Synthesis and Characterization of Responsive Poly(Alkyl Methacrylate) Topologies

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Abstract

Dimethacrylate monomers containing two cleavable *tert*-butyl ester groups were synthesized and utilized in the synthesis of star-shaped polymers. Star polymer coupling was achieved by reacting the living poly(alkyl methacrylate) using 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) or dicumyl dimethacrylate (DCDMA). These star-shaped polymers were cleaved under hydrolytic conditions, leading to significant reductions in molecular weights. The cleavable star-shaped polymers also underwent uncatalyzed degradation at elevated temperatures. Pressure-sensitive adhesive (PSA) copolymers based on 2-ethylhexyl acrylate (EHA) were synthesized containing cleavable branching comprised of either DHDMA or DCDMA. Extremely high molecular weight branched polymers were obtained, and these branched adhesives exhibited 180° peel strengths that displayed a strong dependence on the weight-average molecular weights. The PSA branching sites were cleaved via acid-catalyzed hydrolysis, drastically lowering the 180° peel strengths of the cleaved linear polymers between 75 and 95 percent.

Branched poly (EHA) PSAs containing 2-hydroxyethyl methacrylate (HEMA) and ethylene glycol dimethacrylate (EGDMA), as well as poly(EHA-*co*-HEMA), were synthesized and modified with photoactive functional groups. Cinnamate functionalized PSAs underwent photocrosslinking under UV light, leading to significant losses in 180° peel strengths. The acrylate functionalized PSAs were mixed with a photoinitiator, and following crosslinking under visible light, these PSAs exhibited excellent deactivation characteristics.

Poly(methyl methacrylate) containing aliphatic diols were synthesized via anionic polymerization utilizing the novel protected functional co-initiator 1,1-bis-4,4’-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene (BTOPE). Following the coupling of BTOPE with *sec*-butyl lithium, methyl methacrylate was polymerized in living fashion at -78 °C in THF. A broad molecular weight range of BTOPE-initiated PMMA samples were synthesized, and molecular weight distributions were as low as 1.03 were observed. Hydrolytic deprotection of the protecting groups resulted in α,α-dihydroxy PMMA.

The graft macromonomers poly(*tert*-butyl styrene-*block*-styrene) methacrylate and poly(styrene-*block*-*tert*-butyl styrene) methacrylate were synthesized from the corresponding diblock copolymer alcohols utilizing acid chloride chemistry. Excellent molecular weight control, narrow molecular weight distributions, and perfect crossover were observed in both types of diblock polymers. The macromonomers were copolymerized with methyl methacrylate via solution free-radical copolymerization. The styrene blocks in the purified graft copolymers were selectively sulfonated using acetyl sulfate.

Results of the research efforts presented herein are written as individual research reports with contributing authors and pertinent literature reviews presented at the beginning of each chapter.

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Synthesis and Characterization of Responsive Branched
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Chapter 1 : Dissertation Overview

1.1 Research Significance and Impact

Living polymerization methodologies have become increasingly important in recent years as polymer development has focused more towards extremely specialized applications. Living polymerization techniques enjoy several important advantages over conventional chain growth polymerizations in addition to achieving narrow molecular weight distributions and good molecular weight control. Two major advantages common to all living polymerization techniques are the ability to both synthesize complex polymer topologies, and introduce telechelic functional groups via a combination of functionalized initiation and functional terminating reagents. Anionic polymerizations of methacrylic monomers also exert increasingly high degrees of control over the backbone tacticity, which allows for some degree of tuneability in polymer T_g. Practical limits on the formation of star-shaped polymers via anionic polymerization produced a need for an improvement in the purification techniques of the crosslinking monomers.

In addition to the structural and topological control imposed on the product polymer by living polymerization, polymer properties can also be tailored via the introduction of reactive functional groups into polymers. The introduction of functional groups can be achieved via numerous different pathways, including the use of reactive monomers, post-polymerization modification, and protected functional anionic polymerization initiators. Due to the extensive efforts of prior research groups, these pathways allow for the introduction of an extremely large variety of functional groups into polymers synthesized via either living or conventional chain polymerization techniques, as well as ring-opening and step-growth polymerizations. Functional groups that could be hydrolyzed, photocrosslinked, or sulfonated were explored intensely in the present work. These functional groups included the tertiary-alkyl ester, cinnamate, methacrylate, and alcohol functional groups.

Functional groups in polymers that cause either the real or apparent polymer molecular weight to change are especially interesting and important. Molecular weight is one of the most significant attributes of a polymer, and the ability to alter polymer molecular weight in response to a stimulus enables the use of such polymers in a variety of specialized applications including microlithography, adhesion, self-healing materials and tissue regenerative scaffolding. The primary goal of this work was to explore how functional groups could be utilized to create novel environmentally responsive materials based on branched poly(alkyl methacrylate) polymers.

Through the synthesis of novel responsive alkyl branched poly(alkyl methacrylate) polymers, it was shown that polymer properties could be controllably altered when desired. Cleavable star polymer cores containing tert-caron ester linkages could be hydrolyzed completely, with drastic results for polymer molecular weight. A novel cleavable high molecular weight pressure sensitive adhesive based on a loss of molecular weight mechanism was designed based on an understanding of the impact that these hydrolysable branching sites had on the cohesive properties of the polymers. The switchable adhesives based on the loss of molecular weight mechanism were complemented by adhesive polymers whose switching mechanism was based on the opposite approach: photocrosslinking resulting in the buildup of molecular weight to infinity. These crosslinkable adhesives were designed to exhibit similar extents of deactivation as the cleavable adhesives.

Ionic domains aggregate strongly into clusters that behave similar to physical crosslinks. However, the use to too much ionic content will eliminate polymer processability. While a great deal of attention was focused on the random statistical introduction of ionic groups, such as styrenesulfonate, very little work was performed on examining the impact of the controlled placement of these domains in a branched polymer topology. Graft copolymers will be synthesized via a combination of anionic and free-radical polymerizations for the purpose of elucidating the impact of controlled ionic domain placement.

Chapter 2 : Recent Advances in Living Polymerization of Methacrylic Monomers

2.1 Abstract

Numerous different acrylic and methacrylic monomers were polymerized previously under living polymerization conditions, resulting in well-defined polymers covering a broad range of molecular weights, glass transition temperatures (T_g), polarities, and functional groups. The application of living radical polymerization techniques to acrylic monomers remains at its infancy, however. A fundamental understanding of living polymerization processes enabled the synthesis of tailored acrylic and methacrylic polymers.

The three most frequently employed living polymerization techniques differ from each other, despite numerous similarities in the product polymers. Anionic polymerization was shown to give the best control over molecular architecture, while the controlled free radical polymerization techniques, such as atom transfer radical polymerization (ATRP) and reversible addition-fragmentation transfer (RAFT), are much more robust in terms of reaction environment and monomer functionality. The different strengths of these techniques can be used to make well-defined polymers not possible by other routes. For example, anionic polymerization is well-suited for making stereoregular polymers and RAFT is compatible with monomers containing reactive side groups, including carboxylic acids.

2.2 Synthesis and Applications of Acrylic and Methacrylic Monomers

2.2.1 Synthetic Routes to Monomers

Acrylic and methacrylic monomers were synthesized since the 1930's. Due to the versatility of these routes, hundreds of these monomers were utilized in chain polymerizations.[1] There are three main methods employed in the synthesis of these monomers. Each of these synthetic routes involves the use of the respective alcohol, which is difficult to completely remove from the monomer. The first, and most versatile, method is the reaction between the alcohol and either acryloyl chloride or methacryloyl chloride. The original preparation was performed without solvents at 65 °C, and Na_2CO_3 was used to scavenge the HCl by-product.[2] This reaction was greatly improved via the use of CH_2Cl_2 as a solvent, pyridine as an HCl scavenger, and a reaction temperature of 0 °C.[3]

Another synthetic method for methacrylic monomers is the reaction between acetone cyanohydrin and the proper alcohol in the presence of H_2SO_4 at 85 °C.[4] Due to the hazards involved with acetone cyanohydrin, this reaction is only used in special circumstances, such as in the case of deuterated monomer synthesis.[5] In addition, this reaction cannot be utilized to synthesize monomers containing acid-sensitive side groups,

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[1] A. Tominaga, "Acrylic Copolymers by Radical and Anionic Mechanisms and Their Practical Applications." *Plast. Eng.*, **1997**, *40(Macromolecular Design of Polymeric Materials)*, 407-428.

[2] H. T. Neher, "Esters of Acrylic Acid" *US* 2,117,349, **1938**.

[3] J. M. Mellor and C. F. Webb, "Stereochemistry of the Diels-Alder Reaction. Steric Effects of the Dienophile on Endo-Selectivity." *J. Chem. Soc. Perkin Trans.*, **1974**, *2*, 17-22.

[4] E. C. G. Clarke, "Improvements in or Relating to the Manufacture of Esters of Methacrylic Acid" *UK* 405,699, **1934**.

[5] K. Hatada, T. Kitayama, S. Okahata, and Y Heimei, "Studies on the Mechanism of Polymerization of MMA in THF with BuLi at -78 °C by Using Perdeuterated Monomer." *Polym. J.*, **1981**, *13*(11), 1045-1054.

such as the *tert*-butyl group. Figure 2.1 illustrates the first two synthetic routes to acrylic and methacrylic monomers. The third synthetic route is the commercially-used ester interchange[6] route. The ester interchange product contains the highest amounts of alcohol contamination, but it is the primary source for commercial monomer.

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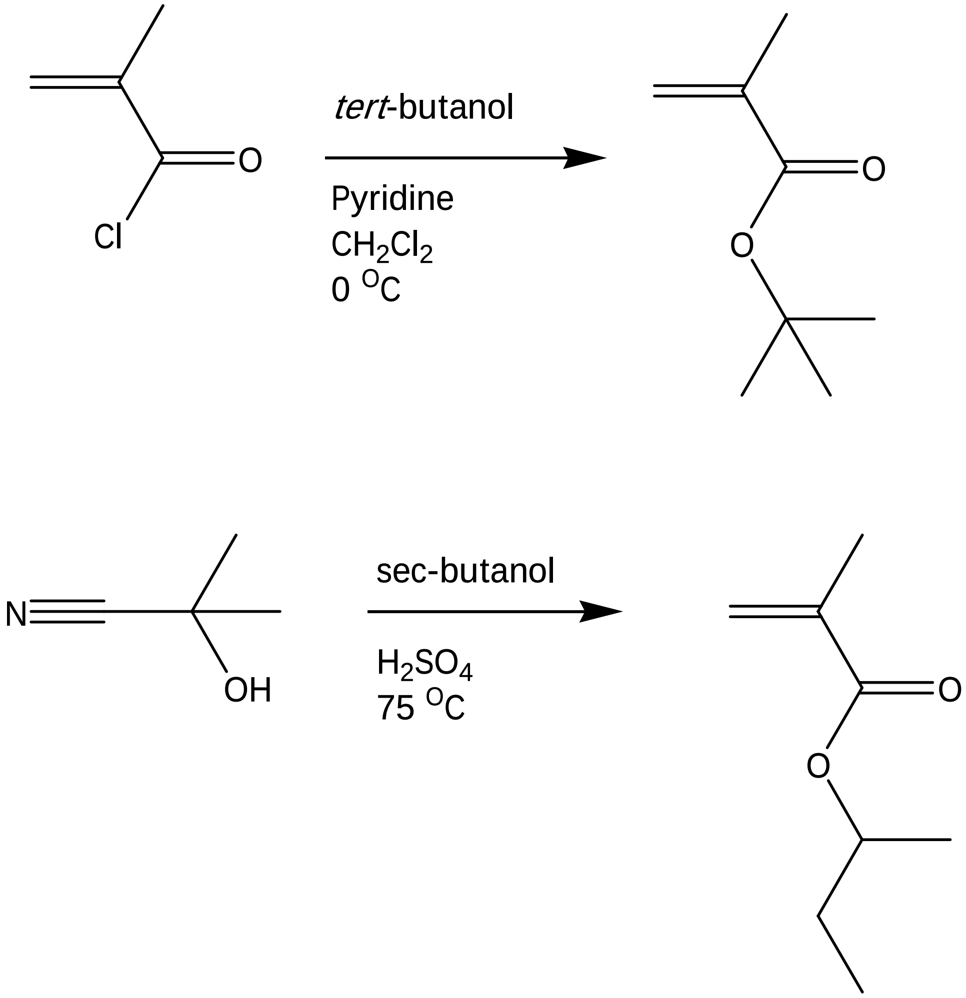
[6] Hyman, M., Jr., “Methacrylic ester and its copolymers.” *US* 2,404,292, **1946**.



`Figure 2.1: Two different common synthetic routes for *tert*-butyl methacrylate and sec-butyl methacrylate

2.2.2 Applications of Acrylic and Methacrylic Polymers

Large-scale commercial uses of methacrylates include poly (methyl methacrylate) (PMMA)-based Plexiglas® and other thermoplastic resins. Acrylic polymers are primarily used in pressure-sensitive adhesives and hydrogels. Both polymer families are also used extensively in academic research. These monomers can be used to synthesize a multitude of polymers due to the versatility of the synthetic routes for these monomers. Acrylic and methacrylic monomers can be tailor-made for specific applications. By changing the side chain, acrylic and methacrylic polymer polarity can be tuned within almost the entire polarity spectrum from hydrophilic to hydrophobic. While poly (acrylic acid) (PAA) is hydrophilic, poly (ethylene glycol) grafted onto a methacrylate-backbone is significantly more hydrophobic.[7] Most acrylic and methacrylic polymers possessing intermediate sidechain polarities are amphiphilic. As a result, they were used extensively in the formation of Langmuir-Blodgett films[8] and micelles.[9,10]

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[7] W. L. Chen and K. R. Shull, "Hydrophilic Surface Coatings from Acrylic Block Copolymers." *Macromolecules*, **1999**, *32*(19), 6298-6306.

[8] S. J. Mumby, J. F. Rabolt, and J. D. Swalen, "Orientation of Poly(Octadecyl Methacrylate) and Poly(Octadecyl Acrylate) in Langmuir-Blodgett Monolayers Investigated by Polarized Infrared Spectroscopy." *Macromolecules*, **1986**, *19*(4), 1054-1059.

[9] C. M. Flanigan, A. J. Crosby, and K. R. Shull, "Structural Development and Adhesion of Acrylic ABA Triblock Copolymer Gels." *Macromolecules*, **1999**, *32*(21), 7251-7262.

[10] J. Kriz, J. Brus, J. Plestil, D. Kurkova, B. Masar, J. Dybal, C. Zune, and R. Jerome, "Polymer Dynamics in an Interface-Confined Space: NMR Study of Poly(Hexyl Ethacrylate)-*Block*-Poly(Acrylic Acid) and Poly(Dodecyl Methacrylate)-*Block*-Poly(Acrylic Acid) Micelles in D_2O." *Macromolecules*, **2000**, *33*(11), 4108-4115.

2.3 Historic Developments in Living Polymerization

Living polymerization was first observed when sodium naphthalide was used to initiate the anionic polymerization of styrene.[11] The propagating polymer consumed monomer at both termini, in the absence of termination and chain transfer. From this single reaction, an entire area of synthetic polymer research evolved over the years.[12,13,14,15] The main obstacle to the employment of this reaction is its sensitivity to proton-donating contaminants. Despite the subsequent discovery of living radical polymerizations, [16,17] the chief means of producing living polymers remains anionic polymerization, which is typically initiated using alkyl lithium [18] or alkylamino lithium[19] initiators.

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[11] M. Szwarc, M. Levy, and R. Milkovich, "Polymerization Initiated by Electron Transfer to Monomer. A New Method of Formation of Block Polymers." *J. Am. Chem. Soc.*, **1956**, *78*(11), 2656-2657.

[12] M. Maurice, *Anionic Polymerization : Principles and Practice*, New York: Academic Press, 1983.

[13] M. Szwarc, "Living Polymers and Mechanisms of Anionic Polymerization." in *Advances in Polymer Science*, Berlin: Springer-Verlag, 1983.

[14] O. W. Webster, "Living Polymerization Methods." *Science*, **1991**, *251*(4996), 887-892.

[15] M. Szwarc, "Living Polymers. Their Discovery, Characterization, and Properties." *J. Polym. Sci. A Polym. Chem.*, **1998**, *36*(1), ix-xv.

[16] K. Matyjaszewski and J. Xia, "Atom Transfer Radical Polymerization." *Chem. Rev.*, **2001**, *101*(9), 2921-2990.

[17] M. Kamigaito, T. Ando, and M. Sawamoto, "Metal-Catalyzed Living Radical Polymerization." *Chem. Rev.*, **2001**, *101*(12), 3689-3746.

[18] D. M. Wiles and S. Bywater, "Polymerization of Methyl Methacrylate Initiated by 1,1-Diphenylhexyl Lithium." *Trans. Faraday Soc.*, **1965**, *61*(1), 150-158.

[19] T. E. Long, R. A. Guistina, B. A. Schell, and J. E. McGrath, "Hindered Lithium Dialkylamide Initiators for the Living Anionic-Polymerization of Methacrylic Esters." *J. Polym. Sci. A Polym. Chem.*, **1994**, *33*(13), 2425-2430.

The first key improvement in the living anionic polymerizations of methacrylates was the use of bulky initiators,[20] which prevented the addition of the initiating carbanion to the methacrylate ester carbonyl. The most common of these initiators is diphenylhexyl lithium, which is formed *in situ* from sec-butyl lithium and 1,1-diphenylethylene.[21] However, the synthesis of acrylic polymers via living anionic polymerizations was not possible without reducing the reactivity of the propagating lithium enolate. The poly(alkyl acrylate) backbone ester α-hydrogen is acidic enough to be abstracted by the polymerizing anion. The use of ligating agents including LiCl[22] has enabled the use of acrylic monomers in anionic polymerizations.

Historically, the major impediment to the use of methacrylic monomers in anionic polymerization was that protic impurities were not removed completely from the monomer.[23] The most significant of these contaminations was shown to be the alcohols remaining from monomer synthesis. The presence of this contaminant quenches anionic polymerization either fully or partially, which leads to a loss of molecular weight control. Trialkyl aluminum Lewis acids remove any protic impurities from the monomers, and their use prior to vacuum distillation of the monomer enable the synthesis of poly(alkyl methacrylates) via anionic polymerization. The first and most widely used cleansing

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[20] D. M. Wiles and S. Bywater, "Polymerization of Methyl Methacrylate Initiated by 1,1-Diphenylhexyl Lithium." *Trans. Faraday Soc.*, **1965**, *61*(1), 150-158.

[21] G. D. Andrews and L. R. Melby, "New Functional Methacrylate Polymers by Anionic Polymerization." *Poly. Sci. Tech.*, **1984**, *25(New Monomers Polym.)*, 357-380.

[22] P. Teyssie, R. Fayt, J. P. Hautekeeper, C. Jacobs, R. Jerome, L. Leemans, and S. K. Varshney, "New Prospects for Living Anionic- Polymerization of (Meth)Acrylic Esters." *Makromol. Chem.- M. Symp.*, **1990**, *32(Invited Lect. Int. Symp. Cationic Polym. Relat. Ionic Processes, 9th, 1989)*, 61-73.

[23] R. D. Allen, "Synthesis of Novel Methacrylate-Containing Polymers by Anionic Polymerization." Dissertation, VA Polytech. Inst. & State Univ., 1985.

agent is $AlEt_3$.[24] The polymerization of $AlEt_3$–treated methacrylic monomers proceeded successfully, yielding low molecular weight distribution polymers with well-controlled molecular weights.

2.4 Properties of Living Polymerization

2.4.1 Structural Control

Following the discovery of controlled free radical polymerization, the technique quickly became diversified as more capping agents were discovered and employed. The reversible capping agent defines the type of living radical reaction. Controlled free-radical polymerization enabled the living polymerization of acrylic and methacrylic monomers without scrupulous purification. However, the alcohol impurity in the monomer can act as a chain transfer agent in radical polymerizations, necessitating minimization of this impurity.

All living polymers share several characteristics that must be present in the reaction.[25,26] The most significant and defining characteristic of living polymerizations is the lack of irreversible terminating side reactions. Thus, controlled free radical polymerizations are considered living only if no terminating reactions accompany the reversible capping of the growing polymer chain. If termination occurs at a limited rate,

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[24] R. D. Allen and T. E. Long, "Synthesis of Tactic Poly(Alkyl Methacrylate) Homo and Copolymers." in *Advances in Polymer Synthesis*, ed. B. M. Culbertson, McGrath, J. E., New York: Plenum Publishing Co., 1985.

[25] K. Matyjaszewski and A. H. E. Mueller, "Naming of Controlled, Living and "Living" Polymerizations." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1997**, *38*(1), 6-9.

[26] R. P. Quirk and B. Lee, "Experimental Criteria for Living Polymerizations." *Polym. Int.*, **1992**, *27*(4), 359-367.

the polymerization is identified as 'controlled'. Due to the lack of termination in living polymerizations, the degree of polymerization increases linearly with the extent of the reaction.[27] Thus, it is possible to distinguish living and controlled polymerizations from conventional polymerizations through the analysis of the reaction kinetics. The two main routes for living polymerization are anionic polymerization and controlled free radical polymerization.[28,29] Controlled free radical polymerization can be achieved through atom transfer free radical polymerization (ATRP),[30] nitroxide-mediated stable free-radical polymerization (SFRP),[31] and reversible addition-fragmentation chain transfer (RAFT) polymerization.[32] Figure 2.2 illustrates the nitroxide- mediated stable free radical polymerization (SFRP)[33] of styrene; other works treat SFRP in great detail.[34]

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[27] H. L. Hsieh and R. P. Quirk, *Anionic Polymerization : Principles and Practical Applications*, New York: Marcel Dekker, 1996.

[28] M. P. Stevens, *Polymer Chemistry- an Introduction*, Third ed., New York: Oxford University Press, 1999, 551.

[29] C.J. Hawker, '"Living" Free Radical Polymerization: A Unique Technique for the Preparation of Controlled Macromolecular Architectures." *Acc. Chem. Res.*, **1997**, *30*(9), 373-382.

[30] A. Muhlebach, S. G. Gaynor, and K. Matyjaszewski, "Synthesis of Amphiphilic Block Copolymers by Atom Transfer Radical Polymerization (ATRP)." *Macromolecules*, **1998**, *31*(18), 6046-6052.

[31] C. Detrembleur, P. Lecomte, J. R. Caille, S. Creutz, P. Dubois, P. Teyssie, and R. Jerome, "4-Methoxypyridine N-Oxide: A New Regulator for the Controlled Free Radical Polymerization of Methyl Methacrylate." *Macromolecules*, **1998**, *31*(20), 7115-7117.

[32] B. Y. K. Chong, T. P. T. Le, G. Moad, Rizzardo E., and Thang S. H., "A More Versatile Route to Block Copolymers and Other Polymers of Complex Architecture by Living Radical Polymerization: The RAFT Process." *Macromolecules*, **1999**, *32*(6), 2071-2074.

[33] C. Burguiere, M. A. Dourges, B. Charleux, and J. P. Vairon, "Synthesis and Characterization of Omega-Unsaturated Poly(Styrene-*B*-N-Butyl Methacrylate) Block Copolymers Using TEMPO-Mediated Controlled Radical Polymerization." *Macromolecules*, **1999**, *32*(12), 3883-3890.

[34] J. R. Lizotte, "Synthesis and Characterization of Tailored Macromolecules Via Stable Free Radical Polymerization Methodologies." Dissertation, VA Polytech Inst. & State Univ., 2003.

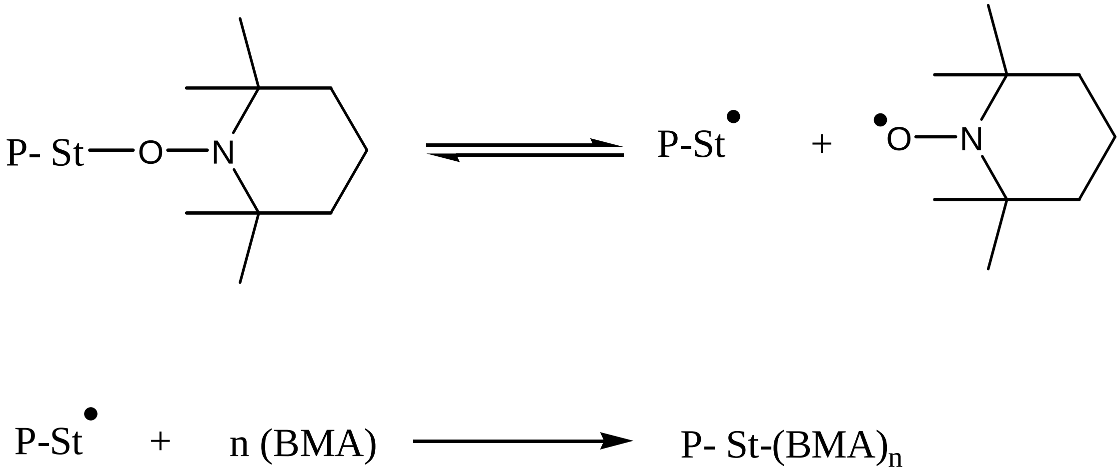

Figure 2.2: TEMPO-mediated polymerization of poly(styrene-*block*-*n*-butyl methacrylate)

Living polymerization distinguishes itself from conventional chain polymerizations by the lack of termination and chain transfer reactions. This results in a highly controlled polymer architecture.[35,36,37,38] A living polymer's molecular weight distribution (MWD) is very low, typically between 1.0 and 1.1. Often, however, living techniques result in polymers that exhibit a MWD of slightly more than 1.1 due to the pendent group reactivity of the monomers employed. Much debate remains over a polymers' extent of livingness, even for well-studied polymerizations, such as the anionic

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[35] O. W. Webster, "Living Polymerization Methods." *Science*, **1991**, *251*(4996), 887-892.

[36] K. Hatada, "Uniform Poly(Methyl Methacrylate)s with Controlled Architecture." *Trends Polym. Sci.*, **1997**, *5*(7), 223-229.

[37] K. Hatada, T. Kitayama, K. Ute, and T. Nishiura, "Structurally Controlled Polymers with Ultimate Precision- Synthesis, Characterization, and Properties." *Macromol. Symp.*, **1999**, *143(World Polymer Congress, 37th International Symposium on Macromolecules, 1998),* 111-120.

[38] R. Milkovich, "Synthesis of Controlled Polymer Structures." in *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*, ed. J. E. McGrath, *ACS Symposium Series*, Washington: American Chemical Society, 1981.

polymerization of *tert*-butyl methacrylate (*t*-BMA).[39] The authors of this study claimed that the polymerization exhibits no 'livingness' between –78 °C and 0 °C in toluene despite compelling evidence to the contrary.[40,41]

Another key benefit resulting from the lack of termination and chain transfer reactions is that the number average molecular weight (M_n) is determined by the ratio of initiator to monomer. Experimentally, M_n equals the grams of monomer divided by the moles of initiator[42] to a good approximation. Thus, a molecular weight range of well-defined polymers can be synthesized with different molecular weights by simply varying the initiator amounts. Meaningful diffusion and rheological experiments can be carried out on polymers that comprise both controlled molecular weights and low molecular weight distributions. Since both experiment types are strongly dependent on molecular weight, a polymer with a broad range of molecular weights makes a poor specimen for such a study.

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[39] C. Zune, P. Dubois, and R. Jerome, "Anionic Polymerization of (Meth)Acrylic Monomers: Anionic Polymerization of *Tert*-Butyl Methacrylate in Toluene." *Polym. Int.*, **1999**, *48*(7), 565-570.

[40] T. E. Long, C. D. DePorter, N. Patel, D. W. Dwight, G. L. Wilkes, and J. E. McGrath, "Poly(Alkyl Methacrylate-Methacrylate Carboxylate) Ion-Containing Block Copolymers." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1987**, *28*, 214-216.

[41] T. E. Long, "Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems." Dissertation, VA Polytech. Inst. & State Univ., 1987.

[42] M. Maurice, *Anionic Polymerization : Principles and Practice*, New York: Academic Press, 1983.

2.4.2 Block Copolymers and Branched Topologies

Following consumption of the monomer in a living polymerization, the propagating center remains active, sometimes for days. The subsequent initiation of a different monomer by the first block leads to diblock copolymers, a very versatile group of polymers.[43,44,45,46] Monomer addition can be repeated to form triblock[47] and multiblock polymers.[48] Block copolymers exhibit different properties than homopolymers, due to the fact that the covalent linkage of two otherwise incompatible polymer chains leads to microphase separation.[49] Applications of block polymers range from thermoplastic elastomers[50,51] to polymer blend compatibalizers.[52] The oldest and most widely used thermoplastic elastomer is poly (styrene-*block*-butadiene-*block*-

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[43] J. Moacanin, G. Holden, and N. W. Tshoegl, eds., *Block Copolymers*, vol. 26, *J. Polym. Sci. C: Polym. Symp.*, New York: Interscience Publishers, 1969.

[44] J. E. McGrath, "An Introductory View of Block Copolymers." in *Block Copolymers: Science and Technology*, ed. D. J. Meier, *MMI Press Symposium Series*, New York: Harwood Academic Publishers, 1979.

[45] A. Noshay and J. E. McGrath, *Block Copolymers: Overview and Critical Survey*, New York: Academic Press, 1977, 516.

[46] W. H. Tang, "Confinement of Symmetric Diblock Copolymer Thin Films." *Macromolecules*, **2000**, *33*(4), 1370-1384.

[47] T. E. Long, A. D. Broske, D. J. Bradley, and J. E. McGrath, "Synthesis and Characterization of Poly (*Tert*-Butyl Methacrylate-*B*-Isoprene-*B*-*Tert*-Butyl Methacrylate) Block Copolymers by Anionic Techniques," *J. Polym. Sci. A Polym. Chem.*, **1989**, *27*(12), 4001-4012.

[48] J. M. Yu, P. Dubois, and R. Jerome, "Poly[Poly(Isobornyl Methacrylate-*Co*-Methyl Methacrylate)(Poly(IBMA-*co*-MMA))-*B*-Polybutadiene-*B*-Poly(IBMA-*co*-MMA)] Copolymers: Synthesis, Morphology, and Properties." *Macromolecules*, **1997**, *30*(21), 6536-6543.

[49] T. Hashimoto, M. Shibayama, M. Fujimura, and H. Kawai, "Microphase Separation and the Polymer-Polymer Interphase in Block Copolymers." in *Block Copolymers: Science and Technology*, ed. D. J. Meier, *Mmi Press Symposium Series*, New York: Harwood Academic Publishers, 1979.

[50] N. R. Legge, G. Holden, and H. E. Schoreder, eds., *Thermoplastic Elastomers: A Comprehensive Review*, New York: Hanser Publishers, 1987.

[51] J. M. Yu and R. Jerome, "Stereocomplexation of sPMMA-PBD-sPMMA Triblock Copolymers with Isotactic PMMA. II: Effect of Molecular Weight." *Polymer*, **1998**, *39*(25), 6567-6575.

[52] D. C. Allport and W. H. James, ed., *Block Copolymers*, London: Applied Science Publishers, Ltd., 1973, 620.

styrene). This triblock copolymer was developed in the 1970s[53] and remains the most successful commercial block copolymer to date. Poly (styrene-*block*-methyl methacrylate) diblock copolymers were used to study dewetting behavior on silicon substrates.[54] Branched polymer topologies were also accessible via living anionic polymerization.[55,56]

Block copolymers are significant, due to the fact that it is often difficult to blend polymers together, even when they are very similar in structure. Since block copolymers feature different polymer chains that are covalently linked, they facilitate blending of otherwise incompatible polymers.[57] Another application of block copolymers is as stabilizers in emulsion polymerization, a very significant commercial process.[58] An example of a polymeric emulsifier is the polyelectrolyte diblock copolymer poly(styrenesulfonate-*block*-butene), which was successfully used to stabilize the emulsion polymerization of styrene.[59]

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[53] A. Keller and J. A. Odell, "The Interrelation between Microstructure and Properties of Block Copolymers." in *Processing, Structure and Properties of Block Copolymers*, ed. M. J. Folkes, New York: Elsevier Science Publishers, 1985.

[54] R. Limary and P. F. Green, "Hierarchical Pattern Formation in Thin Film Diblock Copolymers above the Order-Disorder Transition Temperature." *Macromolecules*, **1999**, *32*(24), 8167-8172.

[55] B. Le Khac and L. J. Fetters, "Synthesis and Properties of Block Copolymers. 3. Polystyrene-Polydiene Star Block Copolymers." *Macromolecules*, **1976**, *9*(5), 732-739.

[56] R. P. Quirk, "Recent Advances in Anionic Polymerization." *Poly. Sci. Tech.*, **1986**, *31(Adv. Polym. Synth.)*, 321-346.

[57] J. K. Kim, "Compatibilization Effect of a Block- Copolymer in 2 Random Copolymer Blends," *Polymer*, **1995**, *36*(6), 1243-1252.

[58] G. E. Molau, ed., *Colloidal and Morphological Behavior of Block and Graft Copolymers*, New York: Plenum Press, 1971.

[59] H. Muller, W. Leube, K. Tauer, S. Forster, and M. Antonietti, "Polyelectrolyte Block Copolymers as Effective Stabilizers in Emulsion Polymerization." *Macromolecules*, **1997**, *30*(8), 2288-2293.

The use of living polymerization also enables the functionalization of the polymer chain by end-capping.[60] The end capping of PMMA by a cyclic anhydride[61] is an example of such a functionalization. It was possible to synthesize graft polymers via this modification, when a polymerizable unsaturated group was introduced.[62] By capping the growing poly (t-butyl acrylate) chain with acryloyl chloride, a macromonomer resulted which was copolymerized with methyl acrylate to form a graft copolymer.[63] Figure 2.3 shows the synthetic scheme for this graft polymer.

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[60] M. A. Peters, A. M. Belu, R. W. Linton, L. Dupray, T. J. Meyer, and J. M. DeSimone, "Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers." *J. Am. Chem. Soc.*, **1995**, *117*(12), 3380-3388.

[61] I. Fallais, N. Pantoustier, J. Devaux, C. Zune, and R. Jerome, "Anionic Synthesis of Cyclic Anhydride End-Capped Poly(Methyl Methacrylate)." *Polymer*, **2000**, *41*(14), 5535-5539.

[62] O. W. Webster, "Living Polymerization Methods." *Science*, **1991**, *251*(4996), 887-892.

[63] K. Antolin, J.-P. Lamps, P. Rempp, and Y. Gnanou, "Synthesis of Poly (*T*-Butyl Acrylate) Macromonomers." *Polymer*, **1990**, *31*(5), 967-970.

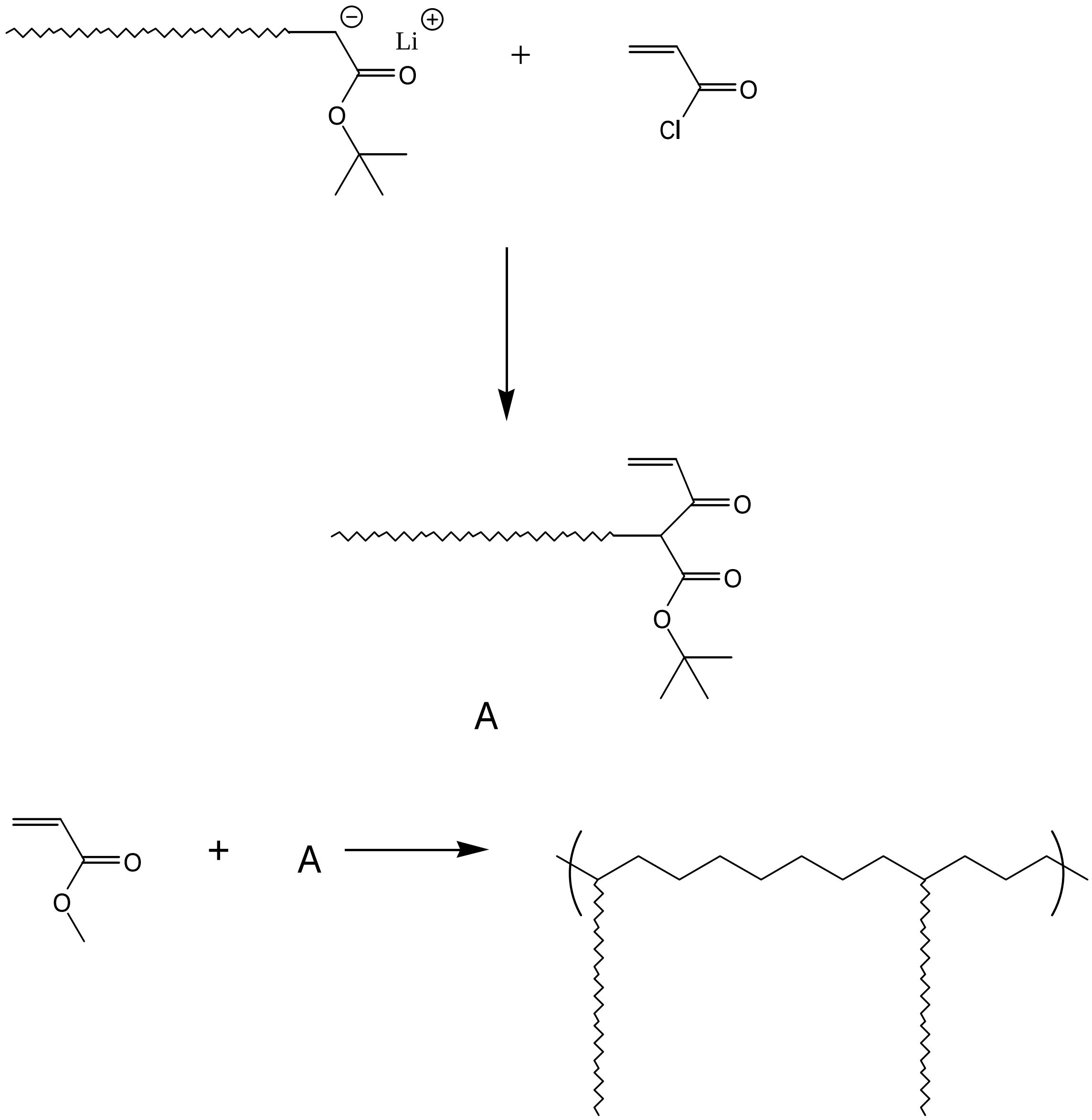

Figure 2.3: Graft copolymerization of poly(*tert*-butyl methacrylate) macromonomer

2.5 Anionic Polymerization

Despite the advent of controlled free-radical polymerizations, anionic polymerization remains the most significant methodology for the living polymerization of acrylic and methacrylic monomers.[64,65] A very strongly nucleophilic initiator, typically an alkyllithium, initiates this reaction. Alkylmagnesium initiators were also studied,[66] as well as other counter-ions.[67,68] For initiation to occur, the initiating anion must be more reactive than the propagating species. More recently, non-carbanionic initiators such as lithium diisopropylamide (LDA),[69,70] and metal-free initiators[71] were utilized. The propagating anion continues to polymerize monomers to form polymers with very low molecular weight distributions. The effects of the lack of chain- termination on molecular weight were discussed in section 4.1.1.

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[64] R. Jerome, P. Teyssie, B. Vuillemin, T. Zundel, and C. Zune, "Recent Achievements in Anionic Polymerization of (Meth)Acrylates." *J. Polym. Sci. A Polym. Chem.*, **1999**, *37*(1), 1-10.

[65] P. Teyssie, P. Bayard, J. Robert, S. K. Varshney, J.-S. Wang, P. Heim, and B. Vuillemin, "Control of Living Anionic Polymerization of (Meth)Acrylates. Active Complex Species, Macromolecular Engineering and Possible Scaling-Up." *Macromol. Symp.*, **1995**, *98(35th IUPAC International Symposium on Macromolecules, 1995)*, 171-183.

[66] K. Ute, T. Kitayama, and K. Hatada, "Studies on the Polymerization of Methyl Methacrylate with Butylmagnesium Chloride by the Aid of Totally Deuterated Monomer- Structures of Polymerization Products and Fate of Initiator." *Polym. J.*, **1986**, *18*(3), 249-261.

[67] T. Ishizone, K. Yoshimura, E. Yanase, and S. Nakahama, "Controlled Anionic Polymerization of Tert-Butyl Acrylate with Diphenylmethyl Anions in the Presence of Dialkylzinc." *Macromolecules*, **1998**, *31*(25), 8706-8712.

[68] W. H. Liu, M. Nakano, and Y. Okamoto, "Polymerization of T-Butyl Acrylate Using Organoaluminum Complexes and Correlation between Main-Chain Tacticity and Glass Transition Temperature of the Obtained Polymers," *Polymer*, **2000**, *41*(12), 4467-4472.

[69] T. E. Long, R. A. Guistina, B. A. Schell, and J. E. McGrath, "Hindered Lithium Dialkylamide Initiators for the Living Anionic-Polymerization of Methacrylic Esters," *J. Polym. Sci. A Polym. Chem.*, **1994**, *33*(13), 2425-2430.

[70] S. Antoun, P. Teyssie, and R. Jerome, "Lithium Diisopropylamide as Initiator for the Anionic Polymerization of Methacrylates." *Macromolecules*, **1997**, *30*(6), 1556-1561.

[71] D. Baskaran, S. Chakrapani, S. Sivaram, T. E. Hogen-Esch, and A. H. Mueller, "Anionic Polymerization of Alkyl (Meth)Acrylates Using Metal-Free Initiators: Effect of Ion Pairing on Initiation Equillibria." *Macromolecules*, **1999**, *32*(9), 2865-2871.

One of the most significant recent advances in anionic polymerization was in the area of ligating reagents,[72] an important topic that was the subject of several recent review articles.[73,74,75,76] The main benefit to the use of these compounds lies in the reduction of the relative rates of terminating reactions that occur with certain monomers. The use of ligating agents has enabled the successful anionic polymerization of alkyl acrylate monomers. Successful use of ligating agents includes the triethylborane-mediated polymerization initiation via the diphenylmethylpotassium initiator.[77] In this system, *tert*-butyl acrylate was quantitatively polymerized at 0 °C. In many cases of ligated anionic polymerization, however, the reaction temperature must be at –78 °C in order to produce polymers with a molecular weight distributions of less than 1.1. The use of lithium silanolate ligating agents in conjunction with *sec*-butyl lithium is such a case.[78]

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[72] O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, and T. V. Rajanbabu, "Group-Transfer Polymerization. 1. A New Concept for Addition Polymerization with Organosilicon Initiators." *J. Am. Chem. Soc.*, **1983**, *105*(17), 5706-5708.

[73] P. Vlcek and L. Lochmann, "Anionic Polymerization of (Meth)Acrylate Esters in the Presence of Stabilizers of Active Centres." *Prog. Poylm. Sci.*, **1999**, *24*(6), 793-873.

[74] M. Van Beylen, S. Bywater, G. Smets, M. Szwarc, and D. J. Worsfold, "Developments in Anionic-Polymerization- a Critical Review." *Adv. Polym. Sci.*, **1988**, *86*, 87-143.

[75] C. Zune and R. Jerome, "Anionic Polymerization of Methacrylic Monomers: Characterization of the Propagating Species." *Prog. Polym. Sci.*, **1999**, *24*(5), 631-664.

[76] D. Baskaran, "Strategic Developments in Living Anionic Polymerization of Alkyl (Meth)Acrylates." *Prog. Polym. Sci.*, **2003**, *28*(4), 521-581.

[77] T. Ishizone, K. Yoshimura, E. Yanase, and S. Nakahama, "Controlled Anionic Polymerization of *t*BA with Diphenylmethylpotassium in the Presence of Triethylborane." *Macromolecules*, **1999**, *32*(3), 955-957.

[78] T. Zundel, P. Teyssie, and R. Jerome, "New Ligands for the Living High-Molecular-Weight Anionic (Co)Polymerization of Acrylates in Toluene at 0 Degrees C. 3. Ligation of Sec-Butyllithium by Lithium Silanolates." *Macromolecules*, **1998**, *31*(17), 5577-5581.

2.5.1 Polymerization Characteristics

The additives and reaction components and conditions used in the anionic polymerization of acrylic and methacrylic monomers determine many aspects of the product polymer. The use of acrylic and methacrylic monomers required modifications to the original anionic polymerization procedure[79] before living polymers were obtained. The most significant modification consisted of an improved monomer purification, which minimally includes drying over CaH_2, followed by a high-vacuum distillation. Then, Et_3Al is used to consume any remaining proton-donating impurities and the monomer is distilled again.[80] The use of this highly reactive Lewis acid is especially crucial for ensuring the complete removal of hindered alcohols, such as *tert*-butanol.

Both acrylic and methacrylic polymers require low reaction temperatures, especially when short and/or linear chains are present on the ester.[81] Typically, temperatures ranging from –78 to –40 °C are used for these reactions. Higher reaction temperatures make the carbonyl group more susceptible to nucleophilic attack by the enolate,[82] resulting in termination of the reaction. The polymerization solvent is dried over Na/ benzophenone and distilled immediately before polymerization. The most frequently used solvents are THF and toluene, and the solvent polarity has a great impact on the stereoregularity of the polymer backbone.

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[79] M. Szwarc and A. Rembaum, "Polymerization of Methyl Methacrylate Initiated by an Electron Transfer to the Monomer." *J. Poly. Sci.*, **1956**, *22*(100), 189-191.

[80] R. D. Allen, T. E. Long, and J. E. McGrath, "Preparation of High Purity, Anionic Polymerization Grade Alkyl Methacrylate Monomers." *Polym. Bull.*, **1986**, *15*(2), 127-134.

[81] T. E. Long, "Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems." Dissertation, VA Polytech. Inst. & State Univ., 1987.

[82] K. Hatada, T. Kitayama, S. Okahata, and Y Heimei, "Studies on the Mechanism of Polymerization of MMA in THF with BuLi at -78 °C by Using Perdeuterated Monomer." *Polym. J.*, **1981**, *13*(11), 1045-1054.

The use of a sterically-hindered initiator prevents the attack on the ester by the initiating species. The most successful example is the initiation by diphenylhexyllithium (DPHL).[83] This initiator is synthesized *in situ* by adding *sec*-butyl lithium to 1,1-diphenylethylene immediately before polymerization. Figure 2.4 demonstrates the anionic polymerization of *tert*-butyl methacrylate.

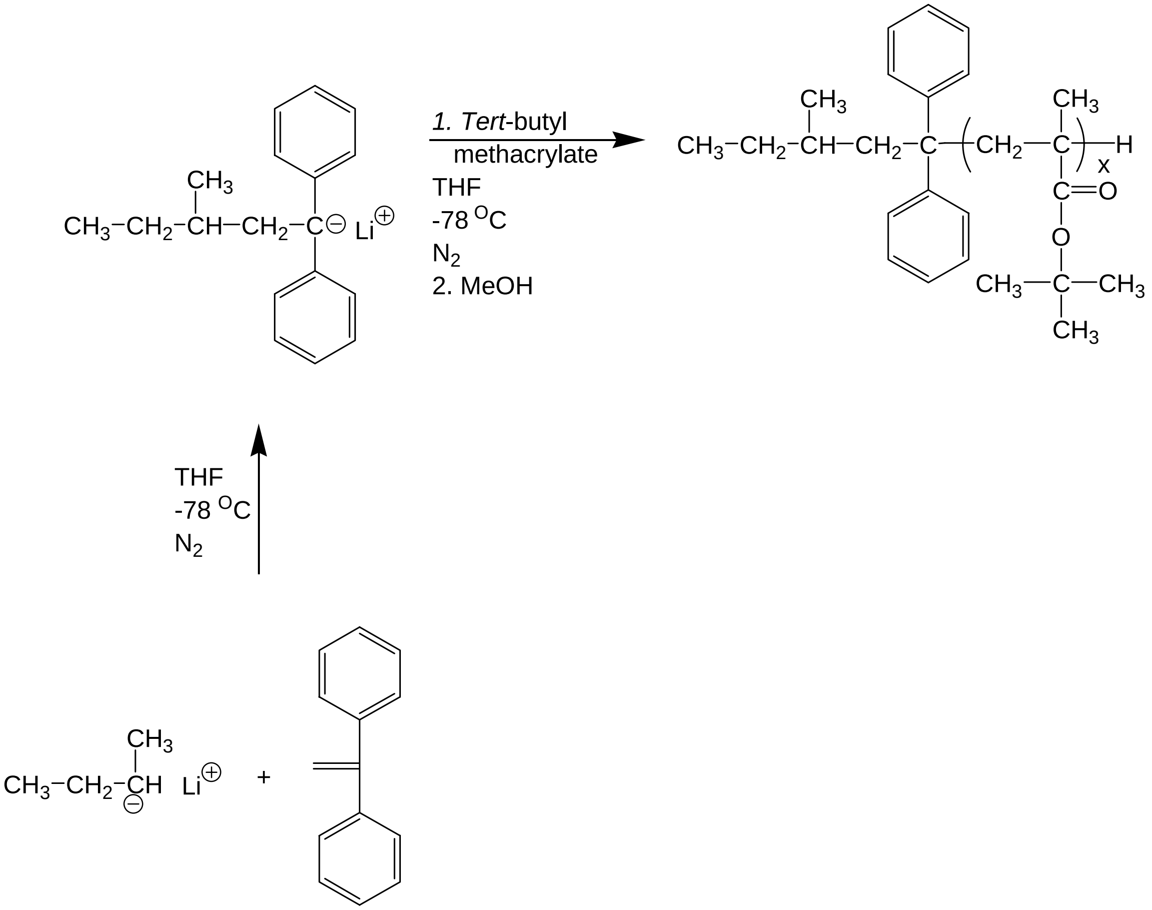

Figure 2.4: Typical anionic synthesis of methacrylic polymers

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[83] D. M. Wiles and S. Bywater, "Polymerization of Methyl Methacrylate Initiated by 1,1-Diphenylhexyl Lithium." *Trans. Faraday Soc.*, **1965**, *61*(1), 150-158.

While methacrylic monomers can be polymerized in the above systems, it is not possible to obtain living acrylic polymers due the acidity of the carbonyl α-hydrogen on the polymer backbone. This proton source quenches the propagating anion. The use of ligating agents in the anionic polymerization of acrylic monomers leads to living polymers.[84,85] The presence of LiCl hinders the aggregation of the reactive centers, leading to a greater number of active species and accelerate the rate of propagation.[86] The improved polymerization control resulting from the use of LiCl dramatically improved the molecular weight distribution and molecular weight control of poly (*t*-BA.[87] The enhancement of the propagation rate reduced the relative rate of termination by hydrogen abstraction until it was kinetically insignificant. However, the use of LiCl in the polymerization of acrylates was completely living only in the case of *t*-BA.[88] LiCl was also shown to improve the polymerization of *tert*-butyl methacrylate.[89] Other

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[84] N. Nugay, T. Nugay, R. Jerome, and P. Teyssie, "Ligated Anionic Block Copolymerization of Methyl Methacrylate with N-Butyl Acrylate and N-Nonyl Acrylate as Promoted by Lithium 2-(2-Methoxyethoxy) Ethoxide Diphenylmethyllithium." *J. Polym. Sci. A Polym. Chem.*, **1997**, *35*(8), 1543-1548.

[85] J. S. Wang, R. Jerome, and P. Teyssie, "Mechanistic Aspects of Ligated Anionic Polymerization (LAP) - the Case of (Meth)Acrylic Ester Monomers." *J. Phys. Org. Chem.*, **1995**, *8*(4), 208-221.

[86] D. Kunkel, A. H. E. Muller, M. Janata, and L. Lochmann, "The Role of Association/Complexation Equilibria in the Anionic-Polymerization of (Meth)Acrylates." *Makromol. Chem.- M. Symp.*, **1992**, *60(Int. Symp. Cationic Polym. Relat. Ionic Processes, 10th, 1991)*, 315-326.

[87] R. Fayt, R. Forte, C. Jacobs, R. Jerome, T. Ouhadi, P. Teyssie, and S. K. Varshney, "New Initiator System for the "Living" Anionic Polymerization of *Tert*-Alkyl Acrylates." *Macromolecules*, **1987**, *20*(6), 1442-1444.

[88] S. Antoun, J. S. Wang, R. Jerome, and P. Teyssie, "Anionic Polymerization of Various Methacrylates Initiated with LiCl-Complexed sBuLi." *Polymer*, **1996**, *37*(25), 5755-5759.

[89] S. K. Varshney, Z. S. Gao, X. F. Zhong, and A. Eisenberg, "Effect of Lithium-Chloride on the Living Polymerization of *Tert*-butyl Methacrylate and Polymer Microstructure Using Monofunctional Initiators." *Macromolecules*, **1994**, *27*(5), 1076-1082.

lithium-containing ligating salts, such as lithium perchlorate[90] and lithium 2-(2-methoxyethoxy) ethoxide,[91] were employed to increase the degree of control over acrylic polymerizations.

2.5.2 Product Polymer Properties

Anionic polymerization is a very effective technique for achieving high degrees of control over the tacticity and molecular composition[92] as well as obtaining very narrow molecular weight distributions (Figure 2.5), as determined using size exclusion chromatography (SEC). The solvent employed in anionic polymerization has a significant impact of the tacticity of methacrylic and acrylic polymers.[93,94] It was shown that the use of a nonpolar solvent, such as toluene, creates slowly-reacting tight-ion pairs consisting of the living enolate and the cationic counterion. As a result, a highly isotactic polymer was formed.[95] More polar solvents such as THF result in more reactive ion pairs, which result in the formation of a mixture of syndiotactic and atactic triads. The presence of bulkier side groups in the methacrylate exacerbates this effect. Table 1 lists some polymerization conditions and the tacticities of different poly(*tert*-butyl

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[90] D. Baskaran and Sivaram S, "Specific Salt Effect of Lithium Perchlorate in Living Anionic Polymerization of Methyl Methacrylate and *Tert*-Butyl Acrylate." *Macromolecules*, **1997**, *30*(6), 1550-1555.

[91] N Nugay, T. Nugay, R. Jerome, and P. Teyssie, "Anionic Polymerization of Primary Acrylates as Promoted by Lithium 2-(2-Methoxyethoxy) Ethoxide." *J. Polym. Sci. A Polym. Chem.*, **1997**, *35*(2), 361-369.

[92] A. Omenat, J. Lub, and H. Fischer, "Liquid-Crystalline Diblock Copolymers Produced by Living Cationic and Anionic Polymerizations." *Chem. Mater.*, **1998**, *10*(2), 518-523.

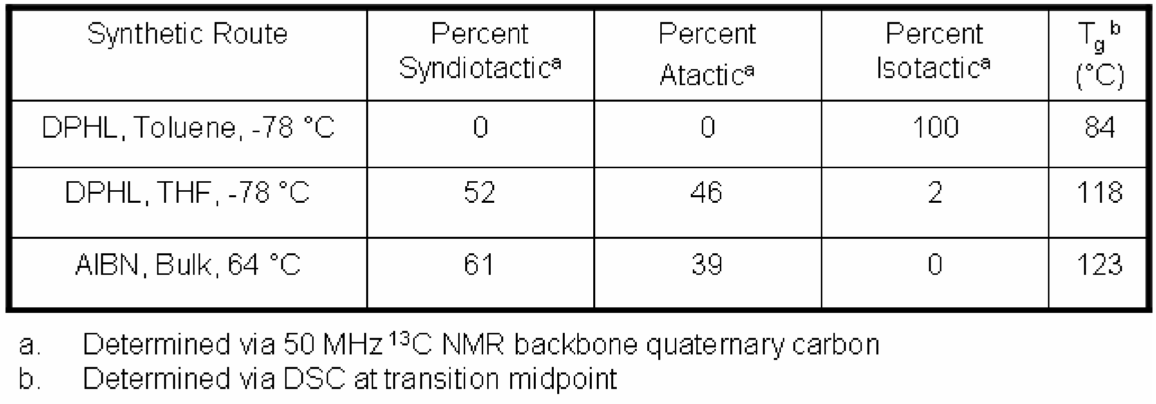
[93] R. D. Allen and T. E. Long, "Synthesis of Tactic Poly(Alkyl Methacrylate) Homo and Copolymers." in *Advances in Polymer Synthesis*, ed. B. M. Culbertson, McGrath, J. E., New York: Plenum Publishing Co., 1985.

[94] W. H. Liu, T. Nakano, and Y. Okamoto, "Stereochemistry of Acrylate Polymerization in Toluene Using N-BuLi." *Polym. J.*, **1999**, *31*(5), 479-481.

[95] T. E. Long, "Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems." Dissertation, VA Polytech. Inst. & State Univ., 1987.

methacrylate) products. The significance of stereoregular polymers is discussed in section 4.5.2. Ligating agents drastically influence polymer microstructure. For example, LiCl was shown to mask the effect of solvent polarity on the tacticity of poly(*tert*-butyl methacrylate) synthesized via anionic polymerization.[96]

Table 2.1: The effect of solvent and temperature on the tacticity of poly (*t*-BMA)



Synthetic Route	Percent Syndiotactic[a]	Percent Atactic[a]	Percent Isotactic[a]	T_g[b] (°C)
DPHL, Toluene, -78 °C	0	0	100	84
DPHL, THF, -78 °C	52	46	2	118
AIBN, Bulk, 64 °C	61	39	0	123

a. Determined via 50 MHz ^{13}C NMR backbone quaternary carbon
b. Determined via DSC at transition midpoint

In addition to stabilizing the growing chain, the use of some ligating agents, such as LiCl,[97] resulted in the selection for a particular polymer tacticity.[98] By increasing the ratio of moles of LiCl to moles of initiator, Teyssie et al.[99] selectively obtained more syndiotactic than isotactic PMMA. The ligating agent $Bu(Me_2)SiOLi$ was used to make

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[96] C. Zune, C. Archambeau, P. Dubois, and R. Jerome, "Effect of the Solvent Polarity on the Living Ligated Anionic Polymerization of *Tert*-Butyl Methacrylate and Copolymerization with Methyl Methacrylate." *J. Polym. Sci. A Polym. Chem.*, **2001**, *39*(10), 1774-1785.

[97] J. B. Pang, G. T. Jin, Y. X. Hou, and H. M. Zhang, "Study on the Anionic Polymerization of *Tert*-Butyl Methacrylate." *J. Polym. Mater.*, **1998**, *15*(1), 67-72.

[98] P. Teyssie, J. Baran, P. Dubois, R. Jerome, J. S. Wang, J. M. Yu, Y. S. Yu, and T. Zundel, "Living Anionic Polymerization of (Meth)Acrylic Esters: New Mechanistic Concepts and Resulting Materials." *Macromol. Symp.*, **1998**, *132(International Symposium on Ionic Polymerization, 1997)*, 303-307.

[99] J. S. Wang, R. Jerome, R. Warin, and P Teyssie, "Anionic-Polymerization of (Meth)Acrylic Monomers. 12. Effect of Lithium- Chloride on the Stereochemistry of the Anionic-Polymerization of Methyl-Methacrylate in THF and in a 9/1 Toluene THF Mixture." *Macromolecules*, **1993**, *26*(22), 5984-5990.

highly isotactic PMMA at a much higher temperatures than what is usually employed for PMMA (0 °C).[100] Ligating agents are usually extremely selective for a certain tacticity. PMMA was stereospecifically polymerized, yielding 96% atactic, 98% syndiotactic, and 100% isotactic polymers.[101]

Phosphonium counterions were also used to control the living anionic polymerization of alkyl methacrylate. One benefit of using tetraphenylphosphonium was that the polymerization of methyl methacrylate could be carried out at ambient temperatures.[102] Metallic ligating agents featuring counter ions other than group I metals were also employed in anionic polymerization.[103] Very recently, Hatada et al.[104] synthesized syndiotactic and atactic living acrylate and methacrylate polymers in high proportions. For syndiotactic polymer, *tert*-butyl lithium was used as the initiator in the presence of trialkylaluminum. Atactic polymers were synthesized using the same initiator in the presence of bis(2,6-di-t-butylphenoxy) methylaluminum. Polymer tacticity or microstructure can be verified using ^{1}H[105,106] and ^{13}C NMR,[107] depending on

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[100] T. Zundel, P. Teyssie, and R. Jerome, "New Ligands for the Living Isotactic Anionic Polymerization of Methyl Methacrylate in Toluene at 0 Degrees C. 1. Ligation of Butyllithium by Lithium Silanolates." *Macromolecules*, **1998**, *31*(8), 2433-2439.

[101] K. Hatada, "Stereoregular Uniform Polymers." *J. Polym. Sci. A Polym. Chem.*, **1999**, *37*(3), 245-260.

[102] A. P. Zagala and T. E. Hogen-Esch, "Living Anionic Polymerization of Methyl Methacrylate at Ambient Temperatures in the Presence of the Tetraphenylphosphonium Cation." *Macromolecules*, **1996**, *29*(8), 3038-3039.

[103] H. Schlaad and A. H. E. Mueller, "Mechanism of Anionic Polymerization of Methyl Methacrylate in the Presence of Aluminum Alkyls." *Macromol. Symp.*, **1995**, *95(Synthesis of Controlled Polymeric Structures through Living Polymerizations and Related Processes)*, 13-26.

[104] K. Hatada and T. Kitayama, "Structurally Controlled Polymerizations of Methacrylates and Acrylates." *Polym. Int.*, **2000**, *49*(1), 11-47.

[105] D. T. Williamson, J. F. Elman, P. H. Madison, A. J. Pasquale, and T. E. Long, "Synthesis and Characterization of Poly(1,3-Cyclohexadiene) Homopolymers and Star-Shaped Polymers." *Macromolecules*, **2001**, *34*(7), 2108-2114.

polymer composition. Phenyl adducts were also used in conjunction with *t*-butyl lithium to yield primarily syndiotactic block copolymers.[108]

2.6 Atom Transfer Radical Polymerization (ATRP)

The termination reactions that plague free-radical polymerizations can be prevented by the reversible capping agent used in atom transfer radical polymerization (ATRP).[109] The growing radical chain does not terminate due to the presence of a metal complex, such as CuBr, which reversibly binds Br to the radical by a continuous redox equilibrium.[110] The overall reaction is shown in Figure 2.6. The equilibrium between uncapped and capped species greatly favors the capped species, resulting in very long polymerization times and the elimination of radical-radical coupling. Since free-radical polymerization is not sensitive to the relative acidity of the acrylic polymer backbone protons, living radical polymerizations of alkyl acrylates such as *t*-butyl acrylate[111] are

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[106] D. T. Williamson, T. E. Glass, and T. E. Long, "Determination of the Stereochemistry of Poly(1,3-Cyclohexadiene) Via End Group Functionalization." *Macromolecules*, **2001**, *34*(17), 6144-6146.

[107] T. Nishiura, T. Kitayama, and K. Hatada, "Carbon-13 NMR Spectra of Stereoregular Copolymers of Methyl and Butyl Methacrylates." *Int. J. Polym. Anal. Ch.*, **2000**, *5*(4-6), 401-413.

[108] J. M. Yu, P. Dubois, P. Teyssie, and R. Jerome, "Syndiotactic Poly(Methyl Methacrylate)(sPMMA)-Polybutadiene (PBD)-sPMMA Triblock Copolymers: Synthesis, Morphology, and Mechanical Properties." *Macromolecules*, **1996**, *29*(19), 6090-6099.

[109] Y. Liu, L. X. Wang, and C. Y. Pan, "Synthesis of Block Copoly(Styrene-*B*-*P*-Nitrophenyl Methacrylate) and Its Derivatives by Atom Transfer Radical Polymerization." *Macromolecules*, **1999**, *32*(25), 8301-8305.

[110] J. S. Wang and K. Matyjaszewski, "Controlled Living Radical Polymerization- Halogen Atom-Transfer Radical Polymerization Promoted by a Cu(I)Cu(II) Redox Process." *Macromolecules*, **1995**, *28*(23), 7901-7910.

[111] K. A. Davis and K. Matyjaszewski, "Atom Transfer Radical Polymerization of *Tert*-Butyl Acrylate and Preparation of Block Copolymers." *Macromolecules*, **2000**, *33*(11), 4039-4047.

possible. Functional monomers including hydroxyethyl methacrylate were also homopolymerized and copolymerized in living fashion via ATRP.[112,113,114]

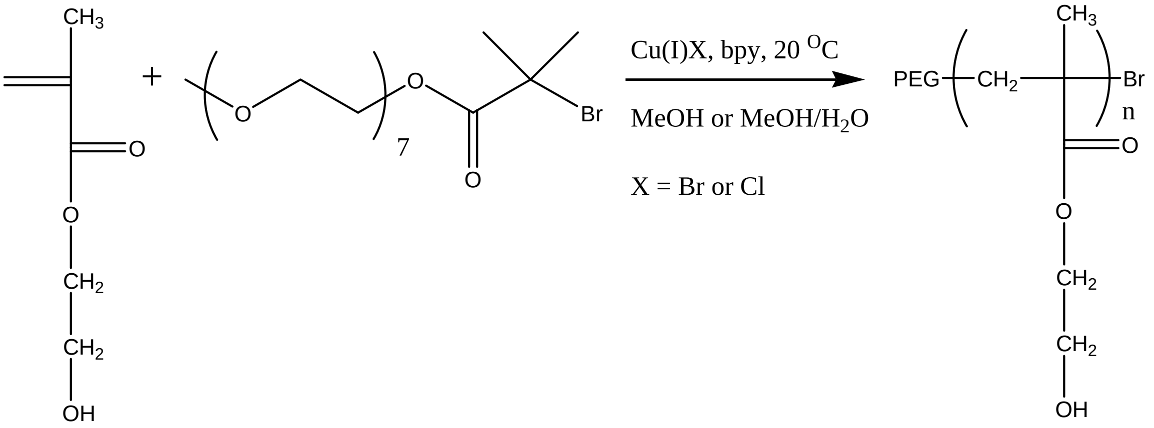

Figure 2.5: ATRP synthesis of poly (PEG-*block*-2-hydroxyethyl methacrylate)

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[112] K.L Robinson, M. A. Khan, M. V. de Paz Banez, X. S. Wang, and S. P. Armes, "Controlled Polymerization of 2-Hydroxyethyl Methacrylate by ATRP at Ambient Temperature." *Macromolecules*, **2001**, *34*(10), 3155-3158.

[113] J. V. M. Weaver, I. Bannister, K. L. Robinson, X. Bories-Azeau, S. P. Armes, M. Smallridge, and P. McKenna, "Stimulus-Responsive Water-Soluble Polymers Based on 2-Hydroxyethyl Methacrylate." *Macromolecules*, **2004**, *37*(7), 2395-2403.

[114] D. Zhang and C. Ortiz, "Synthesis and Single Molecule Force Spectroscopy of Graft Copolymers of Poly(2-Hydroxyethyl Methacrylate-*g*-Ethylene Glycol)." *Macromolecules*, **2004**, *37*(11), 4271-4282.

ATRP can be used in conjunction with many other monomer types, such as the copolymerization of PMMA with a PDMS macroinitiator.[115] Since there is no termination step, these reactions were used to make diblock copolymers as well.[116] This reaction was also used to polymerize several different methacrylate copolymers, as well as networks via end-linking of the living chains.[117]

2.6.1 Polymerization Characteristics

ATRP reactions are typically carried out in a similar fashion as free-radical polymerizations.[118] After drying over CaH_2, the monomer is introduced into the reactor under an inert atmosphere and dissolved in a solvent such as ethyl acetate. The reversible capping agent, CuBr, is introduced, followed by the ligating agent and initiator. The polymerizations are performed at the temperature necessary for the initiator to decompose. Initiation temperatures range from 65 °C (AIBN) to 110 °C (thermal initiation).[119]

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[115] P. J. Miller and K. Matyjaszewski, "Improving the Structural Control of Graft Copolymers by Combining ATRP with the Macromonomer Method." *Macromolecules*, **2000**, *34*(10), 3186-3194.

[116] D. A. Shipp, J. L. Wang, and K. Matyjaszewski, "Synthesis of Acrylate and Methacrylate Block Copolymers Using Atom Transfer Radical Polymerization." *Macromolecules*, **1998**, *31*(23), 8005-8008.

[117] F. Asgarzadeh, P. Ourdouillie, E. Beyou, and P. Chaumont, "Synthesis of Polymer Networks by "Living Free Radical Polymerization and End-Linking Processes." *Macromolecules*, **1999**, *32*(21), 6996-7002.

[118] S. G. Roos, A. H. E. Muller, and K. Matyjaszewski, "Copolymerization of N-Butyl Acrylate with Methyl Methacrylate and PMMA Macromonomers: Comparison of Reactivity Ratios in Conventional and Atom Transfer Radical Copolymerization." *Macromolecules*, **1999**, *32*(25), 8331-8335.

[119] Y. Liu, L. X. Wang, and C. Y. Pan, "Synthesis of Block Copoly(Styrene-*B*-*P*-Nitrophenyl Methacrylate) and Its Derivatives by Atom Transfer Radical Polymerization." *Macromolecules*, **1999**, *32*(25), 8301-8305.

ATRP usually requires a solubilizing ligating agent,[120] which increases the solubility of CuBr in the reaction. These ligating agents are typically either bipyridine (bpy) or a modified version, such as 4,4'-dinonyl-2,2'-bipyridine.[121] The reaction kinetics, shown in Figure 2.7, indicate that the polymerization of MMA is controlled in nature. Unlike conventional free-radical polymerizations, which exhibit fast propagation rates, all controlled free radical polymerizations, including ATRP, display significantly longer polymerization times, typically requiring several hours.

2.6.2 Product Properties

The molecular weight control with ATRP varies with the polymerization system. The molecular weight distribution can be as low as 1.05 for PMMA, [122] well within the molecular weight distributions observed for most living polymerizations. However, the polymerization of poly(nitrophenyl methacrylate) resulted in MWD values as high as 2.45.[123] The authors speculated that the complexation of Cu^{II} to the growing radical prevented the rapid capping equilibrium, leading to a high occurrence of terminating side-reactions.

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[120] T. E. Patten, J. H. Xia, T. Abernathy, and K. Matyjaszewski, "Polymers with Very Low Polydispersities from Atom Transfer Radical Polymerization." *Science*, **1996**, *272*(5263), 866-868.

[121] V. Percec, B. Barboiu, and H.J Kim, "Arenesulfonyl Halides: A Universal Class of Functional Initiators for Metal-Catalyzed "Living" Radical Polymerization of Styrene(s), Methacrylates, and Acrylates." *J. Am. Chem. Soc.*, **1998**, *120*(2), 305-316.

[122] V. Percec, B. Barboiu, and H.J Kim, "Arenesulfonyl Halides: A Universal Class of Functional Initiators for Metal-Catalyzed "Living" Radical Polymerization of Styrene(s), Methacrylates, and Acrylates." *J. Am. Chem. Soc.*, **1998**, *120*(2), 305-316.

[123] Y. Liu, L. X. Wang, and C. Y. Pan, "Synthesis of Block Copoly(Styrene-*B*-*P*-Nitrophenyl Methacrylate) and Its Derivatives by Atom Transfer Radical Polymerization." *Macromolecules*, **1999**, *32*(25), 8301-8305.

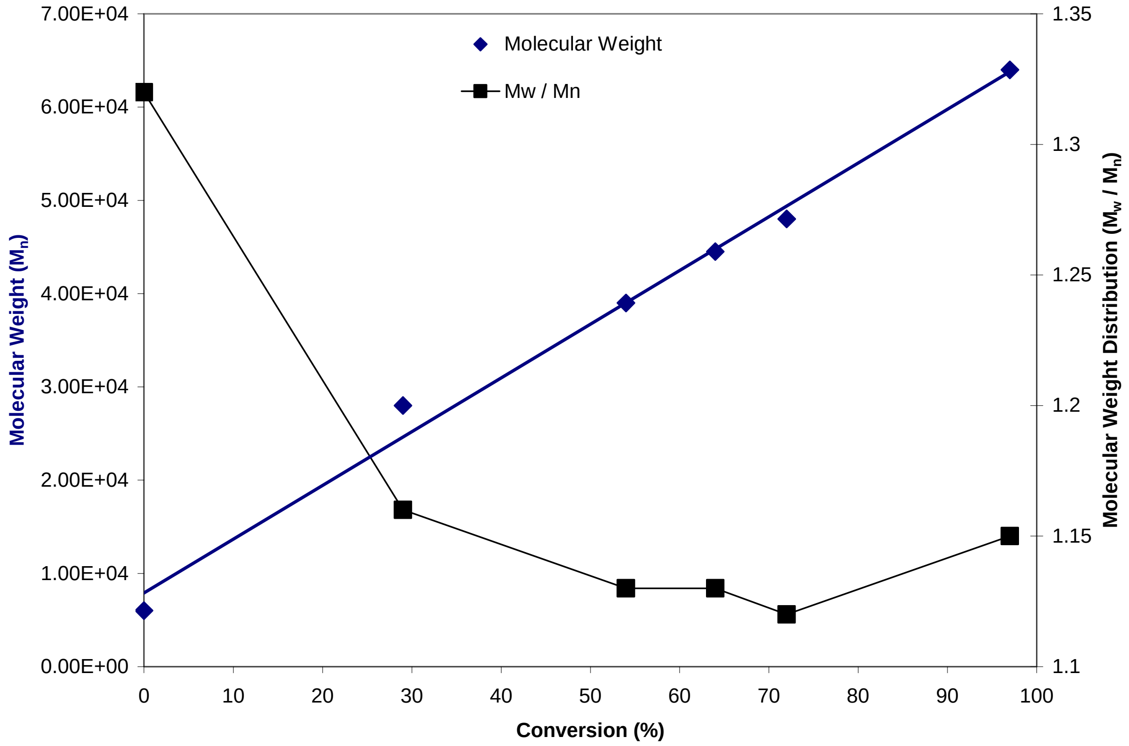

Figure 2.6: Linear polymerization kinetics of MMA in ATRP

ATRP was used to synthesize a variety of methacrylate-containing block copolymers.[124,125] These block copolymers exhibited relatively low molecular weight distributions (1.1-1.15) when the growing methacrylate block initiated the acrylic monomer, but not vice versa. Other amphiphilic methacrylate diblock copolymers were synthesized using ATRP.[126] It is also possible to synthesize styrenic, methacrylic,[127] and acrylic[128] star polymers containing divinylbenzene cores.

Since polymeric Langmuir-Blodgett films form flat substrates, they can be used as the backbones for synthesizing polymer brushes if they possess the functional groups suitable for the ATRP initiation, such as a reactive chlorine group. In one such study, methyl methacrylate was polymerized onto an LB-film of modified poly(trihydroxysilane) by the atom transfer radical polymerization (ATRP) mechanism.[129] The synthetic steps are outlined in Figure 2.8.

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[124] D. A. Shipp, J. L. Wang, and K. Matyjaszewski, "Synthesis of Acrylate and Methacrylate Block Copolymers Using Atom Transfer Radical Polymerization." *Macromolecules*, **1998**, *31*(23), 8005-8008.

[125] K. Matyjaszewski, D. A. Shipp, G. P. McMurtry, S. Gaynor, and T. Pakula, "Simple and Effective One-Pot Synthesis of (Meth)Acrylic Block Copolymers through Atom Transfer Radical Polymerization." *J. Polym. Sci. A Polym. Chem.*, **2000**, *38*(11), 2023-2031.

[126] A. Muhlebach, S. G. Gaynor, and K. Matyjaszewski, "Synthesis of Amphiphilic Block Copolymers by Atom Transfer Radical Polymerization (ATRP)." *Macromolecules*, **1998**, *31*(18), 6046-6052.

[127] S. Angot, D. Taton, G. Hizal, K. S. Murthy, and Y. Gnanou, "Stars and Star-Block Copolymers of Precise Functionality by Atom Transfer Radical Polymerization." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1999**, *40*(2), 348-349.

[128] X. Zhang, J. Xia, and K. Matyjaszewski, "End-Functional Poly(*Tert*-Butyl Acrylate) Star Polymers by Controlled Radical Polymerization." *Macromolecules*, **2000**, *33*(7), 2340-2345.

[129] M. Ejaz, S. Yamamoto, K. Ohno, Y. Tsujii, and T. Fukuda, "Controlled Graft Polymerization of Methyl Methacrylate on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerzation Techniques." *Macromolecules*, **1998**, *31*(17), 5934-5936.

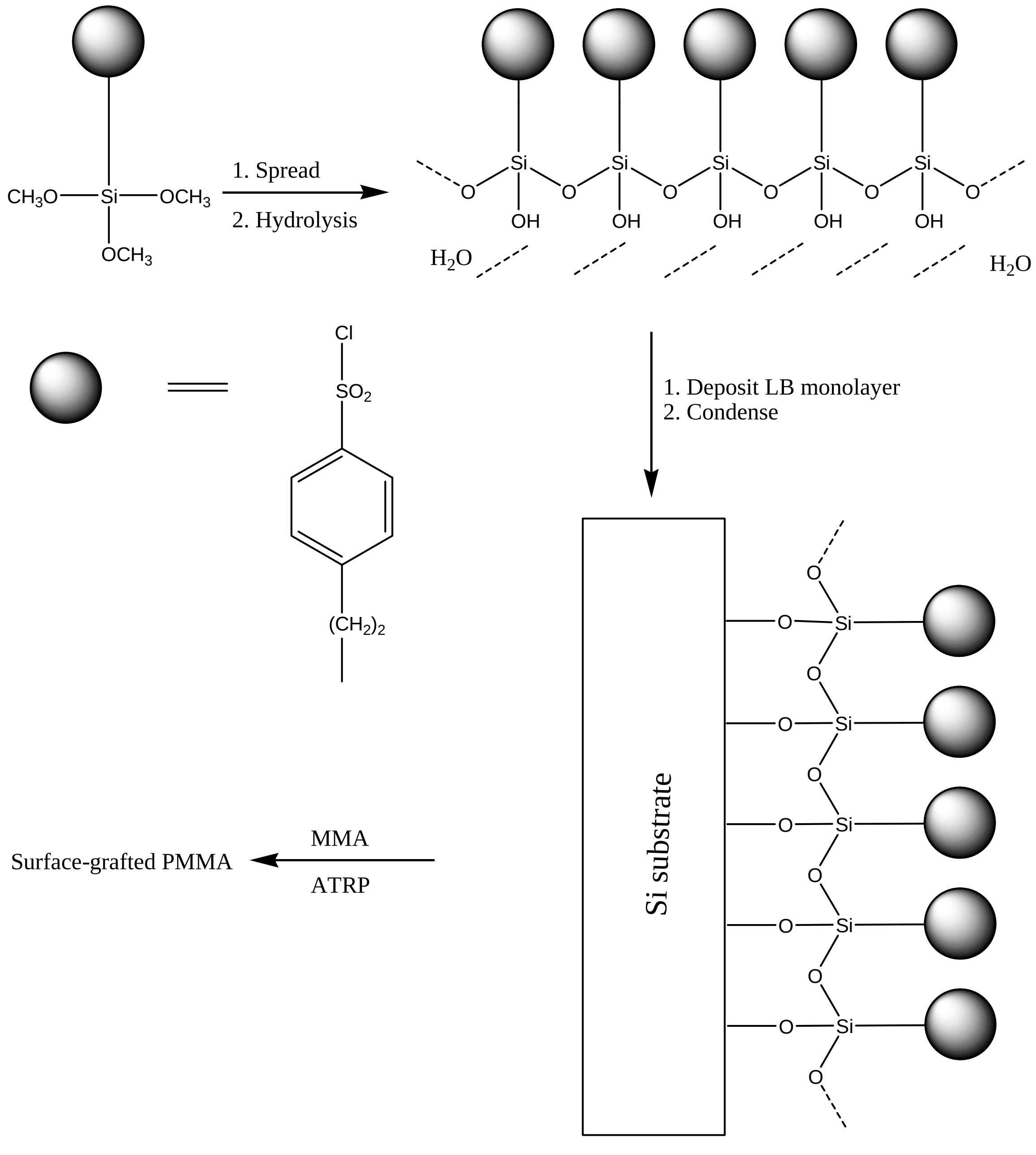

Figure 2.7: Graft polymerization of MMA using a functionalized LB-film

2.7 Reversible Addition-Fragmentation Transfer (RAFT) Polymerization

A newer controlled radical polymerization methodology is the reversible addition-fragmentation chain transfer (RAFT) polymerization, which also involves reversible capping of the growing radical chain.[130,131,132] Figure 9a summarizes the overall reaction that occurs in RAFT, which is initiated using typical free-radical initiators such as benzoyl peroxide (BPO). This reaction features a reversible chain transfer agent, usually a dithioester,[133] which can add to a growing chain and initiate the polymerization of another by a reversible chain transfer. This fragmentation creates a dithio end-cap on the first chain, which can undergo chain transfer to any other active chain and resume growing itself. Figure 9b shows the reversible mechanism of the chain transfer.

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[130] J. Chiefari, Chong Y. K., F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, and S. H. Thang, "Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process." *Macromolecules*, **1998**, *31*(16), 5559-5562.

[131] G. Moad, J. Chiefari, Y. K. Chong, J. Krstina, R. T. A. Mayadunne, A. Postma, E. Rizzardo, and S. H. Thang, "Living Free Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (the Life of RAFT)." *Polym. Int.*, **2000**, *49*(9), 993-1001.

[132] A. Sebenik, "Living Free-Radical Block Copolymerization Using Thio-Iniferters." *Prog. Polym. Sci.*, **1998**, *23*(5), 875-917.

[133] E. Rizzardo, J. Chiefari, G. Moad, R. T. A. Mayadunne, and S. H. Thang, "Preparation of Macromonomers Via Chain Transfer - with and without Added Chain Transfer Agent." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1999**, *40*(2), 342-343.

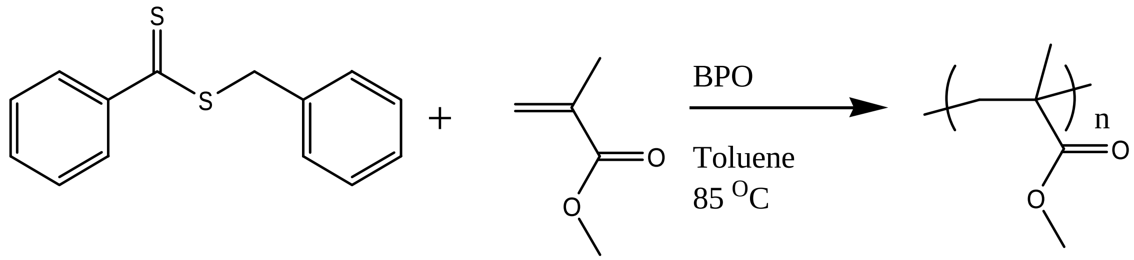

Figure 2.8a: RAFT polymerization of MMA

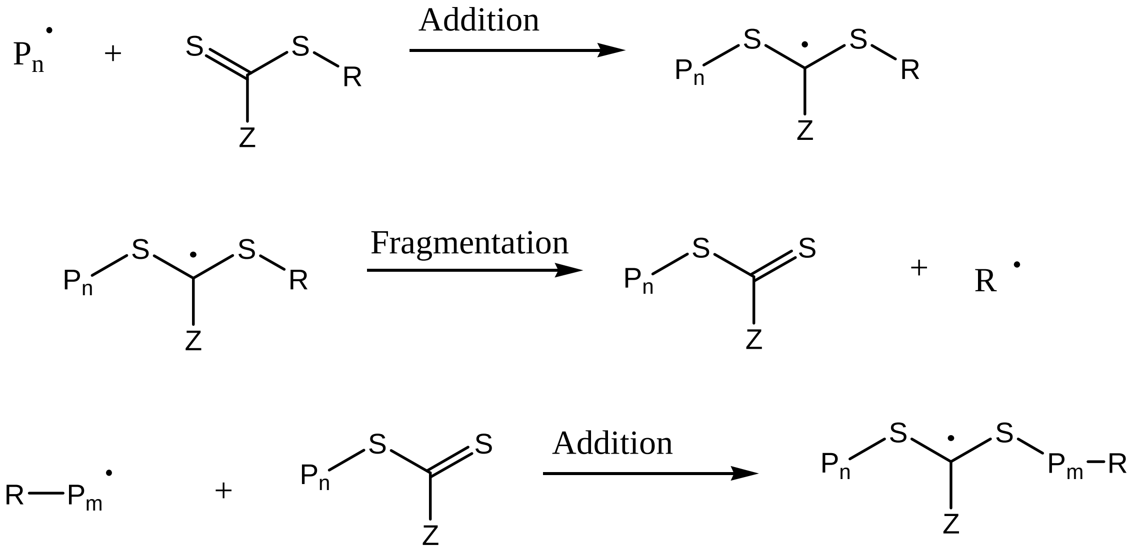

Figure 2.8b: Detailed reversible termination and chain-transfer mechanism in RAFT

As a result of the continually occurring reversible chain transfer reactions, the growing radical chain does not encounter the termination reactions which permanently deactivate the growing ends of polymers created by conventional free-radical polymerizations. In addition, chain transfer to monomer, polymer, or solvent does not occur in RAFT polymerizations. Several diblock copolymers were synthesized using this technique.[134] More recently, more highly-controlled chain transfer agents were developed to achieve more control in the polymerization. The use of dithiocarbamates in the polymerization of poly (styrene-*block*-methyl methacrylate) led to a product having a molecular weight distribution of 1.2.[135]

2.7.1 Reaction Characteristics

The RAFT polymerization is carried out in a variety of solvents, including benzene, DMF, and ethyl acetate. The polymerizations are carried out at elevated temperature, typically 80-90 °C. Higher temperature free-radical initiators, such as AIBN and dibenzoyl peroxide are used in low concentrations.[136] Monomers are freshly distilled with no further modification. The reactions are usually allowed to proceed for 16-24 hours due to the slow reaction kinetics. This reaction is also controlled, as evidenced by

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[134] S. Gaynor, J. S. Wang, and K. Matyjaszewski, "Polymerization by Degenerative Transfer: Effect of the Structure of the Transfer Agent." *Macromolecules*, **1995**, *28*(24), 8051-8056.

[135] R. T. A. Mayadunne, E. Rizzardo, J. Chiefari, Y. K. Chong, G. Moad, and S. H. Thang, "Living Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents." *Macromolecules*, **1999**, *32*(21), 6977-6980.

[136] J. Chiefari, Chong Y. K., F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, and S. H. Thang, "Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process." *Macromolecules*, **1998**, *31*(16), 5559-5562.

the kinetics in the figure below (Fig. 2.11). Typically, conversion rates greater than 50% were necessary to achieve low molecular weight distributions.

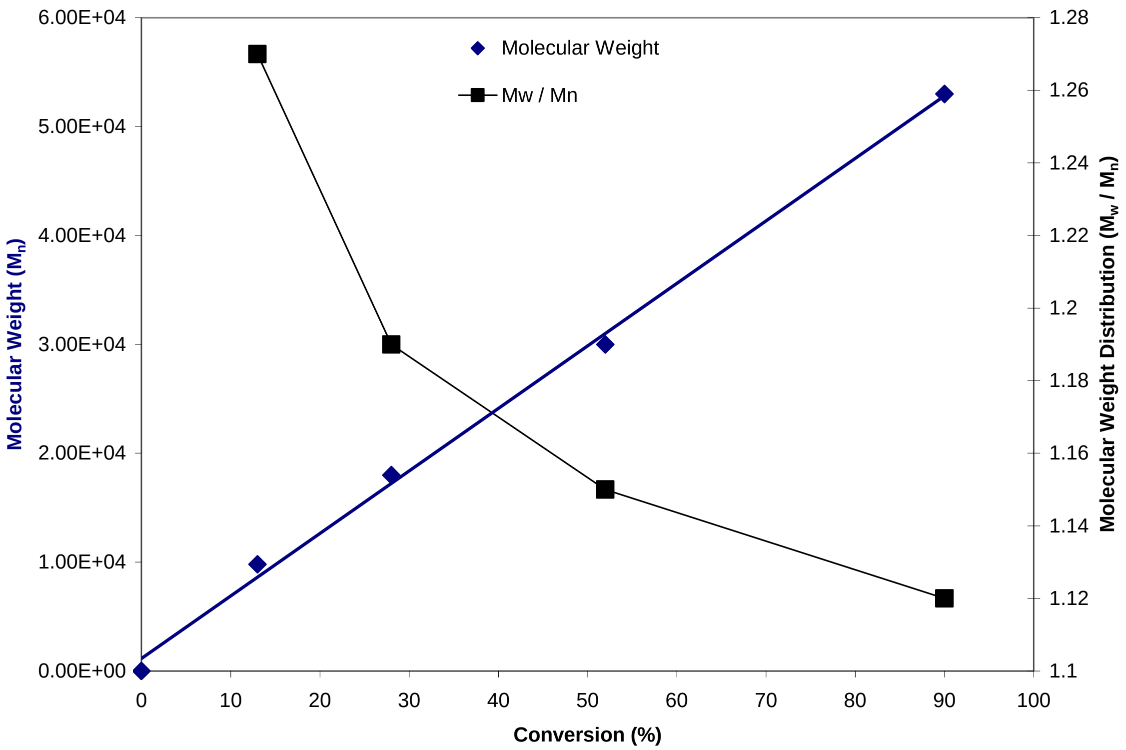

Figure 2.9: Linear RAFT conversion data for styrene indicates the reaction is living.

Several kinds of chain transfer agents are used in RAFT polymerizations, including dithiocarbamates and other (thiocarbonyl)sulfanyl- containing compounds.[137] The chief requirement that these chain transfer agents must meet is that the rates of addition, fragmentation, and re-initiation must be much faster than the propagation rate. In addition, the uncapped radical must be capable of re-initiating polymerization.[138]

2.7.2 Product Properties

The RAFT polymerization technique has enabled the synthesis of block copolymers not possible via anionic or other controlled free-radical polymerizations. Monomers that were previously used in this reaction include acidic, hydroxy, and tertiary amine groups. The wide variety of functional groups that can be incorporated into acrylic and methacrylic polymers[139] is the chief advantage to using RAFT over other living polymerization methods.

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[137] D. G. Hawthorne, G. Moad, E. Rizzardo, and S. H. Thang, "Living Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (Raft): Direct ESR Observation of Intermediate Radicals." *Macromolecules*, **1999**, *32*(16), 5457-5459.

[138] R. T. A. Mayadunne, E. Rizzardo, J. Chiefari, Y. K. Chong, G. Moad, and S. H. Thang, "Living Radical Polymerization with Reversible Addition-Fragmentation Chain Transfer (Raft Polymerization) Using Dithiocarbamates as Chain Transfer Agents." *Macromolecules*, **1999**, *32*(21), 6977-6980.

[139] B. Y. K. Chong, T. P. T. Le, G. Moad, Rizzardo E., and Thang S. H., "A More Versatile Route to Block Copolymers and Other Polymers of Complex Architecture by Living Radical Polymerization: The RAFT Process." *Macromolecules*, **1999**, *32*(6), 2071-2074.

The degree of molecular weight control typically varies with the type of monomer used. The narrowest molecular weight distribution achieved to date by Thang et al.[140] was 1.04 for the polymerization of methyl acrylate in benzene. For the polymerization of monomers containing more reactive functional groups, such as acrylic acid, the molecular weight distribution broadens to 1.23.

2.8 Comparing Anionic and Controlled Free Radical Polymerizations

Even though both techniques are living polymerizations, anionic and controlled free radical polymerizations result in products displaying different characteristics. One such direct comparison was performed very recently by Jerome et al.,[141] in which living poly (methyl methacrylate-*block*-n-butyl methacrylate-*block*-methyl methacrylate) was synthesized using both anionic polymerization and ATRP. Although both products exhibited very similar molecular weights, the anionic product polymer exhibited better characteristics such as lower molecular weight distribution, higher storage modulus, lower viscosity and higher tensile strength. These differences were attributed to significant differences in the rates of initiation relative to propagation. Anionic polymerization is initiated at a much more rapid rate than controlled free radical polymerization.

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[140] J. Chiefari, Chong Y. K., F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, and S. H. Thang, "Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process." *Macromolecules*, **1998**, *31*(16), 5559-5562.

[141] J. D. Tong, G. Moineau, P. Leclere, J. L. Bredas, R. Lazzaroni, and R. Jerome, "Synthesis, Morphology, and Mechanical Properties of Poly(Methyl Methacrylate)-*B*-Poly(N-Butyl Acrylate)-*B*-Poly(Methyl Methacrylate) Triblocks. Ligated Anionic Polymerization vs Atom Transfer Radical Polymerization." *Macromolecules*, **2000**, *33*(2), 470-479.

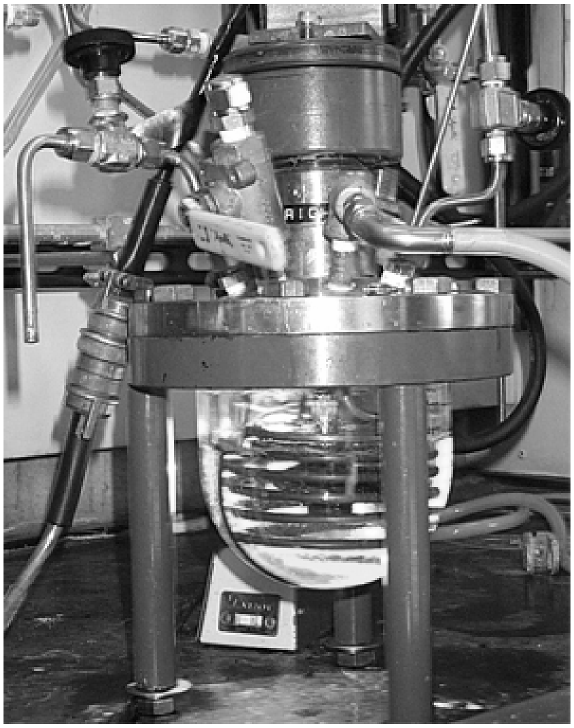

Figure 2.10: Anionic polymerization carried out in pressurized glass reactor system.

The biggest drawback to anionic polymerization is that the reaction is extremely sensitive to the presence of oxygen, water, and any protic impurities.[142] These molecules react with the propagating species and terminate the growing chains. As a result, these reactions must be carefully set up and monitored. This sensitivity has limited the use of anionic polymerization in industrial settings, with the exception of commercial isoprene or butadiene containing polymers. Ultraclean reactors, such as the one depicted in Figure 2.11, are required to prevent premature termination of the reaction. Since free-radical polymerizations are only sensitive to oxygen, they are much easier to perform and were extensively commercialized in the 20th century. Furthermore, anionic polymerization reactions are mostly limited aprotic styrenic, methacrylic, and diene monomers. The sensitivity of anionic polymerization to protic donors precludes the use of numerous commercially available monomers.

Controlled free radical polymerizations are not nearly as sensitive to environmental contaminants. As long as the oxygen is eliminated, the reactions proceed unhindered. A CaH_2 drying is sufficient to prepare the monomer for polymerization. No ultraclean gas supplies or scrupulously clean glassware is required. The rate of reaction failure due to contamination is also much lower for controlled free radical polymerization. However, the very long polymerization time is a drawback to these processes. Since the radical is capped for the majority of the time, it takes a long time to add the monomers. Anionic polymerization in polar solvents at very low temperatures is, in contrast, usually complete in less than five minutes. Living free-radical processes are

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[142] K. Hatada, T. Kitayama, S. Okahata, and Y Heimei, "Studies on the Mechanism of Polymerization of MMA in THF with BuLi at -78 °C by Using Perdeuterated Monomer," *Polym. J.*, **1981**, *13*(11), 1045-1054.

not commercially feasible due to the long polymerization times and difficulties removing the end-cappers. Additionally, are some acrylic monomers that can only be synthesized in a living fashion by anionic polymerization. Some acrylic monomers with bulky substituents in the α- position cannot typically be polymerized free radically due to the reduced reactivity and accessibility of the propagating radical.[143,144]

2.8.1 Reaction Robustness

The greatest advantage of living free radical polymerizations is an enhanced robustness over anionic polymerization. Only the presence of oxygen must be prevented. The requirement of almost absolute cleanliness in addition to low reaction temperatures, has prevented the commercial anionic polymerization of acrylates and methacrylates.[145] Since living free radical polymerizations are based on a free-radical mechanism, they are not affected by protic contaminants as significantly as anionic polymerization. Recently, nitroxide-mediated SFRP,[146] ATRP,[147,148] and RAFT[149] were successfully employed in

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[143] B. Yamada and S. Kobatake, "Radical Polymerization, Co-Polymerization, and Chain Transfer of a-Substituted Acrylic Esters." *Prog. Polym. Sci.*, **1994**, *19*(6), 1089-1131.

[144] T. Kodaira, T. Fujisawa, Q.-Q. Liu, and M. Urushisaki, "Cyclopolymerization. 22. Radical Polymerization of N-Methyl-N-Allyl-2-(Methoxycarbonyl)allylamine: Design of Unconjugated Dienes with High Polymerizability and High Cyclization Tendency Using Functional Groups of Low Polymerizabilities." *Macromolecules*, **1996**, *29*(1), 484-485.

[145] O. W. Webster, "Living Polymerization Methods," *Science*, **1991**, *251*(4996), 887-892.

[146] M. F. Cunningham, "Living/Controlled Radical Polymerizations in Dispersed Phase Systems." *Prog. Polym. Sci.*, **2002**, *27*(6), 1039-1067.

[147] S. Gaynor, J. Qiu, D. A. Shipp, and K. Matyjaszewski, "Controlled/Living Radical Polymerization Applied to Water-Borne Systems." *Polym. Mater. Sci. Eng.*, **1999**, *80*(536-537.

[148] J. Qiu, T. Pintauer, S. Gaynor, K. Matyjaszewski, B. Charleux, and J. P. Vairon, "Mechanistic Aspect of Reverse Atom Transfer Radical Polymerization of N-Butyl Methacrylate in Aqueous Dispersed System." *Macromolecules,* **2000**, *33*(20), 7310-7320.

the controlled emulsion polymerization of methacrylic monomers. The water-based emulsion system is an environment where immediate termination of anionic polymerization would occur.

Living free radical polymerizations are compatible with monomers containing functional groups that prevent a similar polymerization using the anionic route. In some cases, such as in the anionic polymerization of acrylates, bulky initiators were developed to prevent addition to the carbonyl functionality. In addition, ligating agents[150] are required to improve control over the anionic polymerization of acrylates. Functional groups were incorporated into anionically polymerized polymers via the protecting chemistry[151,152] of alcohols,[153] carboxylic acids, and aldehydes.[154] The tolerance of controlled free-radical polymerization to a wide variety of functional groups was recently described in a review by Fréchet, Hawker, et al.[155] ATRP was also used to synthesize

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[149] I. Uzulina, S. Kanagasabapathy, and J. Claverie, "Reversible Addition Fragmentation Transfer (RAFT) Polymerization in Emulsion." *Macromol. Symp.*, **2000**, *150(Polymers in Dispersed Media)*, 33-38.

[150] P. Bayard, R. Jerome, P. Teyssie, S. K. Varshney, and J. S. Wang, "A New Family of "Ligated" Initiators for the "Living" Polymerization of (Meth)Acrylic Esters." *Polym. Bull.*, **1994**, *32*(4), 381-385.

[151] D. N. Schulz, S. Datta, and R. M. Waymouth, "Use of Protecting Groups in Polymerization." *Poly. Mat. Sci. Eng.*, **1997**, *76*(3-5.

[152] A. Hirao and S. Nakahama, "Anionic Living Polymerization of Functionalized Monomers." *Acta Polymerica*, **1998**, *49*(4), 133-144.

[153] H. Ozaki, A. Hirao, and S. Nakahama, "Polymerization of Monomers Containing Functional Silyl Groups. 11. Anionic Living Polymerization of 3-(Tri-2-Propoxysilyl)propyl Methacrylate." *Macromolecules*, **1992**, *25*(5), 1391-1395.

[154] T. Ishizone, T. Utaka, Y. Ishino, A. Hirao, and S. Nakahama, "Anionic Polymerization of Monomers Containing Functional Groups. 10. Anionic Polymerizations of N-Aryl-N-(4-Vinylbenzylidene)Amines." *Macromolecules*, **1997**, *30*(21), 6458-6466.

[155] E. Harth, A. Bosman, D. Benoit, B. Helms, J. M. J. Frechet, and C. J. Hawker, "A Practical Approach to the Living Polymerization of Functionalized Monomers: Application to Block Copolymers and 3-Dimensional Macromolecular Architectures." *Macromol. Symp.*, **2001**, *174(Polymerization Processes and Polymer Materials I)*, 85-92.

block copolymers containing functional monomers such as N-alkyl acrylamide.[156] RAFT polymerization works with an even greater variety of functional monomers. Recently, Thang[157] et al. reported the direct copolymerization of acrylic acid, 2-hydroxyethyl methacrylate, and 2-(dimethylamino)ethyl methacrylate into block copolymers via RAFT polymerization.

The reaction temperatures employed in the living polymerization of acrylic and methacrylic monomers also vary vastly, depending on the method used. Anionic polymerizations must be carried out at much lower temperatures than controlled free radical reactions. For acrylic and methacrylic monomers, the temperatures vary from –78 °C to 0 °C. The extremely low temperatures required in the anionic polymerization of acrylates and methacrylates prevented commercialization. In anionic polymerization of ester-containing monomers, the temperature must be low enough that the propagating anion does not terminate. The anionic polymerization of styrenic and diene monomers did not exhibit similar temperature dependence and these reactions were carried out at temperatures as high as 60 °C. In contrast, ATRP and RAFT temperatures must be high enough that the initiator begins the polymerization. These reaction temperatures typically lie between 60 and 110 °C, depending on the polymerization initiator. Although the use of ligating agents has allowed for higher polymerization temperatures in anionic

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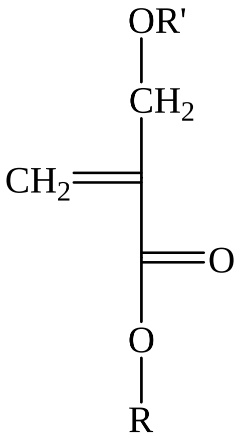
[156] Y. Liu, L. X. Wang, and C. Y. Pan, "Synthesis of Block Copoly(Styrene-*B*-*P*-Nitrophenyl Methacrylate) and Its Derivatives by Atom Transfer Radical Polymerization." *Macromolecules*, **1999**, *32*(25), 8301-8305.

[157] J. Chiefari, Chong Y. K., F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo, and S. H. Thang, "Living Free-Radical Polymerization by Reversible Addition-Fragmentation Chain Transfer: The RAFT Process." *Macromolecules*, **1998**, *31*(16), 5559-5562.

polymerization of (meth)acrylates,[158] the reaction temperatures are still significantly less than those of stable free-radical polymerizations.

2.8.2 Polymer Properties and Applications



R = Bn R' = Me
R = Bn R' = Et
R = Et R' = Et

Figure 2.11: Chemical structure of bulky acrylic monomers polymerized to high stereospecificity.

Polymers produced by anionic and controlled free radical polymerizations differ substantially in several aspects. These aspects can impact the polymers behavior and applications. Propagating controlled radicals are sp^2- planar, and therefore not stereospecific when reacting with monomers. As a result, polymers synthesized via controlled free-radical polymerizations exhibit atactic stereochemistry. A notable

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[158] D. G. H. Ballad, R. J. Bowles, D. M. Haddleton, S. N. Richards, R. Sellens, and D. L. Twose, "Controlled Polymerization of Methyl-Methacrylate Using Lithium Aluminum Alkyls." *Macromolecules*, **1992**, *25*(22), 5907-5913.

exception was the free-radical polymerization of α-(alkoxymethyl)acrylates (Figure 2.12), which were successfully polymerized in the presence of zinc dihalides, resulting in a highly isotactic polymer.[159] Anionic polymerization of this monomer achieved comparable levels of syndiotacticity.

Atactic polymers produced via typical controlled free-radical polymerization techniques cannot be used to study properties such as stereospecific self-assembly. The T_g of many polymers is also dependent of the tacticity. Ligated anionic polymerization can be used in the synthesis of either highly isotactic[160] and syndiotactic[161] methacrylic polymers. These stereoregular polymers are significant, because it was shown that isotactic and syndiotactic poly(methyl methacrylate) polymers self-assemble[162] and form complexes in solution.[163] This self-association of stereotactic PMMA was analyzed at the air-water interface using neutron reflectivity.[164] Very recently, Hatada et al. studied

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[159] S. Habaue, T. Uno, and Y. Okamoto, "Stereospecific Radical Polymerization of α-(Alkoxymethyl)acrylates Controlled by a Catalytic Amount of Zinc Halides." *Macromolecules*, **2000**, *33*(3), 820-824.

[160] K. Ute, T. Kitayama, and K. Hatada, "Studies on the Polymerization of Methyl Methacrylate with Butylmagnesium Chloride by the Aid of Totally Deuterated Monomer- Structures of Polymerization Products and Fate of Initiator." *Polym. J.*, **1986**, *18*(3), 249-261.

[161] T. Kitayama, T. Shinozaki, T. Sakamoto, M. Yamamoto, and K. Hatada, "Living and Highly Syndiotactic Polymerization of Metyl-Methacrylate and Other Methacrylates by *Tert*-Butyllithium- Trialkylaluminum in Toluene." *Makromol. Chem., Suppl.*, **1989**, *15*, 167-185.

[162] M. Nakano, M. Deguchi, H. Endo, K. Matsumoto, H. Matsuoka, and H. Yamaoka, "Self-Assembly of Poly(1,1-Diethylsilabutane)-*Block*-Poly(2-Hydroxyethyl Methacrylate) Block Copolymer. 2. Monolayer at the Air-Water Interface." *Macromolecules*, **1999**, *32*(19), 6088-6092.

[163] T. Kitayama, N. Fujimoto, Y. Terawaki, and K. Hatada, "Stereocomplex Formation between Isotactic PMMA and Syndiotactic Polymethacrylates in Bulk and in Solution." *Polym. Bull.*, **1990**, *23*(3), 279-286.

[164] J. A. Henderson and R. W. Richards, "Neutron Reflectometry from Stereotactic Isomers of Poly(Methyl Methacrylate) Monolayers Spread at the Air-Water Interface." *Polymer*, **1991**, *32*(18), 3284-3294.

the self-assembly of stereoregular methacrylic polymers on a quartz-crystal microbalance.[165]

Anionic polymerization remains the most widely used technique from which acrylic and methacrylic block copolymers can be obtained.[166] While controlled free-radical polymerizations can also afford block copolymers, those synthesized anionically usually exhibit lower molecular weight distributions.[167] Block copolymers typically exhibit higher molecular weight distributions than homopolymers, due to the terminating contaminants introduced upon addition of subsequent block monomers. In cases where the homopolymers contain high molecular weight distributions, anionic polymerization is sometimes the only viable technique for the preparation of low molecular weight distribution block copolymers containing those monomers.

The end products of both anionic and controlled free radical polymerizations are contaminated to some degree by the polymerization components present in the reaction. However, the product from a typical anionic polymerization contains only residual lithium counterions and the polymerization solvent. Both are easily removed when the polymer is precipitated. Sometimes, this step is repeated, to ensure polymer purity.

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[165] T. Serizawa, K. Hamada, T. Kitayama, N. Fujimoto, K. Hatada, and M. Akashi, "Stepwise Stereocomplex Assembly of Stereoregular Poly(Methyl Methacrylate)s on a Substrate." *J. Am. Chem. Soc.*, **2000**, *122*(9), 1891-1899.

[166] E. Ruckenstein and H. M. Zhang, "Living Anionic Copolymerization of 1-(Alkoxy)ethyl Methacrylates with Polar and/or Nonpolar Monomers and the Preparation of Amphiphilic Block Copolymers Containing Poly(Methacrylic Acid) Hydrophilic Segments at Higher Temperatures Than Usually Employed." *Macromolecules*, **1998**, *31*(26), 9127-9133.

[167] C. D. DePorter, T. E. Long, and J. E. McGrath, "Methacrylate- Based Block Ionomers. 1. Synthesis of Block Ionomers Derived from *T*-Butyl Methacrylate and Alkyl Methacrylates." *Polym. Int.*, **1994**, *33*(2), 205-216.

Polymeric systems that are studied in polymer physical chemistry often rely on anionically-polymerized polymers due to this lack of reaction contaminants and narrow molecular weight distributions.

The capping agents used in controlled free radical polymerizations become incorporated into the product polymer. This causes problems in applications where pure polymeric materials are required. A negative feature of ATRP is that the final product contains some CuBr which was difficult to remove. The presence of CuBr is very undesirable, since it is toxic. Some progress was made in removing this capping agent using an ion exchange resin;[168] however, this approach is not commercially feasible. The RAFT polymerization also suffers from a similar contamination. The incorporation of the dithio-containing transfer reagent into the product results in a yellow color, which makes the polymer less appealing as a commercial product.

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[168] K. Matyjaszewski, T. Pintauer, and S. Gaynor, "Removal of Copper-Based Catalyst in Atom Transfer Radical Polymerization Using Ion Exchange Resins." *Macromolecules*, **2000**, *33*(4), 1476-1478.

Chapter 3: Investigations of Chemical Cleavage of Branched Polymers for Performance and Characterization

3.1 Controlled Hydrolytic Cleavage of Branching Sites

3.1.1 Cleavable Network Topologies

Polyester-based hydrolyzable polymers were designed for a number of applications from biomedical materials to recyclable thermoplastics. Linear and branched biocompatible polymers enjoy widespread use in the medical field as sutures[169] and in structural tissue applications.[170] Many biocompatible polymers are designed to slowly hydrolyze to prevent subsequent removal from the body. Tailoring biodegradable polymers enables the use of these materials in different applications that require very different degradation rates. For example, a surgical suture needs to be intact for a much shorter time than a scaffold material used for the regeneration of bone tissue. Crosslinking functional groups were also incorporated into hydrogels that were sensitive to enzymatic degradation. For example, phenylazo crosslinking units were incorporated into hydrogels (Figure 3.1) via the dimerization reactions between two types of network precursor polymer functional groups.[171] These hydrogels were cleaved in the presence of rat cecum. Hydrolysis rates were most strongly dependent on crosslinking density.

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[169] A. K. Agrawal and R. Bhalla, "Advances in the Production of Poly(Lactic Acid) Fibers. A Review." *J. Macromol. Sci. C Polym. Rev.*, **2003**, *43*(4), 479-503.

[170] X. H. Liu and P. X. Ma, "Polymeric Scaffolds for Bone Tissue Engineering." *Ann. Biomed. Eng.*, **2004**, *32*(3), 477-486.

[171] D. Wang, K. Dusek, P. Kopeckova, M. Duskova-Smrckova, and J. Kopecek, "Novel Aromatic Azo-Containing pH-Sensitive Hydrogels: Synthesis and Characterization." *Macromolecules*, **2002**, *35*(20), 7791-7803.

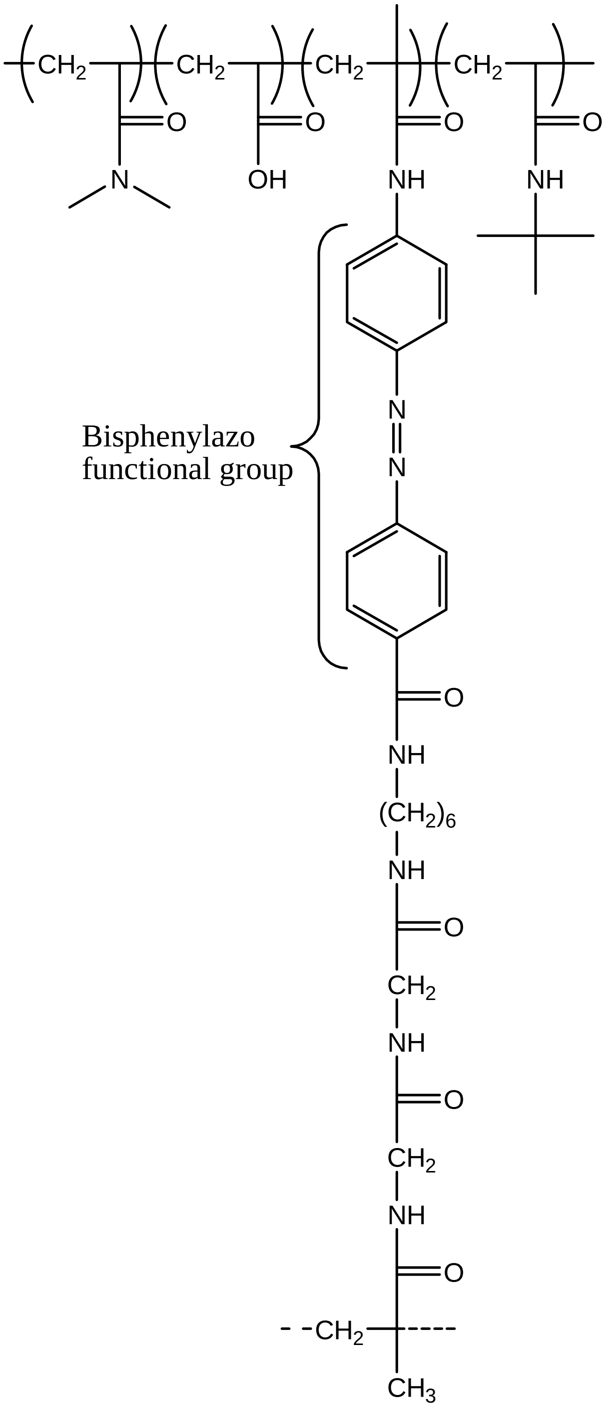

Figure 3.1: Structure of a hydrogel containing the enzymatically cleavable bisphenylazo crosslinking group

Hemiacetal esters were utilized in the synthesis of highly degradable polymer topologies, due to the sensitivity of the functional group to hydrolysis. The novel monomer 1-methoxyallyl methacrylate (MOAMA) was synthesized and homopolymerized under either conventional free-radical or living anionic polymerization (Figure 3.2).[172] The topology of the product polymer was determined by the polymerization, due to the fact that the allyl functional group copolymerized under free-radical conditions, leading to crosslinking. The propagating living enolate anion, in contrast, could not propagate through the allyl functional groups. Thus, network and linear poly(MOAMA) were produced that underwent rapid degradation when subjected to hydrolytic conditions. Hydrolyzable hydrophilic network polymers were synthesized by Frechét et al. that contained reactive phenylacetal functional groups in the crosslinking units. These networks underwent hydrolysis, releasing the bovine serum albumin drug analog gradually (Figure 3.3).[173,174]

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[172] H. Otsuka, K.-I. Mori, and T. Endo, "Novel Reactive Polymers Containing Hemiacetal Ester and Vinyl Moieties: Synthesis and Selective Polymerization of 1-Methoxyallyl Methacrylate Derived from Methacrylic Acid and Methoxyallene." *Macromol. Rapid Comm.*, **2001**, *22*(16), 1335-1339.

[173] N. Murthy, Y. X. Thng, S. Schuck, M .C. Xu, and J. M. J. Frechét, "A Novel Strategy for Encapsulation and Release of Proteins: Hydrogels and Microgels with Acid-Labile Acetal Cross-Linkers." *J. Am. Chem. Soc.*, **2002**, *124*(42), 12398-12399.

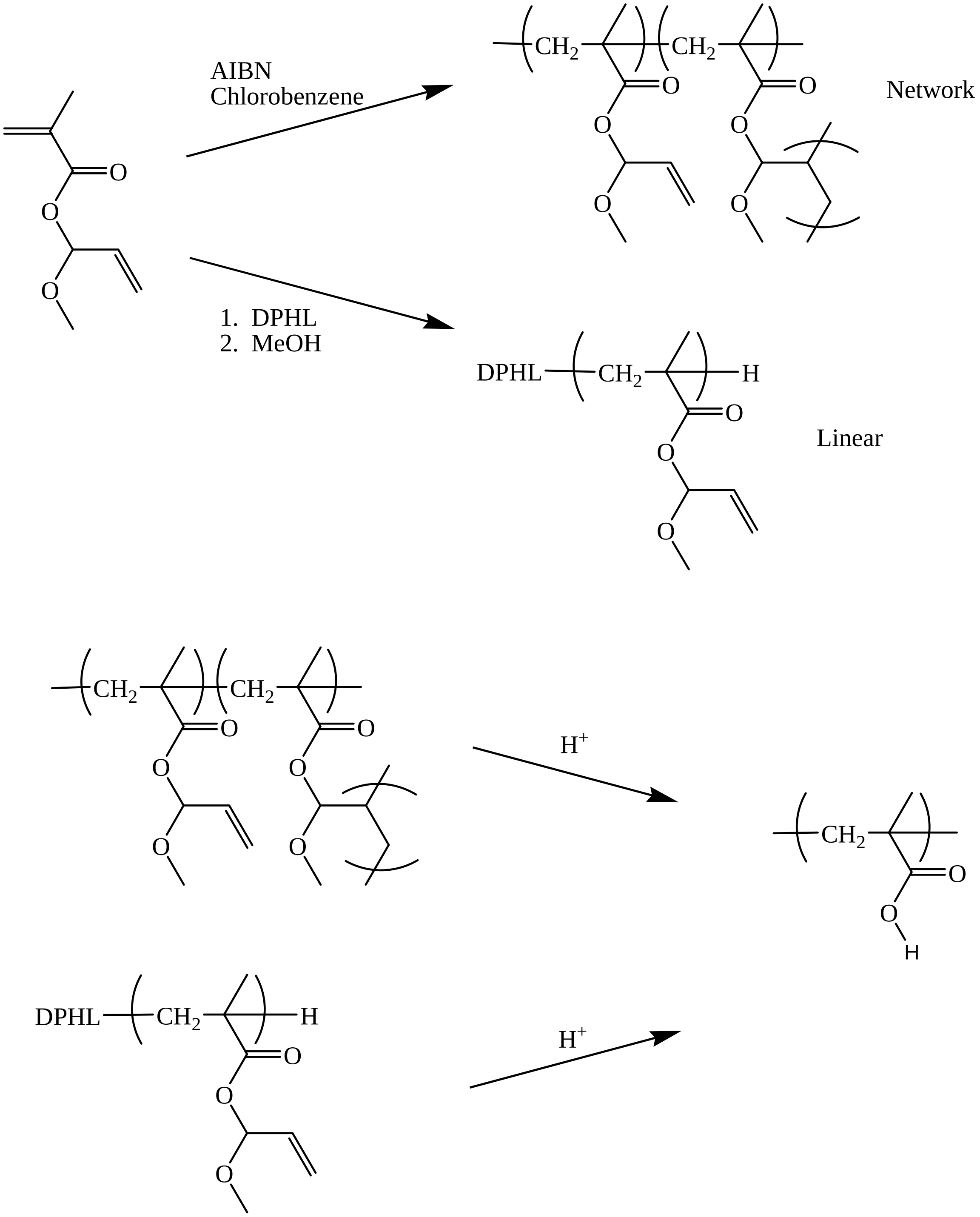

Figure 3.2: Polymer topology of poly(MOAMA) depended on the polymerization

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[174] J. M. J. Frechét and N. Murthy, "Microgel Particles for the Delivery of Bioactive Materials." *WO* 2003082316, **2003**.

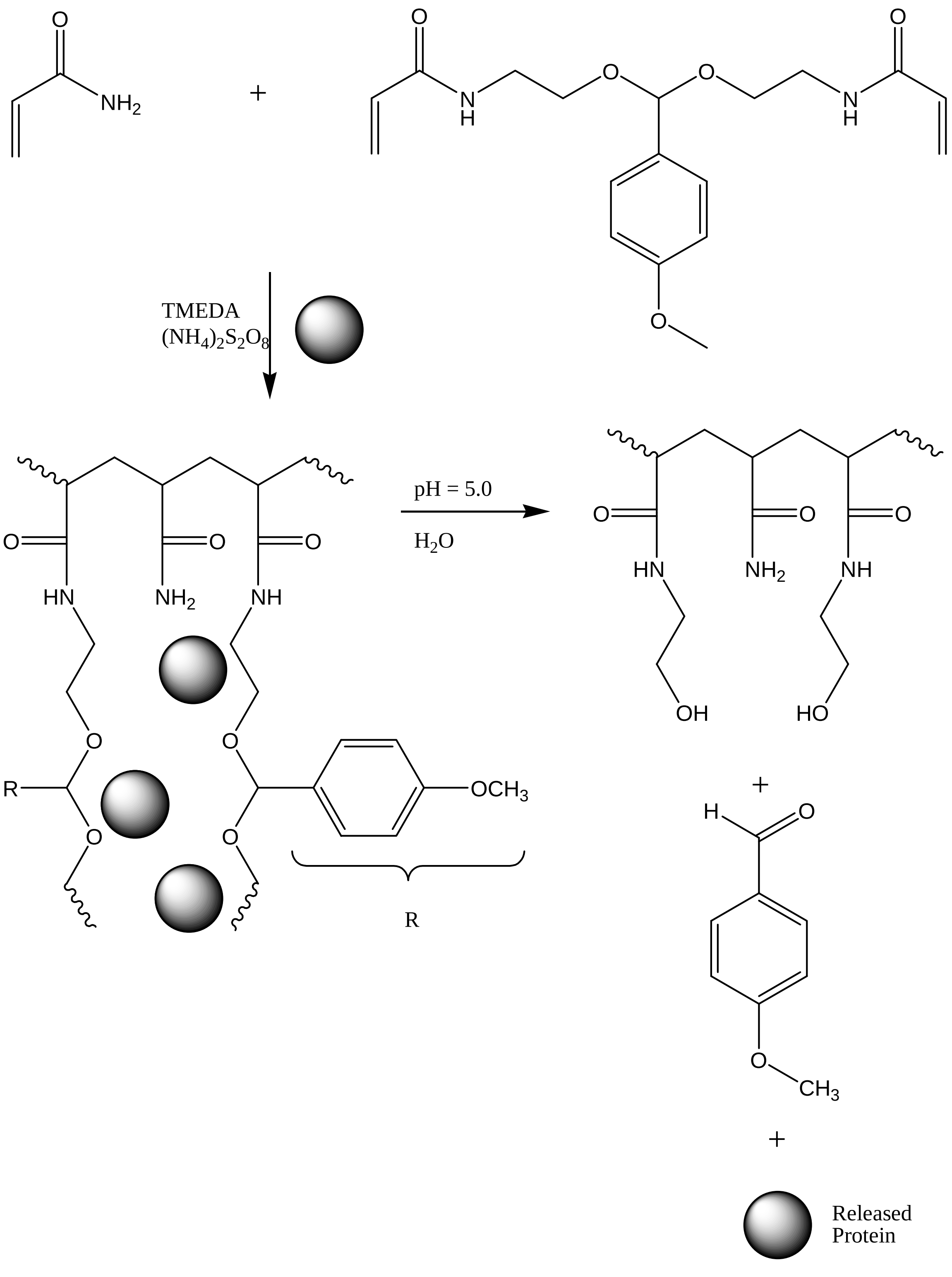

Figure 3.3: Drug delivery system based on hemiacetal hydrolysis

Hemiacetal ester-containing hydrolytically unstable star polymers containing unreactive arm polymers were also synthesized via the arm-first approach. Poly(methyl methacrylate) arm polymers were synthesized via living anionic polymerization, and the living arms were coupled using a novel dimethacrylate monomer containing two hemiacetal functional groups.[175] These star polymers rapidly cleaved in slightly acidic water and room temperatures (Figure 3.4). Cleavable network polymers containing this di(hemiacetal) were also synthesized, and these polymers exhibited slower degradation kinetics than the star polymers under identical conditions. Star-shaped polymers containing other types of cleavable functional groups were also synthesized previously. Most cleavable star-shaped polymers reported previously were designed to exhibit significant sensitivity to water-based hydrolysis under either catalyzed or uncatalyzed environments. Star-shaped polymers were synthesized via an arm-first approach containing divinylbenzene cores and polycaprolactone arm polymers. These star polymers slowly cleaved after dissolution in water as the caprolactone functional units were hydrolyzed.

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[175] E. Ruckenstein and H. Zhang, "A Novel Breakable Cross-Linker and pH-Responsive Star-Shaped and Gel Polymers." *Macromolecules*, **1999**, *32*(12), 3979-3983.

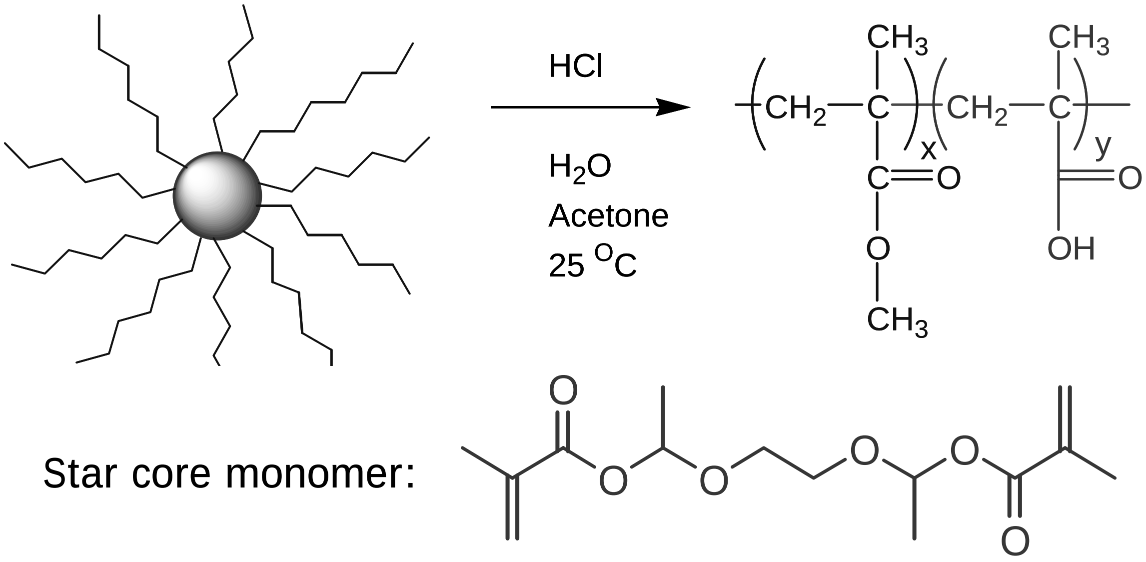

Figure 3.4: Acid-catalyzed hydrolysis of star polymers containing dihemiacetal cores.

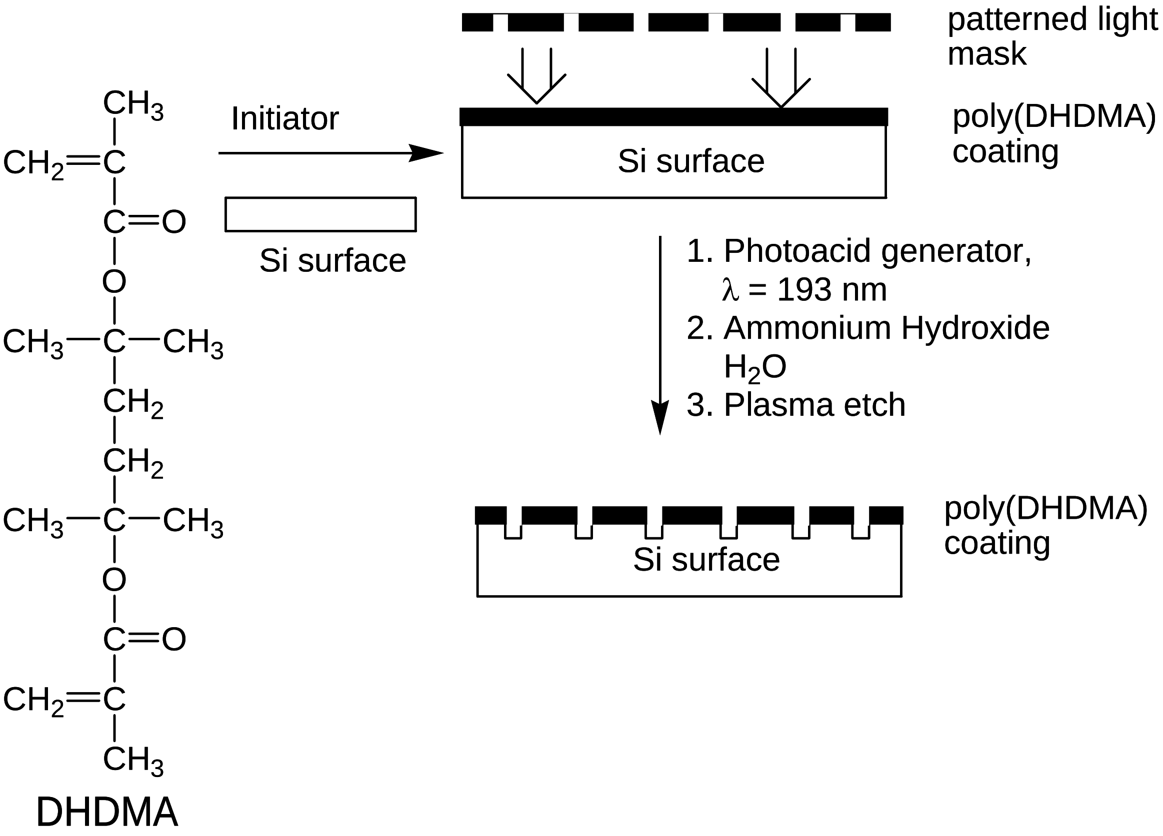

Figure 3.5: Utilization of acid-cleavable DHDMA in nanolithographic coatings

The most common functional group utilized in the hydrolysis of biodegradable polymers were secondary and tertiary ester linkages, whose degradation is accelerated under acidic conditions. Cleavable polymers containing *tert*-butyl ester bonds were designed to be sensitive to either hydrolytic or anhydrous acidic conditions. The monomer 2,5-dimethyl-2,5-hexanediol, which was used previously to synthesize cleavable crosslinked coatings for microlithography (Figure 3.5),[176] coupled living poly(isobutyl methacrylate) arm polymers into cleavable star polymers.[177,178] These star polymers were cleaved into linear arm polymers containing a short polymethacrylic acid block upon acid-catalyzed hydrolysis at elevated temperatures. Star polymer sensitivity to hydrolysis was tuned by introducing a benzene ring to the crosslinking monomers, which stabilized both the hydrolysis intermediates and the by-product.[179]

Aliphatic ester containing hydrogels[180] and other branched polymer topologies are widely utilized in biomedical applications. Network polymers are the most common polymer topology used in biodegradable polymer systems. Biodegradable scaffold network polymers provide a framework for cells to diffuse into, and they grew in the biocompatible matrix, gradually replacing the destroyed tissue. Applications for scaffold

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[176] P. R. Varanasi, A. D. Katnani, M. M. Khojasteh, and R. W. Kwong, "Photoresist Compositions with Pendant Polar-Functionalized Groups and Acid-Labile Branching." *US* 6,140,015, **2000**.

[177] L. Kilian, Z.-H. Wang, A. R. Esker, and T. E. Long, "Topological Reorganization of Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **2002**, *43*(1), 332-333.

[178] T. E. Long, L. Kilian, Z.-H. Wang, and A. R. Esker, "Synthesis and Characterization of Novel Acid-Sensitive Tert-Butyl Methacrylate and Isobutyl Methacrylate Containing Star-Shaped Polymers." *Proc. SPIE- Soc. Opt. Eng.*, **2001**, *4512(Complex Adaptive Structures)*, 65-74.

[179] L. Kilian, Z.-H. Wang, and T. E. Long, "Synthesis and Cleavage of Core-Labile Poly(Alkyl Methacrylate) Star Polymers." *J. Polym. Sci. A Polym. Chem.*, **2003**, *41*(19), 3083-3093.

[180] A. S. Hoffman, "Hydrogels for Biomedical Applications." *Adv. Drug. Del. Rev.*, **2002**, *43*(1), 3-12.

polymers include the regeneration of cartilage[181] and bone.[182] One of the most important requirements of these systems is that the polymers must cause specific cells to adhere to them and begin growing. For example, the biodegradable poly(lactic acid-*co*-lysine) polymer has been modified with the cell-adhesive polypeptide sequence arginine-glycine-aspartic acid[183,184] to promote cell-adhesion and spreading.[185]

Biocompatible hydrogels were obtained from a large variety of natural and synthetic sources.[186] In addition to the influences of degradation by the chemical composition of the network, the network morphology impacts the degradation behavior. The most significant of these characteristics is the crosslinking density. The rate of hydrolysis of network polymers is often strongly dependent on the crosslink density, in particular hydrogels.[187] The hydrolysis rate dependence is due to the fact that the only restriction to water diffusion into the network is how tightly the chains are crosslinked. When water diffuses into these hydrophilic networks, a great deal of swelling occurs,

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[181] J. S. Temenoff and A. G. Mikos, "Review: Tissue Engineering for Regeneration of Articular Cartilage." *Biomaterials*, **2000**, *21*(5), 431-440.

[182] J. C. Middleton and A. J. Tipton, "Synthetic Biodegradable Polymers as Orthopedic Devices." *Biomaterials*, **2000**, *21*(23), 2335-2346.

[183] D. A. Barrerra, E. Zylstra, P. T. Lansbury, and R. Langer, "Copolymerization and Degradation of Poly(Lactic Acid-*co*-Lysine)." *Macromolecules*, **1995**, *28*(2), 425-432.

[184] D. A. Barrerra, E. Zylstra, P. T. Lansbury, and R. Langer, "Synthesis and RGD Peptide Modification of a New Biodegradable Copolymer Poly(Lactic Acid-*co*-Glycine)." *J. Am. Chem. Soc.*, **1993**, *115*(23), 11010-11011.

[185] M. D. Pierschbacher and E. Ruoslahti, "Cell Attachment Activity of Fibronectin Can Be Duplicated by Small Synthetic Fragments of the Molecule." *Nature*, **1984**, *309*(5936), 30-33.

[186] K. Y. Lee and D. J. Mooney, "Hydrogels for Tissue Engineering." *Chem. Rev.*, **2001**, *101*(7), 1869-1880.

[187] S. J. Bryant, C. R. Nuttelman, and K. S. Anseth, "The Effects of Crosslinking Density of Cartilabe Formation in Photocrosslinkable Hydrogels." *Biomed. Sci. Instrum.*, **1999**, *35*(35), 309-314.

which further accelerates degradation. Conversely, tightly crosslinked networks slow the rate of degradation and promote the surface-erosion degradation pathway.[188]

Although networks based on aggregating physical crosslinks were developed previously,[189] hydrolytic degradation remains the primary methodology for hydrogel degradation. A more hydrophilic biodegradable network is more accessible to water, and hydrolysis proceeds at a faster rate as a result. Anseth et al. showed that methacrylate networks composed of the hydrophilic monomer methacrylated sebacic acid degrade approximately 165 times faster than networks containing the much less polar monomer methacrylated 1,6-bis(*p*-carboxyphenoxy) hexane.[190] Network polymers that were comprised of a mixture of the two monomers (Figure 3.6) exhibited an intermediate degradation behavior. Based on their study, the authors concluded that it was possible to synthesize network systems with specifically designed degradation rates based on the relative amounts of hydrophobic and hydrophilic comonomer. Similarly, the hydrolytic stability of poly(ethylene glycol) networks was tuned so that this slowly degradable polymeric network responded much more rapidly to hydrolytic conditions. A variety of hydrolyzable comonomers were used in PEG networks, including lactide,[191] ε-caprolactone,[192] and propylene fumarate.[193]

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[188] A. K. Burkoth and K. S. Anseth, "A Review of Photocrosslinked Polyanhydrides: In Situ Forming Degradable Networks." *Biomaterials*, **2000**, *21*(23), 2395-2404.

[189] B. Jeong , S. W. Kim , and Y. H. Bae, "Thermosensitive Sol–Gel Reversible Hydrogels." *Adv. Drug. Del. Rev.*, **2002**, *54*(1), 37-51.

[190] A. K. Burkoth and K. S. Anseth, "A Review of Photocrosslinked Polyanhydrides: In Situ Forming Degradable Networks." *Biomaterials*, **2000**, *21*(23), 2395-2404.

[191] D. K. Han and J. A. Hubbell, "Lactide-Based Poly(Ethylene Glycol) Polymer Networks for Scaffolds in Tissue Engineering." *Macromolecules*, **1996**, *29*(15), 5233-5235.

[192] A. B. Argade and N. A. Peppas, "Preparation and Characterization of Novel Biodegradable Tri- and Tetraacrylate Intermediates." *Polym. Bull.*, **1993**, *31*(4), 401-407.

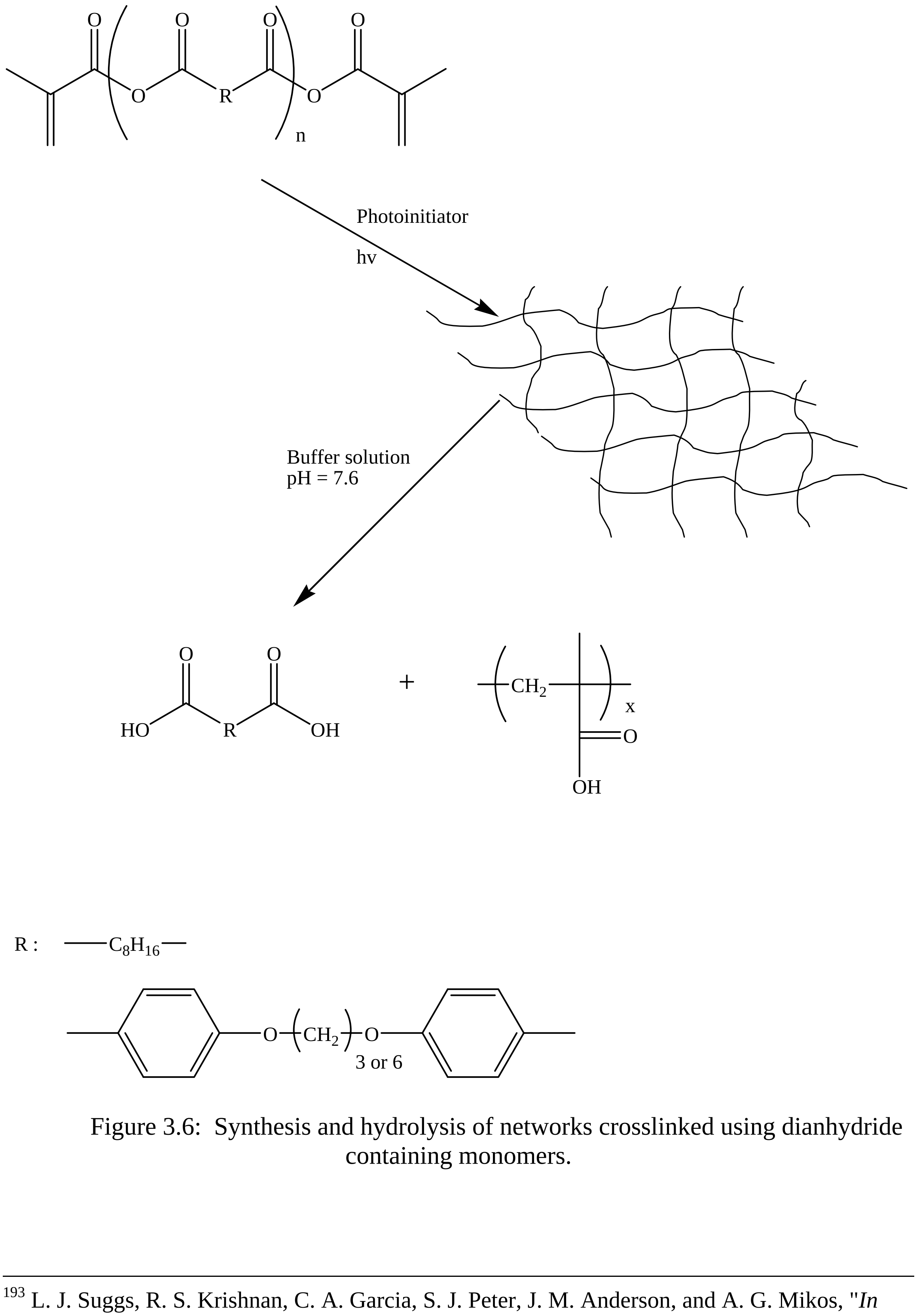

Figure 3.6: Synthesis and hydrolysis of networks crosslinked using dianhydride containing monomers.

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[193] L. J. Suggs, R. S. Krishnan, C. A. Garcia, S. J. Peter, J. M. Anderson, and A. G. Mikos, "*In Vitro and in Vivo* Degradation of Poly(Propylene Fumarate-*co*-Ethylene Glycol) Hydrogels," *J. Biomed. Mater. Res.*, **1998**, *42*(2), 312-320.

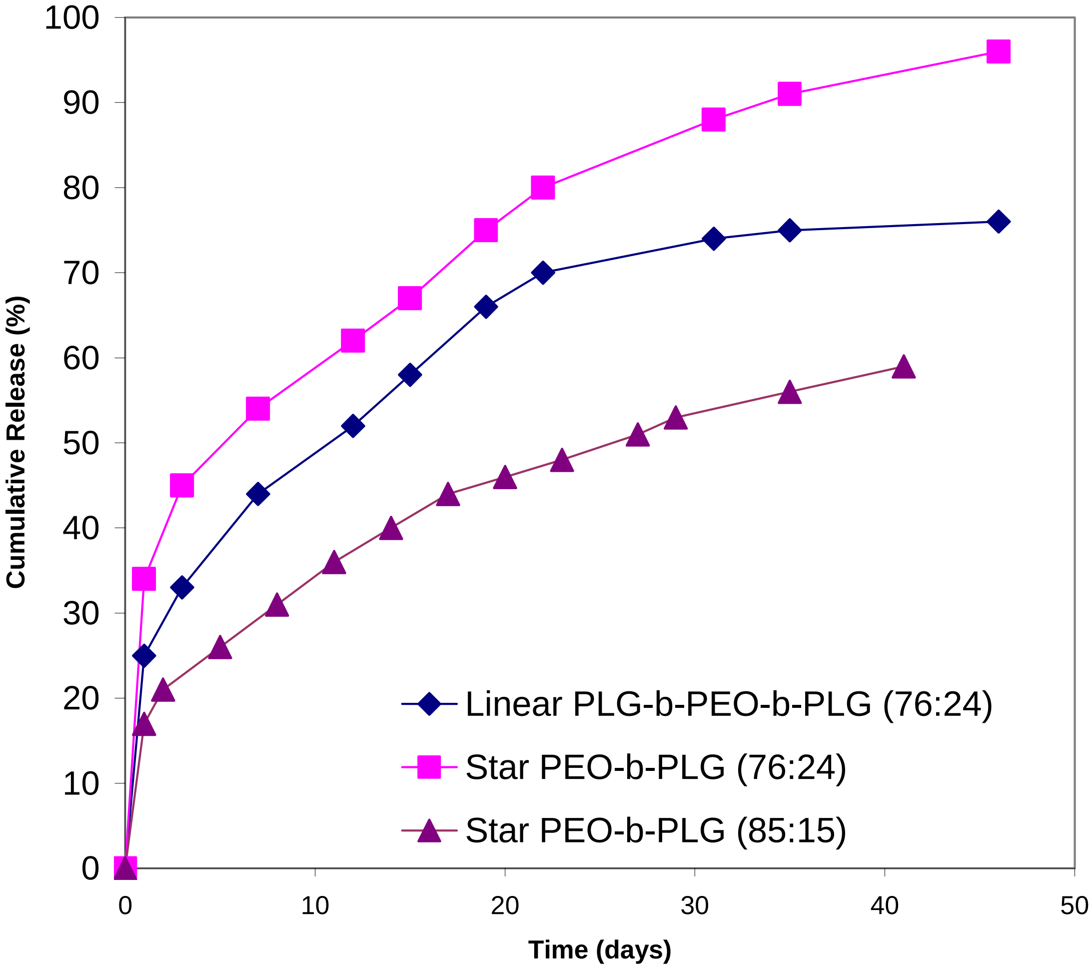

Figure 3.7: Topology effects on drug release of PEO-*block*-PLG delivery systems

Network polymers used in the controlled release of small molecules must exhibit a pore size that is small enough to trap the small molecules. Otherwise, the molecules can diffuse out of the network and controlled release is not possible. The pore size of networks such as a poly(ethylene glycol) network containing labile α-hydroxy acid groups can change as a function of the degree of hydrolysis,[194] as the molecular weight between crosslinks increased. Hydrolyzable networks can be designed to minimize changes in pore size, so that the network does not release all of the trapped molecules after only limited degradation. Drug-releasing hydrolyzable network polymers containing anhydride crosslinking points were also synthesized previously.[195,196] These polymers hydrolyzed very rapidly due to the high reactivity of anhydrides towards hydrolysis. In some biodegradable polymers, anhydride cleavage was shown to occur more rapidly than the subsequent dissolution of the hydrolysis products into water.[197] Linear degradable polymers are not suitable for the steady release of high-molecular weight proteins and other therapeutic molecules, because of the significant impact of diffusion on the release of these molecules.[198] Star, graft, and network polymers were synthesized to overcome this shortcoming (Figure 3.7).[199]

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[194] S. Lu and K. S. Anseth, "Release Behavior of High Molecular Weight Solutes from Poly(Ethylene Glycol)-Based Degradable Networks." *Macromolecules*, **2000**, *33*(7), 2509-2515.

[195] K. Uhrich, K. Whitaker, and R. Schmeltzer, "Poly(Anhydride-Ester) Degradation: Mechanical Changes and Correlation to Antibiotic Release." *Poly. Mat. Sci. Eng.*, **2001**, *84*, 215.

[196] G. Cheng, M. A. Aponte, and C. A. Ramirez, "Synthesis and Characterization of Cross-Linked Amino Acid-Containing Polyanhydrides for Controlled Drug Release Applications." *Poly. Mat. Sci. Eng.*, **2003**, *89*, 618-619.

[197] J. O. Seidel, K. E. Uhrich, C. T. Laurencin, and R. Langer, "Erosion of Poly(Anhydride-*co*-Imides): A Preliminary Mechanistic Study." *J. Appl. Polym. Sci.*, **1996**, *62*(8), 1277-1283.

[198] D. Bodmer, T. Kissel, and E. Traechslin, "Factors Influencing the Release of Peptides and Proteins from Biodegradable Parenteral Depot Systems." *J. Controlled Release*, **1992**, *21*(1-3), 129–138.

[199] A. Breitenbach, Y. X. Li, and T. Kissel, "Branched Biodegradable Polyesters for Parenteral Drug Delivery Systems." *J. Controlled Release*, **2000**, *64*(2-3), 167-178.

3.1.2 Cleavable Branched Topologies

Graft copolymers containing hydrolyzable graft chains and/or cleavable branching sites were synthesized and hydrolyzed. 2-Hydroxypropyl methacrylamide was copolymerized with acrylamide-terminated polylactide.[200] The polylactide graft chains were hydrolyzed, and hydrolysis times could be tuned by changing the relative amounts of polylactide macromonomer. The controlled hydrolysis of graft copolymers was investigated further a possible controlled drug release application. Graft polyester containing polyglycolic acid graft chains were synthesized from several polyalcohol backbones via ring-opening polymerization. The graft chains exhibited hydrolysis kinetics were strongly dependent on the hydrophilicity of the backbone.[201]

Dendrimer and hyperbranched polymers contain many more end groups per polymer than other branched topologies. The properties of the end-groups exert greater influence of the overall polymer properties as a result. Amine-terminated PAMAM dendrimers were functionalized with polylactide graft chains, and the starburst dendrimer degradation relative to linear polylactide was evaluated.[202] The dendrimer exhibited greater water solubility due to the greatly increased number of alcohol end groups. The faster PLA degradation rates in the dendrimers were attributed to the end group concentrations and relatively lower PLA molecular weights.

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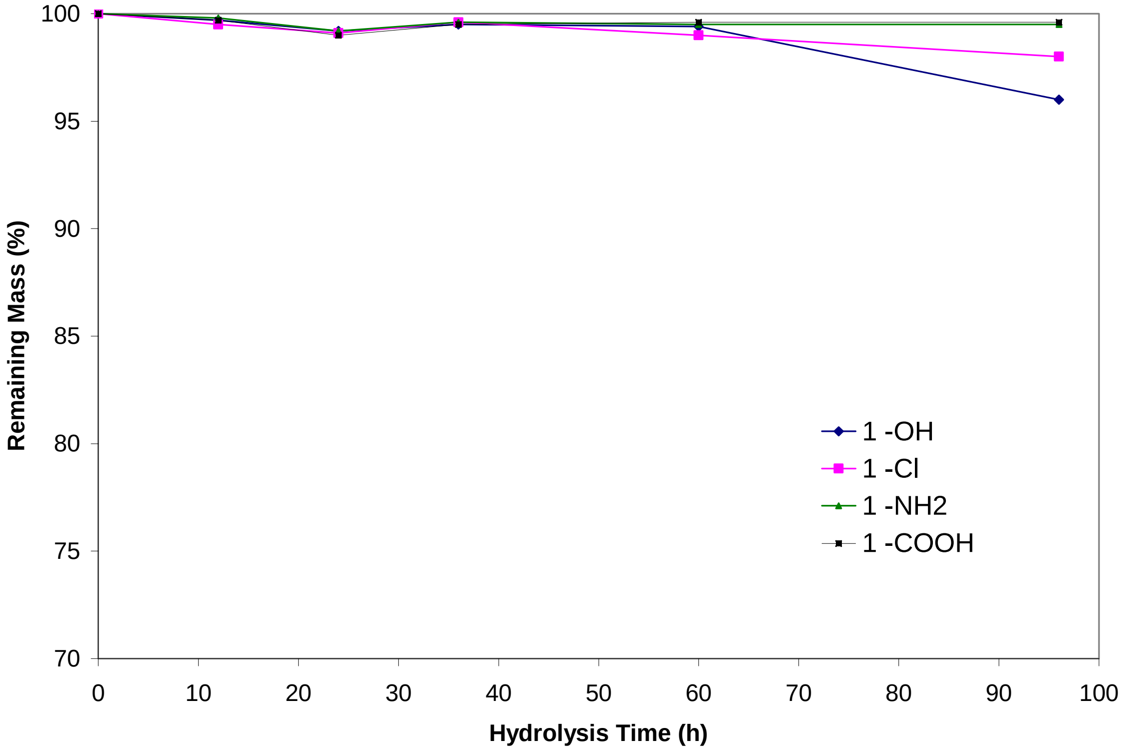
[200] C. F. van Nostrum, T. F. J. Veldhuis, G. W. Bos, and W. E. Hennink, "Tuning the Degradation Rate of Poly(2-Hydroxypropyl Methacrylamide)-*Graft*-Oligo(Lactic Acid) Stereocomplex Hydrogels." *Macromolecules*, **2004**, *37*(6), 2113-2118.

[201] A. Breitenbach, Y. X. Li, and T. Kissel, "Branched Biodegradable Polyesters for Parenteral Drug Delivery Systems." *J. Controlled Release*, **2000**, *64*(2-3), 167-178.

[202] Q. Cai, Y. Zhao, J. Bei, F. Xi, and S. Wang, "Synthesis and Properties of Star-Shaped Polylactide Attached to Poly(Amidoamine) Dendrimer." *Biomacromolecules*, **2004**, *4*(3), 828-834.



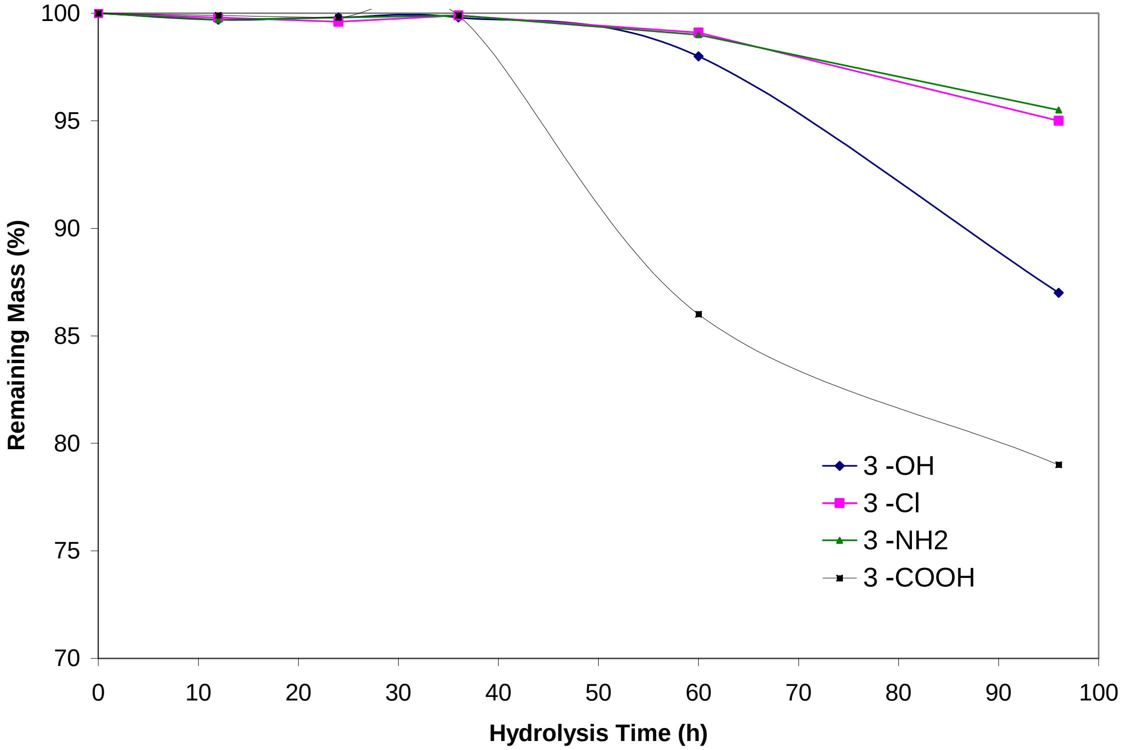


Figure 3.8: Effect of topology on hydrolytic degradation of polylactide in phosphate buffer.

The end group effect on stability was also examined in polylactide topologies. Linear and star polylactides were synthesized bearing either hydroxy, chloro, amino, or carboxylic acid end groups.[203] The carboxylic acid and alcohol containing polymers exhibited the least thermal stability, presumably due to the presence of the acidic functional group, which catalyzes ester cleavage. The stability effects were magnified in the star polymers initiated from pentaerythritol due to the higher amounts of end groups in the star polymer relative to the linear polymer (4:1). Similar effects were observed in the hydrolytic degradation of these polymers due to the increased solubility that was afforded by the end groups. The three-armed star polymers containing either the hydroxy or acid groups degraded much faster than the linear polylactides (Figure 3.8) In a related work, it was shown that microspheres comprised of alcohol-terminated four-armed polylactide star polymers released drug molecule analogs much faster than the linear polymers due to the enhanced degradation rate.[204]

Polymer brushes were useful in the modification of surface properties of inorganic solids[205] and organic polymers. Extremely fine microlithographic surface details were also created via a combination of conventional microlithography with the growth of surface-bound brushes exhibiting controlled molecular-weight, and thus

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[203] S.-H. Lee, S. H. Kim, Y.-K. Han, and Y. H. Kim, "Synthesis and Degradation of End-Group-Functionalized Polylactide." *J. Polym. Sci. A Poly. Chem.*, **2001**, *39*(7), 973-985.

[204] A. Breitenbach, Y. X. Li, and T. Kissel, "Branched Biodegradable Polyesters for Parenteral Drug Delivery Systems." *J. Controlled Release*, **2000**, *64*(2-3), 167-178.

[205] J. Wang, S. Kara, T. E. Long, and T. C. Ward, "Synthesis of Central Functionalized Asymmetric Triblock Copolymers for Surface Modification and Switchable Surface Properties." *J. Polym. Sci. A Poly. Chem.*, **2000**, *38*(20), 3742-3750.

thickness.[206] Although well-defined polymers were covalently attached to the substrate surfaces previously,[207] this technique often suffers from low grafting densities. An alternate approach to the synthesis of polymer brushes is the grafting from approach,[208] in which the surface was functionalized with a high density of polymerization initiating sites, followed by the living polymerization of the polymer brushes. However, these brush polymers are difficult to analyze, since they were covalently bound to the surface. Ester hydrolysis provided an excellent means for the cleavage to brush attachment sites. ATRP initiating sites containing a tert-butyl ester functional group were typically used in the synthesis of removable brushes. Brush cleavage was utilized in the development of a model that enabled molecular weight approximations of polymer brushes based on AFM.[209]

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[206] T. A. von Werne, D. S. Germack, E. C. Hagberg, V. V. Sheares, C. J. Hawker, and K. R. Carter, "A Versatile Method for Tuning the Chemistry and Size of Nanoscopic Features by Living Free Radical Polymerization." *J. Am. Chem. Soc.*, **2003**, *125*(13), 3831-3838.

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[208] M. Husemann, M. Morrison, D. Benoit, K. J. Frommer, C. M. Mate, W. D. Hinsberg, J. L. Hedrick, and C. J. Hawker, "Manipulation of Surface Properties by Patterning of Covalently Bound Polymer Brushes." *J. Am. Chem. Soc.*, **2000**, *122*(8), 1844-1845.

[209] D. Goodman, J. N. Kizhakkedathu, and D. E. Brooks, "Evaluation of an Atomic Force Microscopy Pull-Off Method for Measuring Molecular Weight and Polydispersity of Polymer Brushes: Effect of Grafting Density." *Langmuir*, **2004**, *20*(15), 6238-6245.

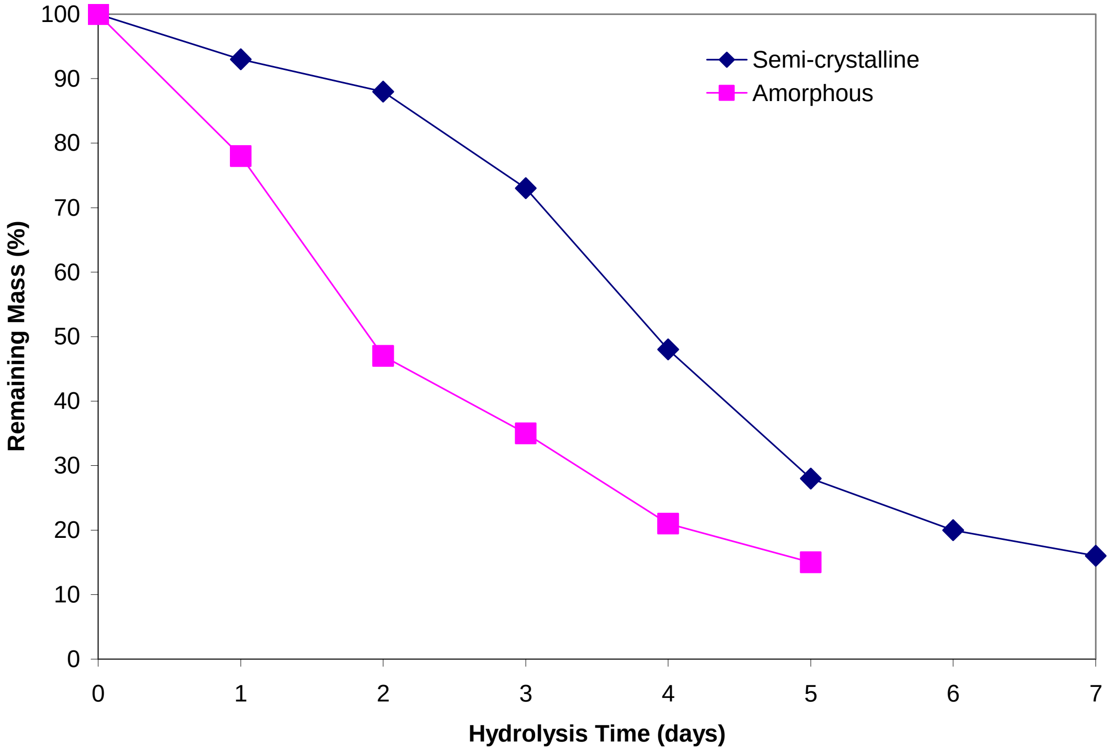

Figure 3.9: Weight loss dependence on the crystallinity of 9:1 poly(glycolic acid-*co*-lactic acid)

Diffusion of water into degradable polymers and subsequent hydrolysis is much more readily accomplished in amorphous polymers than in semicrystalline ones. A representative study of the effects of the presence of polymeric crystals was carried out by Hsiao et al. on biodegradable polymers containing glycolide.[210] The polymer crystals were shown to be much more resistant to hydrolysis than the amorphous phase. Similarly, semicrystalline poly(L-lactide) hydrolyzes very quickly if it is quenched from the melt relative to the semicrystalline morphology (Figure 3.9).[211] Branching sites are known to hinder polymer crystallization,[212] and as a result, branching sites can be used to accelerate degradation kinetics. A branched anhydride-containing polyester was synthesized previously which contained the polyol glycerin.[213] This branched hydrolyzable polymer exhibited lower levels of crystallinity than the linear counterpart. Faster morphine release was observed when a 1,3,5 benzenetricarboxylic acid- branched polyanhydride was hydrolyzed relative to the linear polyanhydride lacking the branching reagent.[214]

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[210] W.-H. Zong, Z.-G. Wang, B. S. Hsiao, B. Chu, J. J. Zhou, D. D. Jamiolkowski, E. Muse, and E. Dormier, "Structure and Morphology Changes in Absorbable Poly(Glycolide) and Poly(Glycolide-*co*-Lactide) During *in Vitro* Degradation." *Macromolecules*, **1999**, *32*(24), 8107-8114.

[211] A. Browning and C. C. Chu, "The Effect of Annealing Treatments on the Tensile Properties and Hydrolytic Degradative Properties of Polyglycolic Acid Sutures." *J. Biomed. Mater. Res.*, **1986**, *20*(5), 613-632.

[212] J. C. Sworen, J. A. Smith, K. B. Wagner, L. S. Baugh, and S. P. Rucker, "Modeling Random Methyl Branching in Ethylene/ Propylene Copolymers Using Metathesis Chemistry: Synthesis and Thermal Behavior." *J. Am. Chem. Soc.*, **2003**, *125*(8), 2228-2240.

[213] C.-K. Chan and I.-M. Chu, "Synthesis and Characterization of Highly Branched Poly(Anhydride-Co-Glycol) with Glycerin as Branching Agent." *J. Appl. Polym. Sci.*, **2003**, *90*(3), 886-893.

[214] M. Maniar, X. Xie, and A. J. Domb, "Polyanhydrides. V. Branched Polyanhydrides." *Biomaterials,* **1990**, *11*(9), 690-694.

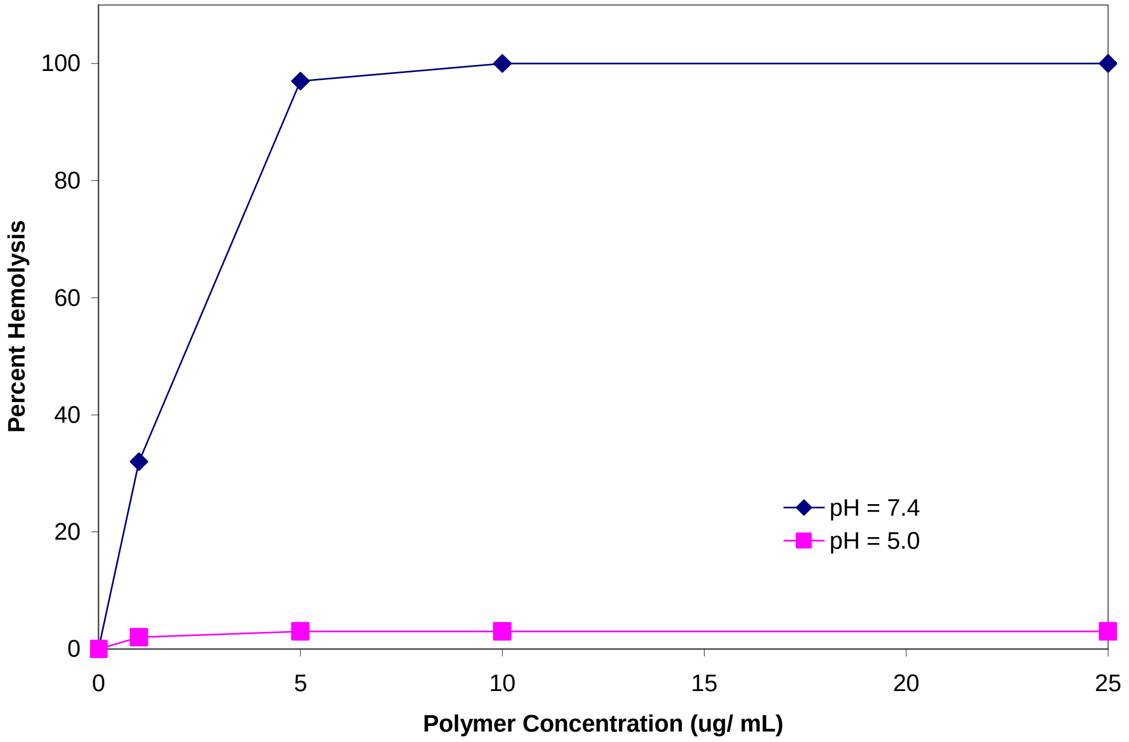

Figure 3.10: Dependence of hydrolyzable graft copolymer physiological activity on pH

Graft copolymers containing phenylacetal branching sites were synthesized in order to be utilized as targeted biodelivery reagents.[215] The phenylacetal functional group underwent very slow hydrolysis at physiological pH, and rapidly hydrolyzed at a pH of 5.4. The initial graft copolymer was not biologically active; however, the graft copolymer backbone liberated as a result of hydrolysis was designed to disrupted cellular membranes.[216] Complete membrane disruption by the graft copolymer hydrolysis product occurred rapidly and selectively at a pH of 5.0, while very little occurred at pH = 7.4 (Figure 3.10).

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[215] N. Murthy, J. Campbell, N. Fausto, A. S. Hoffman, and P. S. Stayton, "Bioinspired pH-Responsive Polymers for the Intracellular Delivery of Biomolecular Drugs." *Bioconjugate Chem.*, **2003**, *14*(2), 412-419.

[216] N. Murthy, I. Chang, P. Stayton, and A. Hoffman, "Ph-Sensitive Hemolysis by Random Copolymers of Alkyl Acrylates and Acrylic Acid," *Macromol. Symp.*, **2003**, *172(Polymers in Medicine)*, 49-55.

3.2 Thermoreversible Polymer Topologies via Diels-Alder Dimerization

Numerous linear and branched thermoreversible polymers were previously developed utilizing a variety of reactive functional groups. Polyesters containing hemiacetal ester functional groups in the main chain were synthesized and the main chains underwent thermal degradation at temperatures above 200 C.[217] However, this example of thermoreversibility is permanent, and a great deal of interest exists in thermoreversible polymers than can re-form upon cooling. The thermoreversibility of the nitroxide functional group utilized in SFRP makes it a good functional group for thermoreversible polymers. The nitroxide containing monomer 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-1-oxy (MTEMPO) was copolymerized with styrene at temperatures where the nitroxide was inactive.[218] The MTEMPO was then utilized to initiate the SFRP of polystyrene graft chains. These graft chains were thermoreversible when heated above 100 °C, resulting in cleavage to the linear chains.

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[217] H. Otsuka and T. Endo, "Poly(Hemiacetal Ester)s: New Class of Polymers with Thermally Dissociative Units in the Main Chain." *Macromolecules*, **1999**, *32*(26), 9059-9061.

[218] A. Niu, C. Li, Y. Zhao, J. He, Y. Yang, and C. Wu, "Thermal Decomposition Kinetics and Structure of Novel Polystyrene Clusters with MTEMPO as a Branching Agent." *Macromolecules*, **2001**, *34*(3), 460-464.

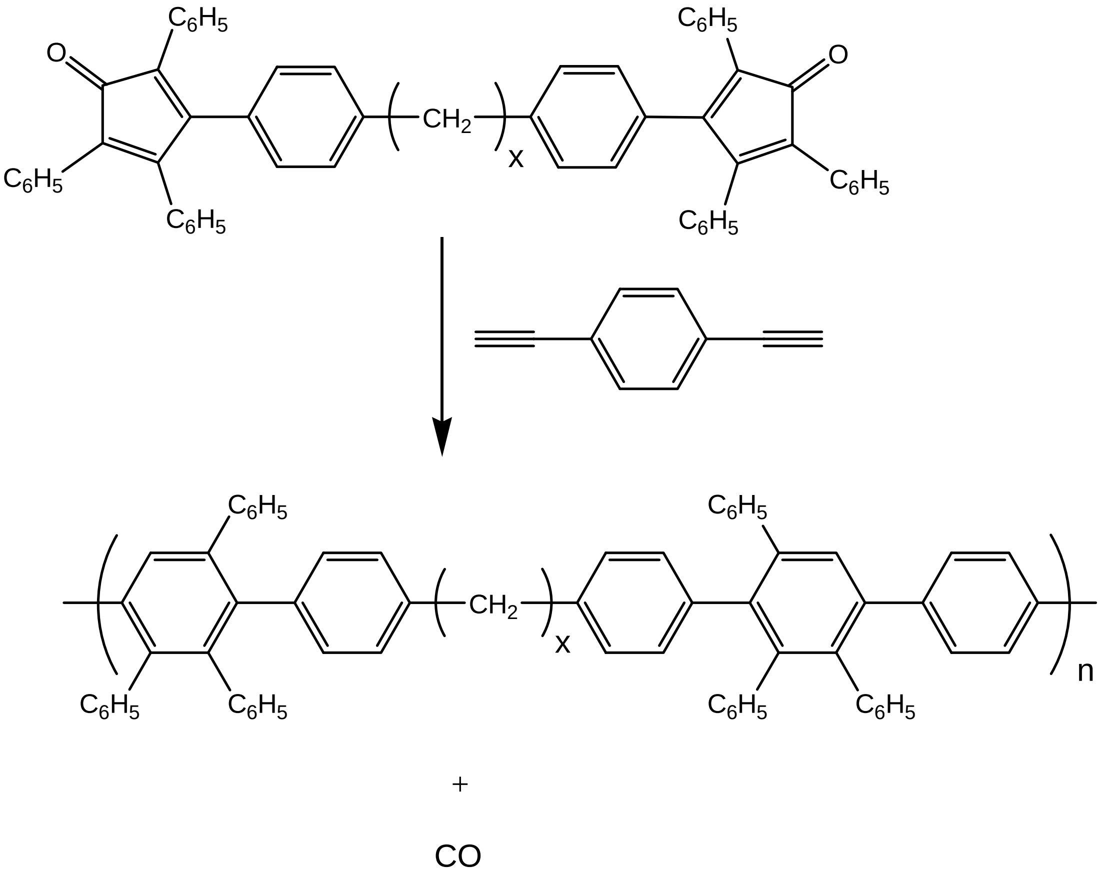

Figure 3.11: Synthesis of tractable polyphenylene via Diels Alder dimerization.

3.2.1 Diels-Alder Polymerization

Diels-Alder dimerization was used in the synthesis of numerous small molecules, including monomers containing polar or functional groups.[219,220] High molecular weight step-growth polymers were synthesized via the spontaneous Diels-Alder polymerization of bis(diene)s and bis(dienophile)s. Although Diels-Alder dimerization was proposed as a step-growth polymerization methodology over a half-century ago,[221] these polymers were not widely studied until the 1980s. Stille et al. synthesized a series of polymers from cyclic monomers containing dicyclopentadienones and diethynylbenzene at 300 °C (Figure 3.11).[222,223,224] Although Diels-Alder dimerizations are typically reversible at elevated temperatures, these polymers lost CO upon dimerization, making polymerization irreversible. As a result, these phenylene polymers exhibited high temperature stability in addition to solubility in a wide variety of solvents. These polymers were synthesized with molecular weights up to $<M_n> = 200{,}000$ and thermal stabilities under N_2 up to

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[219] A. J. Pasquale, A. Fornof, and T. E. Long, "Synthesis of Norbornene Derivatives by Diels-Alder Cycloaddition and Subsequent Copolymerization with Maleic Anhydride." *Macromol. Chem. Phys.*, **2004**, *205*(5), 621-627.

[220] I. Bicu and F. Mustata, "Ketone Derivatives of Diels-Alder Adducts of Levopimaric Acid with Acrylic Acid and Maleic Anhydride: Synthesis, Characterization, and Polymerization.." *J. Appl. Polym. Sci.*, **2004**, *92*(4), 2240-2252.

[221] N. E. Searle, "N-Arylmaleimides" *US* 2,444,536, **1947**.

[222] J. K. Stille and L. Plummer, "Polymerization by the Diels-Alder Reaction." *J. Org. Chem.*, **1961**, *26*, 4026-4029.

[223] J. K. Stille and T. Anyos, "A Novel Diels-Alder Polymerization." *J. Poly. Sci.*, **1964**, *2*(3, Pt. A), 1487-1491.

[224] J. K. Stille, F. W. Harris, R. O. Rakutis, and H. Mukamal, "Diels-Alder Polymerizations. Polymers Containing Controlled Aromatic Segments." *J. Poly. Sci. Poly. Lett.*, **1966**, *4*(10), 791-793.

530 °C.[225] Polymers containing chiral repeat units were also synthesized via Diels Alder dimerization.[226]

Although numerous polyphenylene polymers were synthesized earlier via irreversible Diels-Alder condensation, thermoreversible polymers based on retro-Diels Alder dimerization[227] were also developed. Dimerization occurred at ambient to slightly elevated temperatures, while depolymerization was observed at high temperatures; ceiling temperatures as high as 300 °C were reported for these reversible polymers.[228] The monomers re-polymerized upon cooling. The most commonly utilized functional group pair for retro-diels Alder dimerizations are furan and maleimide functional groups. When mixed in perfect stoichiometric ratios, bismaleimide dienophiles and numerous bisdienes were polymerized to high molecular weight polymers.[229] For example, molecular weights as high as $\langle M_n \rangle = 34{,}000$ were obtained when the α-pyrone functional group was used as the diene;[230] bisfurans are also frequently utilized in the

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[225] U. Kumar and T. X. Neenan, "Diels-Alder Polymerization between Bis(Cyclopentadienones) and Acetylenes. A Versatile Route to New Highly Aromatic Polymers." *Macromolecules*, **1995**, *28*(1), 124-130.

[226] S. E. Mallakpour, A-R. Hajipour, A.-R. Mahdavian, and F. Rafiemanzelat, "Highly Diastereoselective Synthesis of Novel Polymers Via Tandem Diels-Alder-Ene Reactions." *Polym. Int.*, **1999**, *48*(2), 109-116.

[227] H. Kwart and K. King, "The Reverse Diels-Alder or Retrodiene Reaction." *Chem. Rev.*, **1968**, *68*(4), 415-447.

[228] V. V Zuev, J. J. Kever, and Y. N. Sazanov, "Synthesis of Soluble Polyarylates with a Propeller-Like Structure Via Diels-Alder Reaction." *Macromol. Rapid Comm.*, **1998**, *19*(12), 631-634.

[229] A. L. Rusanov, Z. B. Shifrina, E. G. Bulycheva, M. L. Keshtov, M. S. Averina, Y. I. Fogel, K. Muellen, and F. W. Harris, "New Monomers and Polymers Via Diels-Alder Cycloaddition." *Macromol. Symp.*, **2003**, *199(Polycondensation 2002,* (97-107.

[230] G. Alhakimi, H. Goerls, and E. Klemm, "Polyimides by Diels-Alder Polyaddition of α-Pyrones." *Macromol. Chem. Phys.*, **1994**, *195*(5), 1569-1576.

synthesis of thermoreversible polymers.[231] These polymers cleaved to monomers at high temperatures (>100 °C) and re-polymerized at cooler temperatures. Polymers synthesized via an AB-type monomer containing both the diene and dienophile on the same monomer were also reported previously.[232]

3.2.2 Reversible DA Branched Topologies

Thermoreversible Diels-Alder dimerization led to the development of several reversible network polymers.[233] Epoxy-based structural network adhesives containing furan and maleimide functional groups were synthesized that exhibited extremely high fracture strengths below 90 °C.[234] Depolymerization occurred at temperatures above 90 °C, while reversible crosslinking occurred when the sample was cooled to 60 °C. Wudl et al. developed thermoreversible network polymers based on retro-Diels-Alder dimerization chemistry.[235] These tightly crosslinked networks were synthesized from multifunctional monomers containing four furan dienes and tris(maleimide) dienophile monomers, which formed network polymers at 40 °C as the A_4 and B_3 monomers crosslinked (Figure 3.12). Upon further heating, these network polymers reverted to the linear polymer form. It was shown that this topological rearrangement could be carried out repeatedly on the same sample while limiting the introduction of thermal hysteresis.

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[231] C. Gousse and A. Gandini, "Diels-Alder Polymerization of Difurans with Bismaleimides." *Polym. Int.*, **1999**, *48*(8), 723-731.

[232] V. Gaina and C. Gaina, "Ab Monomers. I. Synthesis and Polymerization of Furyl-Maleimide Monomers." *Rev. Roum. de Chim.*, **2003**, *48*(11), 881-890.

[233] H. D. Stenzenberger, "Thermosetting Polyimides from Bismaleimides Via Diels-Alder Reaction." in *Polyimides Other High-Temp. Polym., Proc. Eur. Tech. Symp.*, Amsterdam: Elsevier, 1991.

[234] J. H. Aubert, "Thermally Removable Epoxy Adhesives Incorporating Thermally Reversible Diels-Alder Adducts." *J. Adhes.*, **2003**, *79*(6), 609-161.

Samples of these polymers were fractured and re-mended via heating to 120 °C and cooling to room temperature.[236,237]

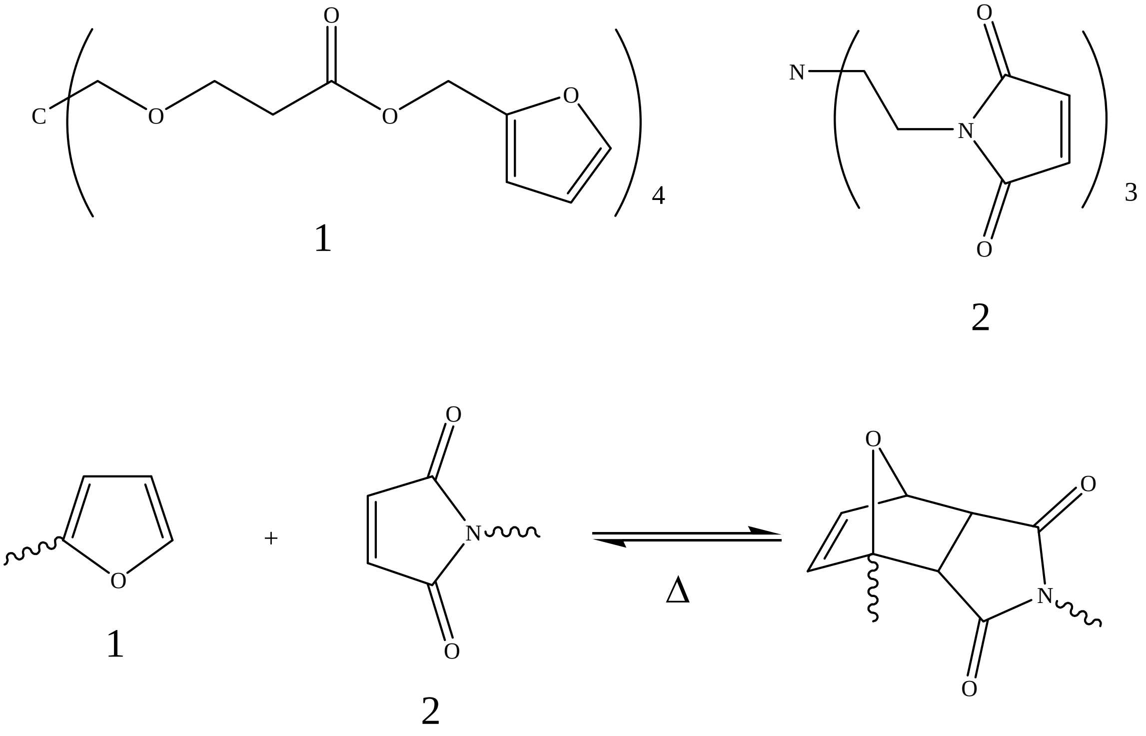

Figure 3.12: Reversible network assembly via Diels Alder dimerization of A_4 and B_3 monomers.

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[235] X. Chen, M. A. Dam, K. Ono, A. Mal, H. Shen, S. R. Nut, K. Sheran, and F. Wudl, "A Thermally Re-Mendable Cross-Linked Polymeric Material." *Science*, **2002**, *295*(5560), 1698-1702.

[236] X. Chen, F. Wudl, A. K. Mal, H. Shen, and S. R. Nutt, "New Thermally Remendable Highly Cross-Linked Polymeric Materials." *Macromolecules*, **2003**, *36*(6), 1802-1807.

[237] X. Chen and F. Wudl, "New Thermally Re-Mendable Highly Cross-Linked Polymeric Materials." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **2003**, *44*(1), 87-88.

Thermoreversible siloxane and methacrylate polymers containing pendent furan and maleimide functional groups were synthesized.[238] These polymers were copolymerized using furfuryl methacrylate and functionalized with the crosslinkable groups following polymerization. Immediate crosslinking occurred upon functionalization (Figure 3.13); these networks were reversibly cleavable at elevated temperatures. A furan containing styrenic monomer was synthesized and copolymerized with styrene to yield statistical copolymers.[239] These polymers rapidly crosslinked upon mixing with diphenylbismaleimide. These crosslinking dimers cleaved when the polymers were heated to 130 °C. The networks were heated in the presence of a large excess of 2-methylfuran to trap the diene and prevent re-crosslinking. Polyurethanes containing furan functional groups in the backbone were synthesized via polycondensation.[240] Crosslinking occurred when the polymer was reacted with bismaleimide crosslinking reagents. However, these networks could not be cleaved utilizing retro-Diels Alder chemistry at high temperatures. An example of reversible networks based on polymers synthesized via polycondensation was reported by Schiraldi et al.[241] Polyesters containing anthracene crosslinked reversibly with aliphatic bismaleimides.

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[238] R. Gheneim, C. Perez-Berumen, and A. Alessandro Gandini, "Diels-Alder Reactions with Novel Polymeric Dienes and Dienophiles: Synthesis of Reversibly Cross-Linked Elastomers." *Macromolecules*, **2002**, *35*(19), 7246-7253.

[239] C. Gousse, A. Gandini, and P. Hodge, " Application of the Diels-Alder Reaction to Polymers Bearing Furan Moieties. 2. Diels-Alder and Retro-Diels-Alder Reactions Involving Furan Rings in Some Styrene Copolymers." *Macromolecules*, **1998**, *38*(2), 314-321.

[240] H. Laita, S. Boufi, and A. Gandini, "The Application of the Diels-Alder Reaction to Polymers Bearing Furan Moieties. 1. Reactions with Maleimides." *Eur. Poly. J.*, **1997**, *33*(8), 1203-1211.

[241] J. R. Jones, C. L. Liotta, D. M. Collard, and D. A. Schiraldi, "Cross-Linking and Modification of Poly(Ethylene Terephthalate-*co*-2,6-Anthracenedicarboxylate) by Diels-Alder Reactions with Maleimides." *Macromolecules*, **1999**, *32*(18), 5786-5792.

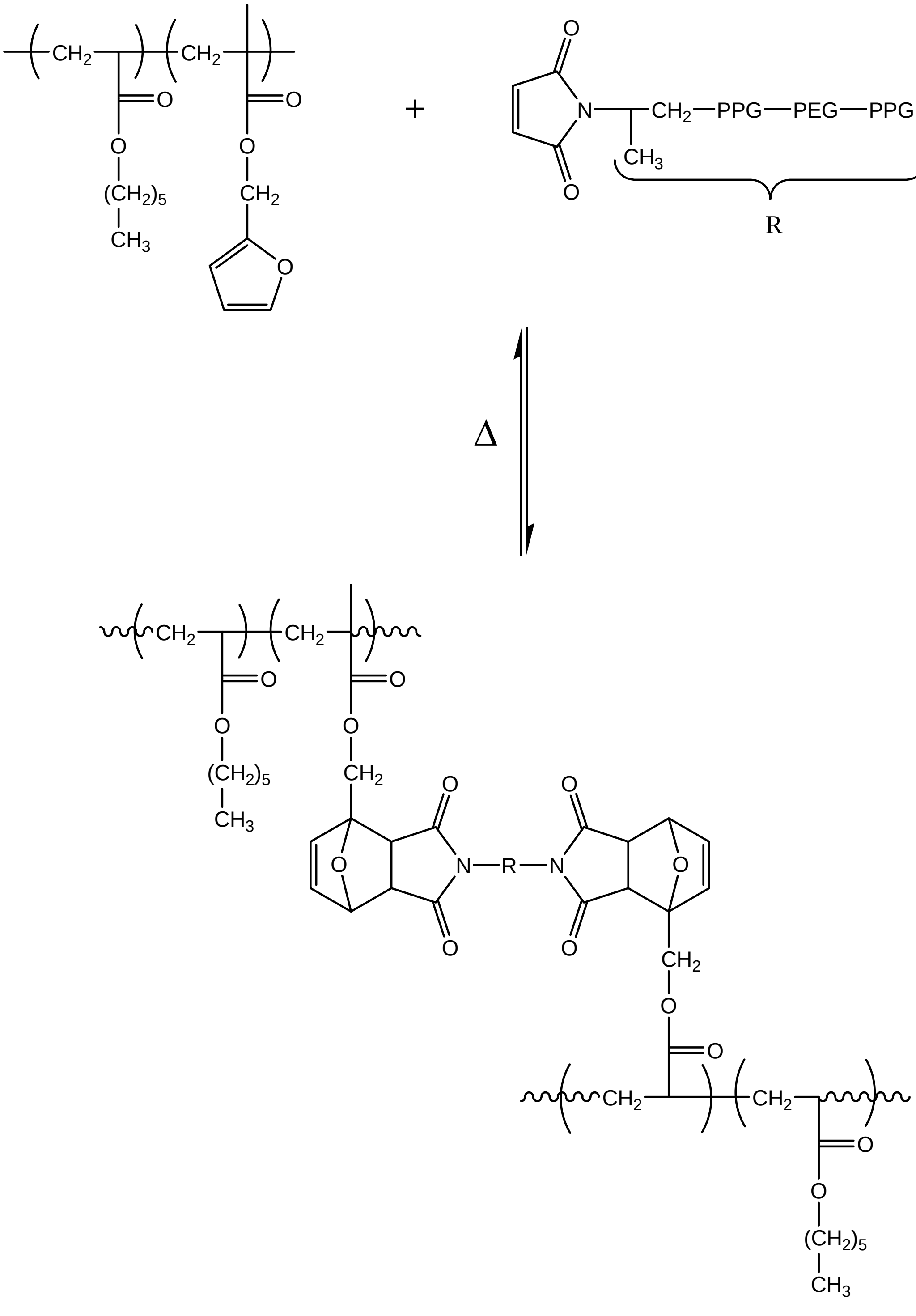

Figure 3.13: Thermoreversible networks were formed using diene containing polymers and a bismaleimide crosslinking oligomers.

Thermally reversible polymer epoxy adhesives were developed containing retro-Diels Alder linkages. The adhesive bonds were drastically weakened upon loss of molecular weight.[242,243] Additionally, polyamide-based Diels-Alder networks were synthesized from tris(maleimide) and either bis(furan)[244] or tris(furan)[245] monomers. These networks improved the mechanical properties in composites with glass fibers when analyzed at ambient temperatures. Another structural use for Diels-Alder dimerized networks was in structural foams. Thermoreversible foams were synthesized that exhibited excellent mechanical properties below the ceiling temperatures.[246,247] These foam polymers depolymerized via retro-Diels Alder at high temperatures.

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[242] J. H. Small, D. A. Loy, D. R. Wheeler, J. R. McElhanon, and R. S. Saunders, "Method of Making Thermally Removable Polymeric Encapsulants." *US* 6,271,335, **2001**.

[243] J. R. McElhanon, E. M. Russick, D. R. Wheeler, D. A. Loy, and J. H. Aubert, "Removable Foams Based on an Epoxy Resin Incorporating Reversible Diels-Alder Adducts." *J. Appl. Polym. Sci.*, **2002**, *85*(7), 1496-1502.

[244] H. S. Patel and V. C. Patel, "Polyimides Containing an S-Triazine Ring." *Des. Monom. Polym.*, **2001**, *4*(4), 369-380.

[245] H. S. Patel and V. C. Patel, "Cross-Linked Polyamides." *Polym. & Polym. Comp.*, **2002**, *10*(4), 315-323.

[246] B. A. Rozenberg, E. A. Dzhavadyan, R. J. Morgan, and E. E. Shin, "The Polyaddition, Chain, and Polycondensation Mechanisms of Formation of Networks Based on Bismaleimides." *Macromol. Symp.*, **2001**, *171(15th Polymer Networks Group Meeting, Polymer Networks '2000)*, 87-96.

[247] L. Dutruch, M. Senneron, M. Bartholin, P. Mison, and B. Sillion, "Preparation of Thermostable Rigid Foams by Control of the Reverse Diels-Alder Reaction During the Crosslinking of Bisnadimide Oligomers." *ACS Symp. Ser.*, **1997**, *669(Polymeric Foams)*, 37-53.

Dendrimer polymer topologies were also synthesized via divergent retro-Diels Alder polymerization. McElhanon and Wheeler developed thermoreversible dendrimers that were synthesized via controlled reversible furan-maleimide dimerizations of AB_2-type monomers (Figure 3.14).[248] Dendrimers that were synthesized up to the third generation were cleaved to the monomers upon heating to 110 °C and regenerated when they were annealed at 65 °C for 24 h. Dendrimers were also irreversibly synthesized from an A_2B monomer comprised of two protected acetylene dienophiles and the furan diene.[249] The dendrimer core was a tetraacetylene-containing biphenyl. The dendrimer was assembled via alternating Diels Alder dimerization and deprotection of the triisopropyl protecting groups. Dendrimeric monomers of the A_4B type were utilized as well to synthesize more highly branched dendrimers. These dendrimers were synthesized up to the third generation.[250]

Hyperbranched polymers exhibiting molecular weights as high as $\langle M_w \rangle$ = 107,000 g/mol were also synthesized via Diels Alder dimerization A_2B monomers were utilized that lacked the protecting groups used in dendrimer synthesis.[251] Third-generation dendrimers were synthesized via alternating Diels-Alder dimerizations and

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[248] J. R. McElhanon and D. R. Wheeler, "Thermally Responsive Dendrons and Dendrimers Based on Reversible Furan-Maleimide Diels-Alder Adducts." *Org. Lett.*, **2001**, *3*(17), 2681-2683.

[249] F. Morgenroth, A. J. Berresheim, M. Wagner, and K. Muellen, "Spherical Polyphenylene Dendrimers Via Diels–Alder Reactions: The First Example of an A_4B Building Block in Dendrimer Chemistry." *Chem. Comm.*, **1997**, *10*(1139-1140.

[250] F. Morgenroth, C. Kuebel, and K. Muellen, "Nanosized Polyphenylene Dendrimers Based Upon Pentaphenylbenzene Units." *J. Mater. Chem.*, **1997**, *7*(7), 1207-1211.

[251] F. Morgenroth and K. Muellen, "Dendritic and Hyperbranched Polyphenylenes Via a Simple Diels-Alder Route." *Tetrahedron*, **1997**, *53*(45), 15349-15366.

Knovenaegel condensations (Figure 3.11).[252] High solubilities and thermal stabilities were observed, similar to the benzyl-substituted linear polyphenylenes synthesized earlier via Diels-Alder dimerization.

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[252] U.-M. Wiesler and K. Müllen, "Polyphenylene Dendrimers Via Diels–Alder Reactions: The Convergent Approach." *Chem. Comm.*, **1999**, 22), 2293–2294.

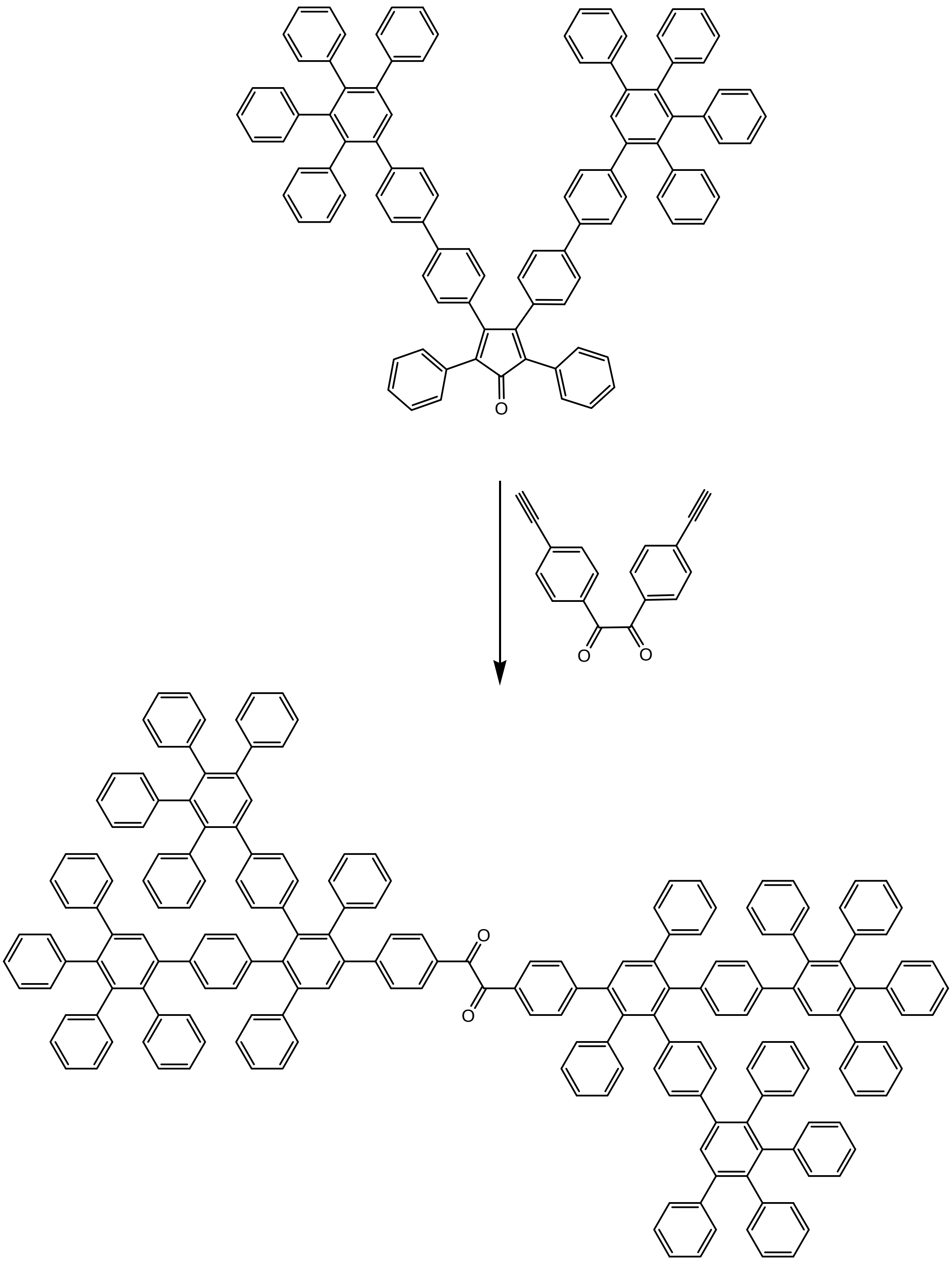

Figure 3.14: Synthesis of 2nd generation polyphenylene dendrimer via Diels-Alder dimerization

Bulky side groups were introduced into phenylene polymers via Diels Alder polymerization of a bisdiene containing six phenyl groups and diethynylbenzene.[253] These high molecular weight polymers were subsequently converted into ribbon-shaped polymers via $AlCl_3$ catalyzed oxidative cyclodehydrogenation, which resulted in the coupling of neighboring phenyl groups. Multiple types of ribbon polymers containing complexed metals were synthesized via Diels-Alder dimerization.[254] These polymers were polymerized from novel phthalocyanine monomers and hemiporphyrazine-based dienes and dienophiles.

A polyarylate containing a pendent 1,2-dihydrobenzocyclobutene functional group was synthesized and utilized to synthesize graft copolymers.[255] The cyclobutenyl functional group reacted with the dienophile functional group in the main chain of an EPDM copolymer. Graft copolymers containing the polyarylate graft chains exhibited significantly improved impact properties over the EPDM starting material. Polybutadiene was similarly converted to a graft copolymer via the Diels-Alder dimerization of the unsaturated sites in the backbone with a diene-terminated bis[4-(1,2,4-triazoline-3,5-dion-4-yl)phenyl]methane containing polymer.[256] Graft copolymers were also synthesized from poly(ethylene terephthalate-*co*-anthracene-2,6-

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[253] Z. B. Shifrina, M. S. Averina, A. L. Rusanov, M. Wagner, and K. Muellen, "Branched Polyphenylenes by Repetitive Diels-Alder Cycloaddition." *Macromolecules*, **2000**, *33*(10), 3525-3529.

[254] B. Hauschel, P. Stihler, and M. Hanack, "Ladder Polymers with Macrocyclic Metal Complexes as Subunits." *Trend. Polym. Sci.*, **1996**, *4*(10), 348-354.

[255] B. D. Dean, "High-Temperature Thermoplastic Elastomers Via the Grafting Reaction of Polyarylate onto EPDM Rubber." *J. Appl. Polym. Sci.*, **1993**, *47*(11), 2013-2017.

[256] M. Kuhrau and R. Stadler, "Synthesis of New Polymers Via Diels-Alder Reaction." *Makromol. Chem. Rapid Comm.*, **1990**, *11*(12), 635-644.

carboxylate).[257] Diels-Alder dimerization of the anthracene functional groups with maleimide-functionalized poly(ethylene glycol) resulted in graft copolymers exhibiting significantly increased hydrophilicity relative to the unreacted polymer. Short chain branches were also introduced using maleimide- functionalized octadecane (Figure 3.15).

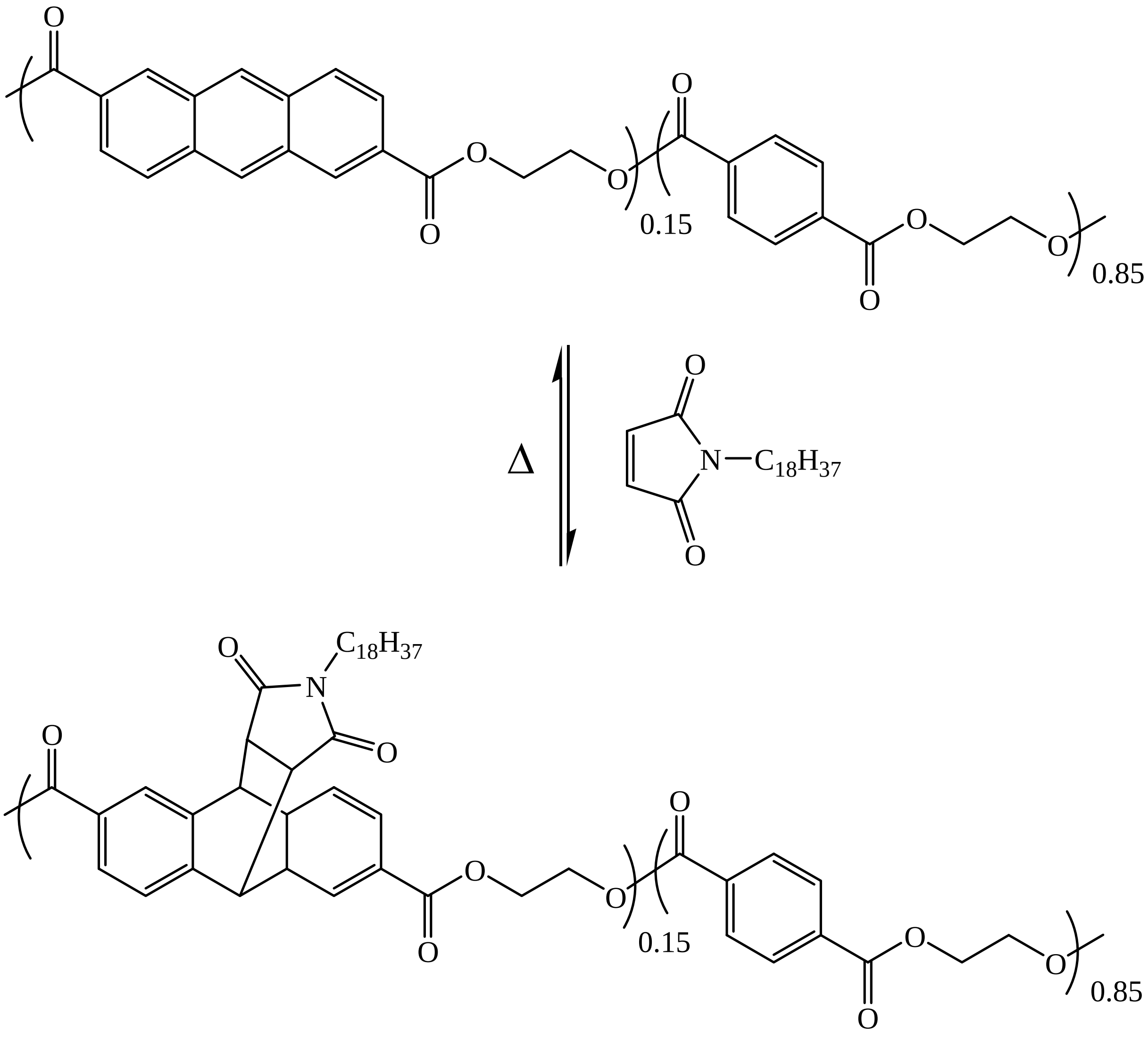

Figure 3.15: Dimerization of maleimide-substituted octadecane and the anthracene functional group in the polyester.

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[257] M. Vargas, R. M. Kriegel, D. M. Collard, and D. A. Schiraldi, "Diels-Alder Modification of Poly(Ethylene Terephthalate-*co*-Anthracene-2,6-Carboxylate) with N-Substituted

3.3 Hydrolytic Cleavage of Esters in Linear Polymers

The introduction of reactive functional groups into polymers resulted in the development of an entire class of compounds that were able to fulfill specialized needs. Numerous polymer modification reactions[258] were developed for acrylates and methacrylates. Most of them involve the removal of protecting groups in order to produce polymers that either cannot be directly synthesized by sensitive living polymerization techniques.[259] Poly(methacrylic acid), for example, can be obtained via the hydrolysis of either the 1-(alkoxy)ethyl,[260] the *tert*-butyl,[261] or the trimethylsiloxy[262] groups. Gaseous HCl successfully converted ultrathin Langmuir-Blodgett[263] (LB) films of poly (*tert*-butyl methacrylate) (*t*-BMA) and poly (*tert*-butyl acrylate) (t-BA) to poly (methacrylic acid) (MAA) and poly (acrylic acid) (AA), respectively[264] without disturbing the layered architecture consisting of the LB-films. Ester hydrolysis was also

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Maleimides." *J. Polym. Sci. A Polym. Chem.*, **2002**, *40*(19), 3256-3263.

[258] J. D. Tong, P. Leclere, C. Doneux, J. L. Bredas, R. Lazzaroni, and R. Jerome, "Synthesis and Bulk Properties of Poly(Methyl Methacrylate)-*B*-Poly(Isooctyl Acrylate)-*B*-Poly(Methyl Methacrylate)." *Polymer*, **2000**, *41*(12), 4617-4624.

[259] A. Hirao, "Functional Polymers Via Anionic Polymerization." *Desk Ref. Funct. Polym.*, **1997**, 19-34.

[260] E. Ruckenstein and H. M. Zhang, "A Novel Route to Poly(2-Hydroxyethyl Methacrylate) and Its Amphiphilic Block Copolymers." *J. Polym. Sci. A Polym. Chem.*, **1998**, *36*(11), 1865-1872.

[261] S. Kawaguchi, T. Takahashi, H. Tajima, Y. Hirose, and K. Ito, "Preparation, Characterization, and Dissociation Properties of Poly(Acrylic Acid) and Poly(Methacrylic Acid) with Narrow Molecular Weight Distribution." *Polym. J.*, **1996**, *28*(9), 735-741.

[262] H. Mori, O. Wakisaka, A. Hirao, and S. Nakahama, "Protection and Polymerization of Functional Monomers. 23. Synthesis of Well-Defined Poly(2-Hydroxyethyl Methacrylate) by Means of Anionic Living Polymerization of Protected Monomers." *Makromol. Chem. Phys.*, **1994**, *159*(9), 3213-3224.

[263] K. J. Naito, "Structure, Deposition Properties, and Function of Polyisobutylmethacrylate (PIBM) Langmuir-Blodgett Films," *J. Colloid Interface Sci.*, **1989**, *131*(1), 218-225.

[264] A. R. Esker, C. Mengel, and G. Wegner, "Ultrathin Films of a Polyelectrolyte with Layered Architecture." *Science*, **1998**, *280*(5365), 892-895.

used to introduce carboxylic acid ends at the termini of dendrimers.[265] Functional groups designed to undergo single or multiple bond cleavages were utilized in the development of hydrolyzable linear and branched polymer topologies. These responsive polymers were designed to break into either smaller subunits or degrade into small molecules entirely.

3.3.1 Structural Effects on Hydrolysis

The hemiacetal and hemiacetal ester functional groups undergo faster hydrolytic degradation than typical esters. Hemiacetal esters are also thermally cleavable (Figure 3.16), and the sensitivity of hemiacetal ester-containing copolymers towards thermal degradation was shown to be tunable by changing the pendent methyl substituents on the hemiacetal functional group to a variety of groups.[266,267] Alkyl groups resulted in thermal degradation temperatures as low as 150 °C while the use of phenyl or phenoxy groups increased thermal stability up to 250 °C. The thermal stability of hemiacetal side groups was also shown to partially depend on the comonomer composition.[268] Isolated hemiacetals do not undergo thermal degradation readily, but hydrolyze very rapidly in the presence of acid.

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[265] J. W. Leon, M. Kawa, and J. M. J. Frechét, "Isophthalate Ester-Terminated Dendrimers: Versatile Nanoscopic Building Blocks with Readily Modifiable Surface Functionalities." *J. Am. Chem. Soc.*, **1996**, *118*(37), 8847-8859.

[266] Y. Nakane, M. Ishidoya, and T. Endo, "Synthesis and Thermal Dissociation of Polymers Having Hemiacetal Ester Moieties." *J. Polym. Sci. A Poly. Chem.*, **1999**, *37*(5), 609-614.

[267] H. Otsuka, H. Fujiwara, and T. Endo, "Thermal Dissociation Behavior of Polymers with Hemiacetal Ester Moieties in the Side Chain: The Effect of Structure on Dissociation Temperature." *J. Polym. Sci. A Poly. Chem.*, **2000**, *37*(24), 4478-4482.

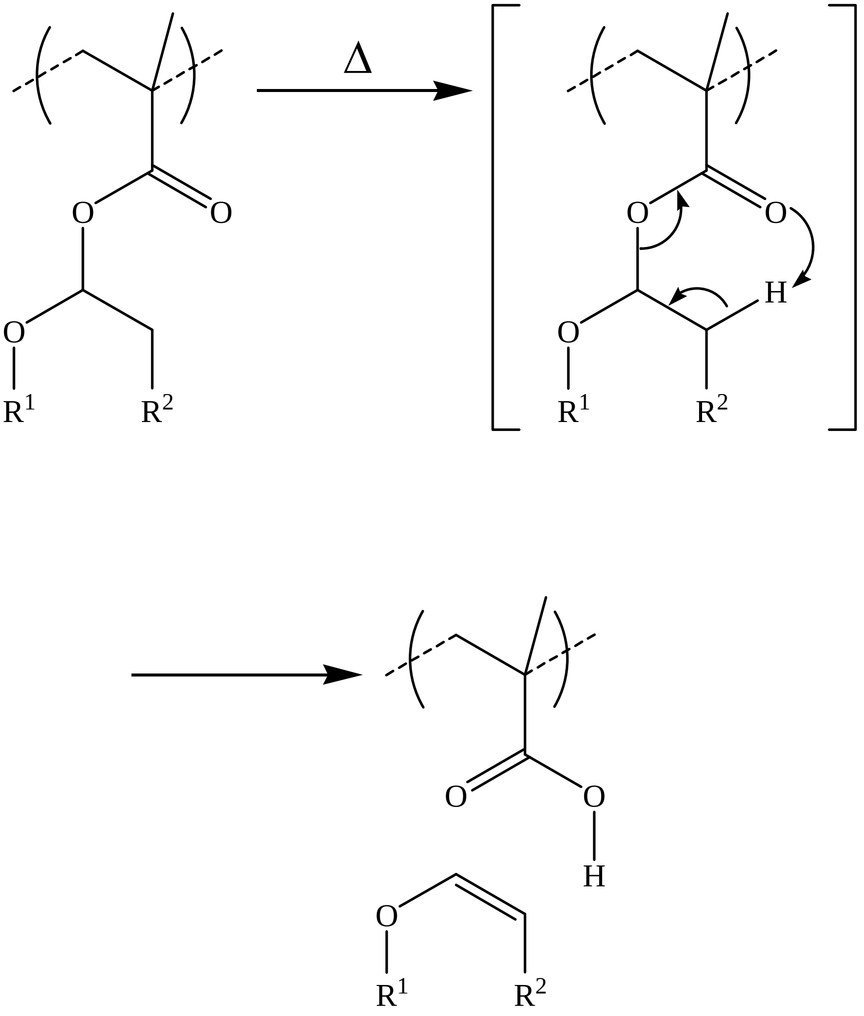

Figure 3.16 Thermal Degradation Mechanism of Hemiacetal Esters

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[268] H. Otsuka, H. Fujiwara, and T. Endo, "Fine-Tuning of Thermal Dissociation Temperature Using Copolymers with Hemiacetal Ester Moieties in the Side Chain: Effect of Comonomer on Dissociation Temperature." *React. Func. Polym.*, **2001**, *46*(3), 293-298.

Copolymers containing a large amount of readily hydrolyzable monomers degrade very rapidly. For example, the extent of poly(ethylene oxide-*block*-ε caprolactone) nanoparticle degradation by the enzyme Lipase PS was dependent on the size of the hydrolyzable ε-caprolactone block, as well as concentration of lipase.[269] The relative amounts of the readily hydrolyzable comonomers must be limited, so that degradation does not occur too quickly. The hydrolysis of poly(vinyl alcohol) was strongly dependent on the relative amounts and types of comonomers in the polymer.[270] Another important characteristic of degradable polymers is the macromolecular architecture. Every macromolecular architecture, including block copolymers, star polymers, graft polymers, and networks, was previously examined in biodegradable polymers. Polymer morphology plays an important part in biodegradation by limiting access of the hydrolyzing solvent water.

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[269] Z. Gan, T. F. Jim, M. Li, Z. Yuer, S. Wang, and C. Wu, "Enzymatic Biodegredation of Poly(Ethylene Oxide-*B*-ε-Caprolactone) Diblock Copolymer and Its Potential Biomedical Applications." *Macromolecules*, **1999**, *32*(3), 590-594.

[270] S. Matsumura, *Biodegradation of Poly(Vinyl Alcohol) and Its Copolymers*, ed. S. Matsumura and A. Steinbuechel, vol. 9, *Biopolymers*, Weinheim, Germany: Wiley-VCH Verlag, 2003, 329-361.

3.3.2 Topological Effects on Hydrolysis

The presence of polymeric crystals will influence both the mechanical properties[271] and degradation[272] of biodegradable polymers. The presence of crystalline lamellae significantly reduces the degradation rate of biodegradable materials, because water must diffuse into the polymer matrix before hydrolysis can occur. Since this diffusion is hindered by lamellae, polymer crystals such as poly(L-lactic acid) typically undergo only surface-degradation initially.[273] When poly(glycolide) and poly(glycolide-*co*-lactide) samples were annealed above T_g and quenched immediately, almost no crystal formation occurred. When this amorphous polymer sample was exposed to hydrolytic conditions, complete degradation occurred rapidly (Figure 3.17). In contrast, the annealed semi-crystalline polymer exhibited much slower degradation kinetics. The introduction of long and short chain branches was shown to hinder the formation of lamellar crystallites. As a result, branched biodegradable polymer degraded faster than their linear counterparts, which exhibited much higher degrees of crystallinity.

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[271] C. C. Chu, "Hydrolytic Degradation of Polyglycolic Acid: Tensile Strength and Crystallinity Study." *J. Appl. Polym. Sci.*, **1981**, *26*(5), 1727-1734.

[272] H. Pistner, D. R. Bendix, J. Muehling, and J. F. Reuther, "Poly(*L*-Lactide): A Long-Term Degradation Study *in Vivo*." *Biomaterials*, **1993**, *14*(4), 291-298.

[273] T. Iwata and Y. Doi, "Morphology and Enzymatic Degradation of Poly(*L*-Lactic Acid) Single Crystals." *Macromolecules*, **1998**, *31*(8), 2461-2467.

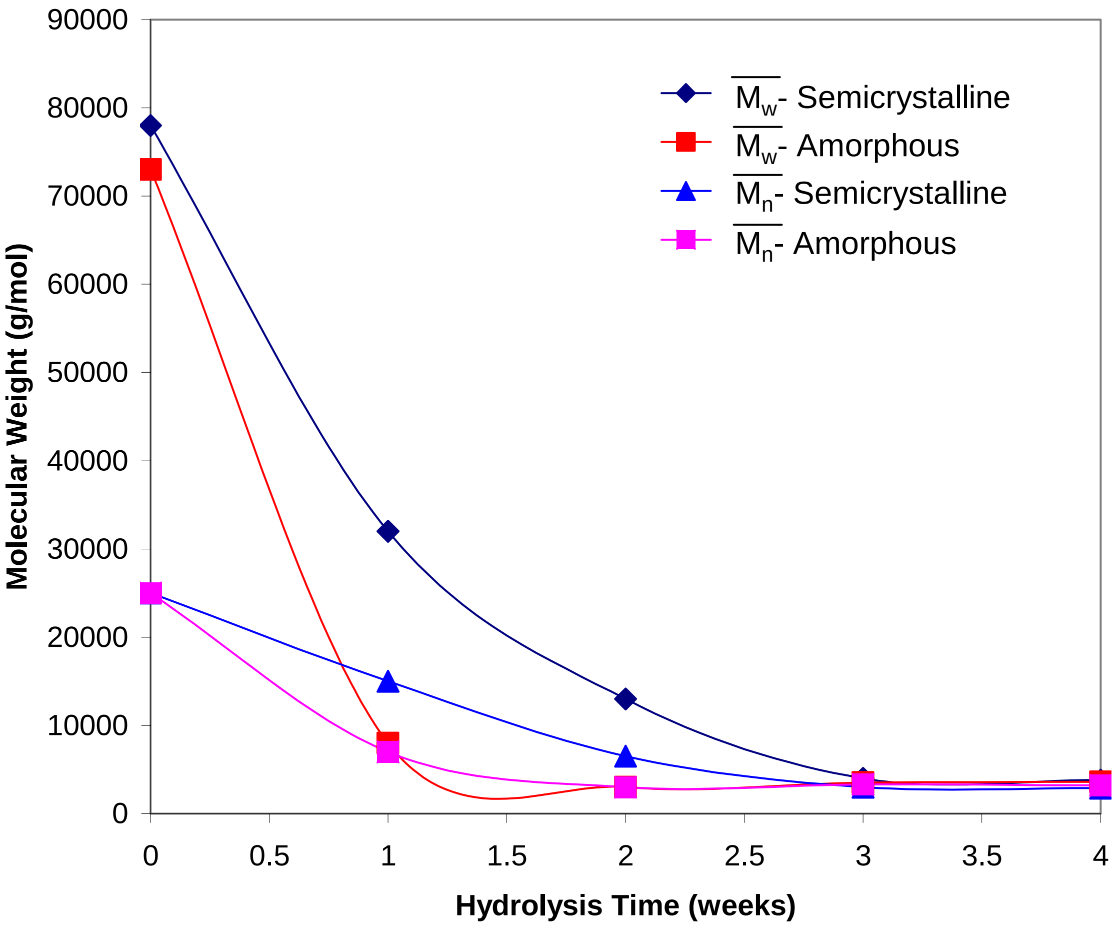

Figure 3.17: Effect of crystallinity of the hydrolysis rate of polylactide

Microphase separation occurs as a result of a low change in entropy (ΔS) as a result of mixing between two or more chemically distinct polymer segments. This effect is typically observed in block copolymers, as well as some end-capped polymers. Microphase-separated domains that aggregate on the surface of a polymer sample can act as a barrier to small hydrolyzing molecules outside the polymer. Gardella et al. synthesized fluorocarbon end-capped poly(lactide) and poly(lactide-*co*-glycolide) copolymers that exhibited slower degradation kinetics as a result of this kind of surface aggregation behavior.[274] The authors demonstrated that the fluorine end-capping segments were aggregated on the surface using elemental analysis obtained by an ESCA. As a result of the water-repelling properties of the end caps, the initial hydrolysis of these polymers was retarded. Once the fluorocarbon layer was removed by hydrolysis, the samples exhibited normal hydrolysis kinetics. In addition to influencing the degradation behavior of block copolymers, microphase separation also plays a role in the biocompatibility aspects of the material. Poly(lactic acid)-*block*-poly(ethylene glycol) diblock copolymers exhibit surface properties that are dependent on the microphase separation due to their differing hydrophilicities. The hydrophilic poly(ethylene glycol) block does not typically promote the adhesion of proteins. Therefore, varying the amount of PEG present on the surface can change the adhesive nature of the diblock surface. Surface PEG content was shown to be dependent on the composition of the diblock.[275]

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[274] W.-K. Lee, D. Losito, J. A. Gardella Jr., and W. L. Hicks Jr., "Synthesis and Surface Properties of Fluorocarbon End-Capped Biodegradable Polyesters." *Macromolecules*, **2001**, *34*(9), 3000-3006.

3.3.3 Drug Delivery via Hydrolysis of Linear Polymers

Biocompatible diblock copolymers such as poly(lactide)-*block*-poly-ethylene glycol were used in studies to determine the feasibility of drug delivery.[276] The anticancer drug paclitaxel can be absorbed into the micelle and the micelles are the used as a controlled release vector for the drug. The micelles released the drug as the diblocks were cleaved by hydrolysis. The use of polymers containing biodegradable esters for drug release has become widespread. Biodegradable polymer systems used for drug delivery are designed to be either directly bonded to the drug molecule or trap the drug molecule. In the first method, drug molecules were released when the covalent ester linkage between the backbone and drug underwent hydrolysis. In the second method, release occurs when the matrix trapping the drug degrades to the point where the drug can diffuse out of the matrix. Alkyl-ester bond hydrolysis was utilized in the controlled drug release of covalently bound drugs. Ibuprofen and indomethacin were attached to methacrylate and methacrylamide monomers and copolymerized.[277] The drugs were released upon ester bond hydrolysis. Covalently-bound drug photorelease was achieved via the cleavage of the nitrobenzyl functional group in the presence of 365 nm light.[278] Drug-release was also achieved via the design of linear biodegradable macromolecules

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[275] A. Lucke, J. Tessmar, E. Schnell, G. Schmeer, and A. Goepferich, "Biodegradable Poly*(D,L*-Lactic Acid)-Poly(Ethylene Glycol." *Biomaterials*, **2000**, *21*(23), 2361-2370.

[276] H. M. Burt, X. Zhang, P. Toleikis, L. Embree, and W. L. Hunter, "Development of Copolymers of Poly(*DL*-Lactide) and Methoxypolyethylene Glycol as Micellar Carriers of Paclitaxel." *Colloids Surf, B*, **1999**, *16*(1-4), 161-171.

[277] D. Soudabeh and E. A. Akbar, "Acrylic Type Polymers Containing Ibuprofen and Indomethacin with Difunctional Spacer Group: Synthesis and Hydrolysis." *J. Controlled Release*, **1997**, *41*(1), 41-49.

[278] C. P. Holmes, "Model Studies for New *O*-Nitrobenzyl Photolabile Linkers: Substituent Effects on the Rates of Photochemical Cleavage." *J. Org. Chem.*, **1997**, *62*(8), 2370-2380.

that directly hydrolyze into the therapeutic molecule, such as salicylic acid.[279,280] Anhydride based polyesters that hydrolyzed into silycylic acid (Figure 3.18) were utilized reduce tissue inflammation for an extended period of time relative to the control.[281] This technique has limited applicability due to the limited number of therapeutic molecules that can be incorporated directly into polyesters.

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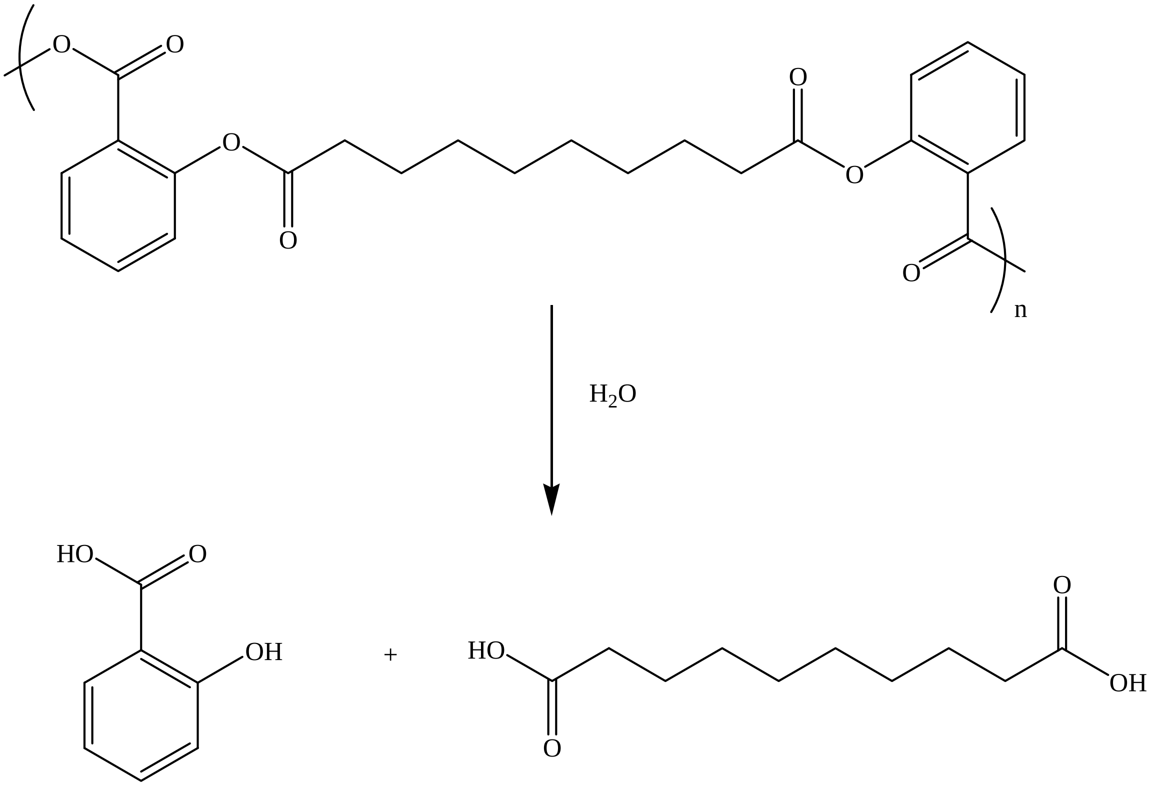
[279] L. Erdmann, C. Campo, C. Bedell, and K. Uhrich, "Polymeric Prodrugs: Novel Polymers with Bioactive Components." *ACS Symp. Ser.*, **1998**, *709(Tailored Polymeric Materials for Controlled Delivery Systems*, 83-91.

[280] L. Erdmann and K. E. Uhrich, "Synthesis and Degradation Characteristics of Salicylic Acid-Derived Poly(Anhydride-Esters)." *Biomaterials*, **2000**, *21*(19), 1941-1946.

[281] L. Erdmann, B. Macedo, and K. E. Uhrich, "Degradable Poly(Anhydride Ester) Implants: Effects of Localized Salicylic Acid Release on Bone." *Biomaterials*, **2000**, *21*(24), 2507-2512.



Salicylic Acid

Figure 3.18: Direct release of salicylic acid (SA) from a hydrolyzable polyanhydride

Chapter 4: Advances in Tailored Branched Macromolecular Design for Adhesion

4.1 Branched Polymers in Thermosetting Adhesives

While the impact of crosslinking on adhesives was known for many decades, improving adhesive performance via the utilization of non-crosslinked branched topologies[282] is a newer field of study. Polymer branching was utilized in the design of polymers with more or less adhesion than the linear counterparts, depending on the desired use of the material. Topologies including star,[283] graft,[284] and branched[285] polymers were used previously to improve the performance of adhesives and coatings. One of the reasons that star polymers were synthesized for use in adhesives was due their relatively low viscosities at higher temperatures, which improved the initial applications of these adhesives to bonds. [286]

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[282] J. W. Hagan, C. B. Mallon, and M. R. Rifi, "Recent Developments in Acrylic Polymers for Latex PSA's." *Adhes. Age*, **1979**, *22*(3), 29-33.

[283] R. D. Harlan, J. E. Schoenberg, C. G. Gore, D. Hariharan, and S. M. Shah, "Use of Star-Branched Polymers in Pressure Sensitive Adhesives." *US* 6,177,540, **2001**.

[284] R. A. Ryntz, "Branched Polyester Macromers for Graft Polymers for Use in Flexible Coatings." *US* 4,873,285, **1989**.

[285] M. S. Brookhart, L. K. Johnson, C. M. Killian, E. F. McCord, S. J. McLain, K. A. Kreutzer, S. D. Ittel, and D. J. Tempel, "Highly Branched Olefin Polymers and Their Uses." *US* 5,880,241, **1999**.

[286] P. M. Petersen, R. D. Harlan, and J. E. Schoenberg, "Multireactivity Polymercaptans, Star Polymers and Methods of Preparation." *US* 6,201,099, **2001**.

The structure of polymer end groups exerts a greater influence over the polymer properties, including adhesion, compared to linear polymers containing only two end groups. Hyperbranched polymers containing terminal epoxy groups were used to drastically increase interfacial adhesion through chemical bonding of the epoxy groups to surface functional sites.[287] The three-dimensional structure of the hyperbranched polymer was cited as the reason for the improved toughening of these adhesive bonds. In addition, branched polyamine adhesion promoters for low-surface energy substrates were developed containing a relatively high number of aliphatic end groups. These adhesion promoters were much better at improving adhesion between polyethylene and a cyanoacrylate adhesive than the linear counterpart.[288]

In order to produce non-adhesive resins, hyperbranched PDMS polymers were synthesized containing numerous pentafluorophenyl end groups, followed by crosslinking with tetraamino pendent PEG macromonomers.[289] These polymers exhibited very little adhesion to human fibrinogen, in contrast to samples based on linear PDMS.

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[287] T. Emrick, H. Chang, J. M. Frechét, J. Woods, and L Baccei, "Hyperbranched Aromatic Epoxides in the Design of Adhesive Materials." *Polym. Bull. (Berlin)*, **2000**, *45*(1), 1-7.

[288] J. G. Woods and J. M. J. Frechét, "Alkyl-Terminated Multi-Amine Compound Primers for Bonding of Polyolefins with Cyanoacrylate Adhesives." *WO* 9915580, **1999**.

[289] D. Gan, A. H. Mueller, and K. L. Wooley, "Amphiphilic and Hydrophobic Surface Patterns Generated from Hyperbranched Fluoropolymer/Linear Polymer Networks: Minimally Adhesive Coatings Via the Crosslinking of Hyperbranched Fluoropolymers." *J. Polym. Sci. A Poly. Chem.*, **2003**, *41*(22), 3531-3540.

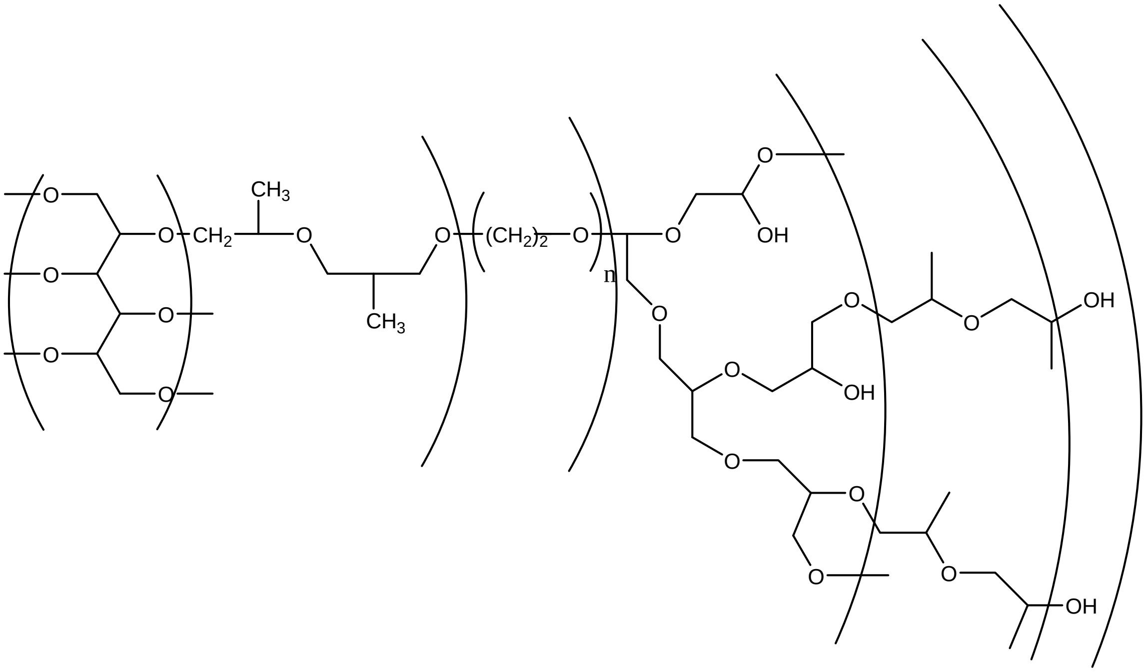

Figure 4.1. Structure of multifunctional epoxy toughening crosslinking reagent prior to functionalization of alcohol to epoxide.[290]

The addition of a multifunctional, highly-branched crosslinking polymer to high-performance thermosetting adhesive blends can help to overcome the brittleness that occurs at high crosslink densities. Highly branched polymers contain significantly greater end groups than linear polymers and were utilized as additives to improve adhesion in moisture-cured isocyanate structural adhesives. The use of either dendrimer or hyperbranched polymers containing terminal alcohol groups in place of the linear diol resulted in increasing shear and peel strengths by up to 80 percent.[291] This unusually beneficial behavior was attributed to an increased crosslink quality resulting from the

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[290] J. Fröhlich, H. Kautz, R. Thomann, H. Frey, and R. Mülhaupt, "Reactive Core/Shell Type Hyperbranched Blockcopolyethers as New Liquid Rubbers for Epoxy Toughening." *Polymer*, **2004**, *45*(7), 2155-2164.

three-dimensional structure of the highly branched crosslinking points, leading to a significant increase in cohesive performance. Hyperbranched[292,293] polymers containing a large number of terminal epoxy groups were also used to improve toughness in an epoxy adhesive. More recently, hyperbranched polymers with a shape analogous to star-burst polymers were synthesized (Figure 4.13) containing extremely large quantities of epoxy end-groups (up to 88 per molecule).[294] These multifunctional crosslinking reagents were used in epoxy adhesives formulations, resulting in significantly greater tensile moduli and fracture toughness.

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[291] H. Dodiuk, Z. Gold, and S. Kenig, "Tailoring New Architectures for Polyurethanes Using Dendritic and Hyper-Branched Polymers and Their Adhesion Behavior. Part 1." *J. Adhes. Sci. Tech.*, **2004**, *18*(3), 301-311.

[292] T. Emrick, H. Chang, J. M. Frechét, J. Woods, and L Baccei, "Hyperbranched Aromatic Epoxides in the Design of Adhesive Materials." *Polym. Bull. (Berlin)*, **2000**, *45*(1), 1-7.

[293] R. Mezzenga, L. Boogh, J.-A. E. Månson, and B. Pettersson, "Effects of the Branching Architecture on the Reactivity of Epoxy-Amine Groups." *Macromolecules*, **2000**, *33*(4373-4379.

[294] J. Fröhlich, H. Kautz, R. Thomann, H. Frey, and R. Mülhaupt, "Reactive Core/Shell Type Hyperbranched Blockcopolyethers as New Liquid Rubbers for Epoxy Toughening." *Polymer*, **2004**, *45*(7), 2155-2164.

4.2 Branched Thermoplastic Adhesives

Conventional pressure-sensitive adhesives offer little or no adhesion to low surface energy substrates such as polypropylene and low density and high density polyethylene since the surface energy of the adhesive must be lower than the surface energy of the adherent.[295] A common method to circumvent this shortcoming was to modify the adherent surface with functional groups to either alter surface energy or act as the initiating site for polymer brushes.[296,297]

Block copolymers exhibiting low T_g's were synthesized for use as unblended PSAs. For example, low molecular weight triblock copolymers consisting of two biodegradable polylactide end blocks coupled to a biocompatible PEG central block were synthesized from the PEG diol macroinitiator.[298] Due to the low molecular weights and subsequent T_g's, these triblock copolymers were utilized as biodegradable tissue adhesives. Block copolymers have also received significant interest as specialty adhesives[299] due to their microphase separated morphologies depicted in Figure 4.14.[300] Microphase separation enables block copolymers to exhibit a wide range of compatibility with adhesive modifiers that are added to improve adhesion. Pressure-sensitive adhesives were also modified using oligomeric tackifiers, which raise T_g and lower the surface

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[295] E. M. Petrie, *Handbook of Adhesives and Sealants*, New York: McGraw-Hill, 2000.

[296] H. Wang and H. R. Brown, "Autoadhesion of High Density Polyethylene (HDPE) to HDPE by Ultraviolet Grafting of Methacrylates and Acrylates." *J. Adhes.*, **2003**, *79*(10), 955-971.

[297] F. Brochard-Wyart, P. G. de Gennes, L. Leger, Y. Marciano, and E. Raphael, "Adhesion Promoters." *J. Chem. Phys.*, **1994**, *98*(38), 9405-9410.

[298] G. Lando and C. Cohn, "Introducing Lactide-Based Biodegradable Tissue Adhesives." *J. Mater. Sci.: Mater. Med.*, **2003**, *14*, 181-186.

[299] K. Huang, B. P. Lee, D. R. Ingram, and P. B. Messersmith, "Synthesis and Characterization of Self-Assembling Block Copolymers Containing Bioadhesive End Groups." *Biomacromolecules*, **2002**, *3*(2), 397-406.

energy of the adhesive. In order for a tackifier to successfully modify these PSA properties, it must not exhibit macrophase separation with the adhesive base polymer. However, the aliphatic tackifiers necessary for low energy surface adhesion are not compatible with standard polyacrylate adhesives due to the polarity of the acrylate polymer. However, well-defined block copolymers are difficult to synthesize industrially, due to the practical limitations inherent to all current living polymerization methodologies.

Graft copolymers, some of which exhibit microphase separation behavior that is very similar to block copolymers, were developed and utilized in a variety of applications ranging from additives to reduce motor oil viscosity[301] to specialty adhesives.[302] The primary advantages of these polymers over pure block copolymers are ease of synthesis and lower materials cost. Graft polymers containing a significant quantity of graft chains undergo microphase separation, leading to distinct glass transition temperatures from backbone polymer domain and the graft chain domains.

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[300] A. Falsafi, F. S. Bates, and M. Tirrell, "Role of Chain Architecture in the Adhesion of Block Copolymers." *Macromolecules*, **2001**, *34*(5), 1323-1327.

[301] W. L. Liu and F. C. Loveless, "Comb Graft Polymers and Their Use in Functional Fluids" *US*, **1996**, 5,508,353.

[302] P. B. Foreman, S. M. Shah, R. Chandran, and P. S. Eaton, "Rubber-Acrylic Adhesive Formulation" *US*, **2003**, 6,670,417.

Recently, graft PSA copolymers were synthesized containing a main chain comprised of 2-ethylhexyl acrylate, methyl methacrylate, and 2-hydroxyethyl methacrylate that exhibited a PSA T_g. The graft chains consisted of poly(ethylene-*co*-butylene) graft chains, which aggregated to form very low-T_g hydrophobic soft domains.[303] The graft chains were incorporated into the graft copolymer via the use of a commercially-available poly(ethylene-*co*-butylene) methacrylate graft macromonomer in a solution free-radical polymerization. Due to the very hydrophobic nature of the EB graft chains, aliphatic tackifiers were successfully blended with these PSAs, drastically lowering the surface energy of the PSA. These graft copolymer PSAs adhered strongly to low surface energy substrates, including polyethylene and polypropylene, due to the solubility of the tackifier in the low T_g domain.

The introduction of polymer brushes on common base polymers were also useful in the design of adhesives for bioadhesion and PSA applications. A significantly more hydrophilic graft polymer was synthesized when starch was exposed to ^{60}Co radiation in the presence of acrylic acid.[304] The radiation induced the formation of free-radical initiating sites throughout the starch polymer. These starch-*graft*-polyacrylic acid graft copolymers exhibited improved tissue adhesion relative to commercially available linear starch-based adhesive polymers. These adhesives were impregnated with testosterone, releasing the model drug in a controlled fashion. Natural rubber latex was modified in a

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[303] P. Foreman, P. Eaton, and S. M. Shah, "The Best of Both Worlds." *Adhes. Age*, **2001**, *44*(9), 50,53-54,56,58,60.

[304] D. Ameye, J. Voorspoels, P. Foreman, J. Tsai, P. Richardson, S. Geresh, and J. P. Remon, "Ex Vivo Bioadhesion and in Vivo Testosterone Bioavailability Study of Different Bioadhesive Formulations Based on Starch-G-Poly(Acrylic Acid) Copolymers and Starch / Poly(Acrylic Acid) Mixtures." *J. Controlled Release*, **2002**, *79*(1-3), 173-182.

similar way; the formation of the grafting sites was induced using a cumene hydroperoxide/ tetraethylene pentamine redox system.[305] Poly(methyl methacrylate) brushes were polymerized from these initiating sites.

Although an improvement in adhesion is desirable for many applications, many materials are designed to exhibit poor adhesion either initially or following exposure to a stimulant that induces a reaction with the polymer. Polymer brushes were used to modify surfaces in order to achieve very poor adhesion to prevent biofouling. PET surfaces were chemically modified with carboxylic acid groups so that moderately high molecular weight PEG chains could be grafted to the surfaces in high densities. The modified surfaces exhibited decreased bacterial adhesion, measured by a bacterial count that was lower than the unmodified surface by multiple orders of magnitude.[306]

A recently developed type of pressure-sensitive adhesive was designed to be deactivated via light-induced crosslinking. The deactivation was desirable in order to facilitate removal of old bandages from sensitive tissue. Methacrylate functional groups were introduced to the PSA pre-polymer following polymerization (Figure 4.??).[307,308] Relatively low molar quantities of the methacrylate group were sufficient to crosslink the polymer when it was exposed to visible light, after it was blended with the free-radical

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[305] D.-Y. Lee, N. Subramaniam, C. M. Fellows, and R. G. Gilbert, "Structure–Property Relationships in Modified Natural Rubber Latexes Grafted with Methyl Methacrylate and Vinyl Neo-Decanoate." *J. Polym. Sci. A Poly. Chem.*, **2002**, *40*, 809–822.

[306] P. Kingshott, J. Wei, D. Bagge-Ravn, N. Gadegaard, and L. Gram, "Covalent Attachment of Poly(Ethylene Glycol) to Surfaces, Critical for Reducing Bacterial Adhesion." *Langmuir*, **2003**, *19*(6912-6921.

[307] I. Webster, "Adhesives." *US* 6,184,264, **2001**.

photoinitiator Irgacure. Photocrosslinking reduced the adhesive peel strengths by up to 98 percent. The photodeactivation rates were primarily dependent on the concentration of photoinitiator.

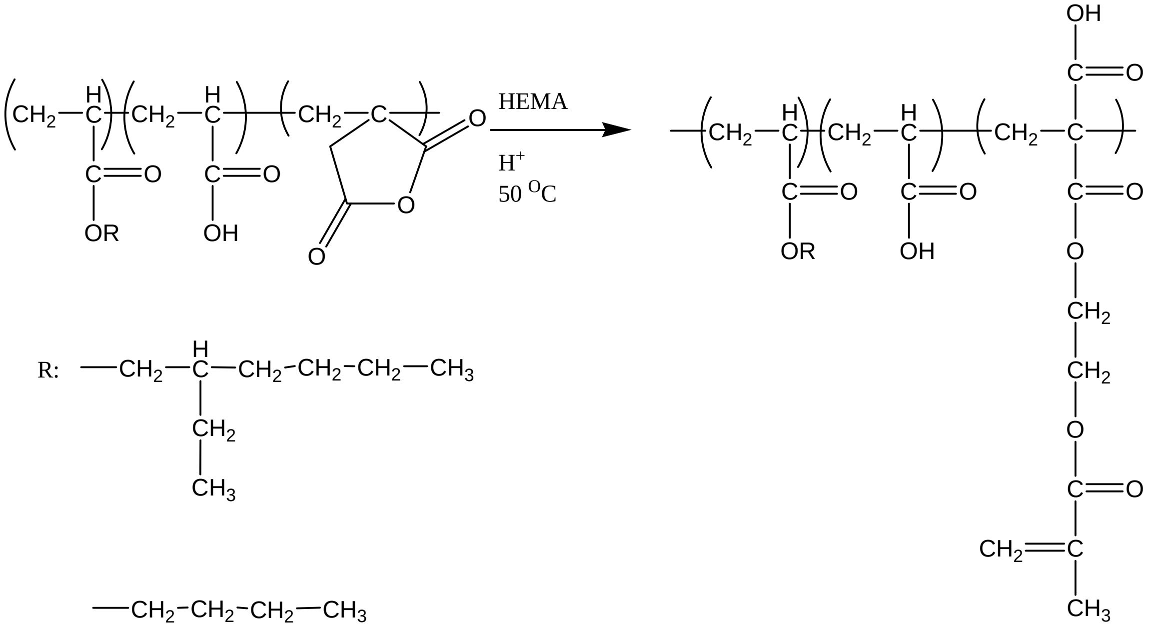

Figure 4.3: Post-polymerization introduction of methacrylate functional group to synthesize a photoswitchable PSA[282]

The crosslink density typically determines whether a pressure-sensitive adhesive exhibits excellent or poor adhesion. In addition to being utilized in deactivatable adhesives, crosslinking was also used to generate excellent adhesives in-situ. The advantage of this technique is rapid and facile application of the pre-polymer prior to crosslinking. This technique has advantages in applications such as wound dressings. Adhesives for wound dressings were synthesized from three-armed star-shaped polymers

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[308] I. Webster, "The Development of a Pressure-Sensitive Adhesive for Trauma-Free Removal." *Int. J. Adhes. Adhesiv.*, **1999**, *19*(1), 29-34.

containing PEG and poly(propylene oxide) (PPO) containing three isocyanate functional groups at the termini.[309] HEMA was reacted with the isocyanate groups, resulting in a material that was photocrosslinkable in the presence of a free-radical photoinitiator. The star-shaped polymer was irradiated following application to a wound site, resulting in excellent adhesive and toughness characteristics in the wound dressing.

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[309] C. C. Capelli and K. Zamzow, "Pressure-Sensitive Adhesive Compositions Suitable for Medical Uses" *US* 5,045,601, **1991**.

Chapter 5: Synthesis and Characterization of Novel Acid-Sensitive *tert*-Butyl Methacrylate and Isobutyl Methacrylate Containing Star-Shaped Polymers

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4512(Complex Adaptive Structures), 65-74.

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5.1 Abstract

Star-shaped polymers containing poly(isobutyl methacrylate) (iBMA) and poly(*tert*-butyl methacrylate) (*t*-BMA) arms coupled to a 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) core were synthesized using arm-first living anionic polymerization. Size exclusion chromatography (SEC) indicated that coupling efficiencies were high and coupled products exhibited a monomodal molecular weight distribution. The star-shaped polymer number-average molecular weights were 8 to 10 times higher than the precursor arm molecular weights. The ratio of coupling reagent to living chain end concentration controlled the molecular weight of the star-shaped polymer and the number of coupled arms. The molecular weight distributions of the star-shaped polymers ranged from 1.5 to 2.0. Due to the labile tertiary-butyl esters contained in the DHDMA cores, these star-shaped polymers were readily hydrolyzed in the presence of acid catalysts. For example, poly(iBMA) star-shaped polymers were hydrolytically stable at 25 °C and hydrolyzed readily at 65 °C in the presence of hydrochloric acid. In addition, the poly(*t*-BMA) containing star-shaped polymers

degraded under similar conditions. The degradation process for the iBMA and *t*-BMA containing star-shaped polymers was confirmed using ^{1}H NMR spectroscopy, and poly(iBMA)-*block*-poly(methacrylic acid) and poly(methacrylic acid) were obtained, respectively.

Keywords: star-shaped polymer, anionic polymerization, degradable, methacrylate, hydrolysis, synthesis, coupling

5.2 Introduction

Living anionic polymerization[310] permits the preparation of star[311,312] and diblock[313] copolymers, which exhibit unique solid-state morphologies and solution properties.[314,315] Living polymerizations distinguish themselves from conventional chain polymerizations by the fact that the active center does not terminate or undergo chain-transfer.[316] As a result, the number-average molecular weight of the polymer chain can

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[310] H. L. Hsieh and R. P. Quirk, *Anionic Polymerization : Principles and Practical Applications*, New York: Marcel Dekker, 1996.

[311] X. Zhang, J. Xia, and K. Matyjaszewski, "End-Functional Poly(*Tert*-Butyl Acrylate) Star Polymers by Controlled Radical Polymerization." *Macromolecules*, **2000**, *33*(7), 2340-2345.

[312] V. R. Raju, E. V. Menezes, G. Marin, W. W. Graessley, and L. J. Fetters, "Concentration and Molecular Weight Dependence of Viscoelastic Properties in Linear and Star Polymers." *Macromolecules*, **1981**, *14*(6), 1668-1676.

[313] A. Noshay and J. E. McGrath, *Block Copolymers: Overview and Critical Survey*, New York: Academic Press, 1977, 516.

[314] B. J. Bauer and L. J.. Fetters, "Synthesis and Dilute-Solution Behavior of Model Star-Branched Polymers." *Rubber Chem. Technol.*, **1978**, *51*(3), 401-436.

[315] T. Hashimoto, M. Shibayama, M. Fujimura, and H. Kawai, "Microphase Separation and the Polymer-Polymer Interphase in Block Copolymers." in *Block Copolymers: Science and Technology*, ed. D. J. Meier, *MMI Press Symposium Series*, New York: Harwood Academic Publishers, 1979.

[316] M. Szwarc, "Living Polymers and Mechanisms of Anionic Polymerization." in *Advances in Polymer Science*, Berlin: Springer-Verlag, 1983.

be controlled,[317] and low molecular weight distributions are typically observed. In addition, many anionic polymerization systems result in controlled stereochemistry[318] through a combination of environmental factors, including temperature, solvent, and use of ligating reagents.[319]

The most common strategy to synthesize star-shaped polymers is to initially prepare the arm macromolecule, followed by subsequent coupling of the arms to form star-shaped polymers; this polymerization strategy is known as the arm-first method. The coupling reagents are typically either divinyl monomers, such as divinylbenzene,[320] or multifunctional end-capping reagents, such as tetrachlorosilane.[321] The use of divinyl monomers enables a large number of coupled arms, while chlorosilanes result in greater control over the specific number of coupled arms. Star-shaped polymers utilizing the coupling monomer ethylene glycol dimethacrylate (EGDMA) received industrial attention as viscosity enhancers[322] and ink fillers.[323]

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[317] M. Maurice, *Anionic Polymerization : Principles and Practice*, New York: Academic Press, 1983.

[318] W. H. Liu, T. Nakano, and Y. Okamoto, "Stereochemistry of Acrylate Polymerization in Toluene Using N-BuLi." *Polym. J.*, **1999**, *31*(5), 479-481.

[319] J. B. Pang, G. T. Jin, Y. X. Hou, and H. M. Zhang, "Study on the Anionic Polymerization of *Tert*-Butyl Methacrylate." *J. Polym. Mater.*, **1998**, *15*(1), 67-72.

[320] J. G. Zilliox, P. Rempp, and J. Parrod, "Preparation of Star-Shaped Macromolecules by Anionic Copolymerization." *J. Polym. Sci. Polym. Symp.*, **1968**, *22*(Pt. 1), 145-156.

[321] T. Masuda, Y. Ohta, and S. Onogi, "Rheological Properties of Anionic Polystyrenes. III. Characterization and Rheological Properties of Four-Branch Polystyrenes." *Macromolecules*, **1971**, *4*(6), 763-768.

[322] R. J. Sutherland, "Process for Making Dispersant Viscosity Index Improvers Containing Star Polymers." *US* 5,486,563, **1996**.

[323] H. J. Spinelli, "Ink Jet Inks Containing Star Polymer Additives." *EP* 1,008,634, **2000**.

An attribute of divinylbenzene and EGDMA is that the resulting star-shaped polymer is not susceptible to core cleavage. An example of a cleavable star-shaped polymer was recently reported by Ruckenstein et al. using the coupling monomer ethylene glycol di(1-methacryloyloxy) ethyl ether, which has two hydrolyzable ester bonds.[324] This monomer was polymerized using organolithium initiators and methyl methacrylate to form star-shaped and crosslinked polymers, which were hydrolyzed using acidic water and acetone at ambient temperatures. Quantitative hydrolysis occurred after a few minutes. Although these cleavable star-shaped polymers undergo facile hydrolysis, acid-catalyzed elimination under anhydrous conditions is not possible.

The utility of the *tert*-butyl group in *tert*-butyl methacrylate (*t*-BMA) as a protecting group was thoroughly investigated previously. The *tert*-butyl group was easily removed from *t*-BMA containing polymers via acid-catalyzed hydrolysis[325,326] and elimination[327] mechanisms. In addition, the *tert*-butyl group was thermally eliminated to yield anhydride groups that were easily hydrolyzed using basic water.[328] These deprotection pathways provide indirect routes for the synthesis of poly(methacrylic acid)

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[324] E. Ruckenstein and H. Zhang, "A Novel Breakable Cross-Linker and pH-Responsive Star-Shaped and Gel Polymers." *Macromolecules*, **1999**, *32*(12), 3979-3983.

[325] S.-H. Qin and K.-Y. Qiu, "Block Copolymerization of *Tert*-Butyl Methacrylate with α,ω-Difunctionalized Polystyrene Macroiniferter and Hydrolysis to Amphiphilic Block Copolymer." *J. Polym. Sci. A Polym. Chem.*, **2001**, *39*(9), 1450-1455.

[326] T. E. Long, C. D. DePorter, N. Patel, D. W. Dwight, G. L. Wilkes, and J. E. McGrath, "Poly(Alkyl Methacrylate-Methacrylate Carboxylate) Ion-Containing Block Copolymers." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1987**, *28*(214-216),

[327] A. R. Esker, C. Mengel, and G. Wegner, "Ultrathin Films of a Polyelectrolyte with Layered Architecture." *Science*, **1998**, *280*(5365), 892-895.

[328] J. Lai, "Thermal Behavior of Random Copolymers of Methacrylic Acid and *Tert*-Butyl Methacrylate." *Macromolecules*, **1984**, *17*(5), 1010-1012.

via anionic polymerization,[329] since a direct polymerization of methacrylic acid is not possible. This polymer modification reaction was selectively performed in poly(*t*-BMA) containing block copolymers[330,331] and star-shaped polymers.[332] Although ester-hydrolysis is particularly useful for the synthesis of controlled poly(methacrylic acid), this approach can be applied to the design of cleavable coupling monomers.

A divinyl coupling reagent containing *tert*-butyl ester bonds will undergo similar elimination mechanisms that occur for *t*-BMA. An example of this type of coupling monomer is 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA). This monomer was used in the synthesis of cleavable network polymers.[333] DHDMA has received commercial attention as a network crosslinking monomer for use in nanolithographic applications,[334,335] acting as a positive photoresist that was spin-coated onto a semiconductor wafer. This photoresist was cleaved using a photoacid generator (PAG) present in catalytic quantities. PAG-induced network cleavage occurred at wavelengths ranging from 190 to 315 nm, depending on the PAG selected. The product was removed

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[329] T. E. Long, R. D. Allen, and J. E. McGrath, "Synthesis and Characterization of Block Copolymers Containing Acid and Ionomeric Functionalities." *ACS Symp. Ser.*, **1988**, *364(Chem. React. Polym.)*, 258-275.

[330] P. Guegan, J. J. Cernohous, A. K. Khandpur, T. R. Hoye, and C. W. Macosko, "Anionic Synthesis, Modification and Characterization of ABC Triblock Copolymers," *Macromolecules*, **1996**, *29*(13), 4605-4612.

[331] C. D. DePorter, T. E. Long, and J. E. McGrath, "Methacrylate- Based Block Ionomers. 1. Synthesis of Block Ionomers Derived from T-Butyl Methacrylate and Alkyl Methacrylates." *Polym. Int.*, **1994**, *33*(2), 205-216.

[332] C. Mengel, W. H. Meyer, and G. Wegner, "Photocrosslinkable Star Polymers: Precursors for Model Polyelectrolyte Networks." *Macromol. Chem. Phys.*, **2001**, *202*(7), 1138-1149.

[333] M. Y. Li, R. C. Liang, F. Raymond, and A. Reiser, "Imaging by Photodecoupling of Crosslinks in Polymer Gels." *J. Imaging Sci.*, **1990**, *34*(6), 259-264.

[334] A. Reiser and M. Y. Li, "Photosensitive Element Comprising a Light-Sensitive Acid-Releasing Component and an Acid-Sensitive Crosslinked Polymer." *EP* 422,628, **1991**.

[335] P. R. Varanasi, A. D. Katnani, M. M. Khojasteh, and R. W. Kwong, "Photoresist Compositions with Pendant Polar-Functionalized Groups and Acid-Labile Branching." *US* 6,140,015, **2000**.

by washing with water containing tetramethyl ammonium hydroxide. Ober et al.[336] have also more recently synthesized poly(DHDMA) networks via free-radical polymerization and studied their uncatalyzed thermal cleavage. It was found that thermal ester-bond cleavage occurred at 200 °C, yielding anhydrides. Subsequent hydrolysis of the anhydride-containing polymer using a sodium hydroxide solution led to a base-soluble polymer.

5.3 Experimental

5.3.1 Materials

Reagents were used without further purification, unless stated. 1,1-Diphenylethylene (Aldrich, 97%) was titrated using *sec*-butyllithium (FMC Lithium Division, 2.21 M) under nitrogen and vacuum distilled (0.08 mm Hg) at 65 °C. Methyl methacrylate (Aldrich, 99%), isobutyl methacrylate (TCI, 98%), and *tert*-butyl methacrylate (TCI, 98%) were dried over CaH_2 (Aldrich, 95%) and vacuum distilled (0.08 mm Hg). The monomers were then treated with triethylaluminum (Aldrich, 1.6 M) and vacuum distilled (0.08 mm Hg). THF (Burdick & Jackson, HPLC) was stirred over sodium (Aldrich, lump) and benzophenone (Aldrich, 99%), and distilled under nitrogen. Dichloromethane (HPLC, Burdick & Jackson) and triethylamine (Aldrich, 99%) were stirred over CaH_2 overnight and distilled under nitrogen. Basic alumina (Aldrich, 150 mesh) was activated at 125 °C for at least one week immediately prior to use.

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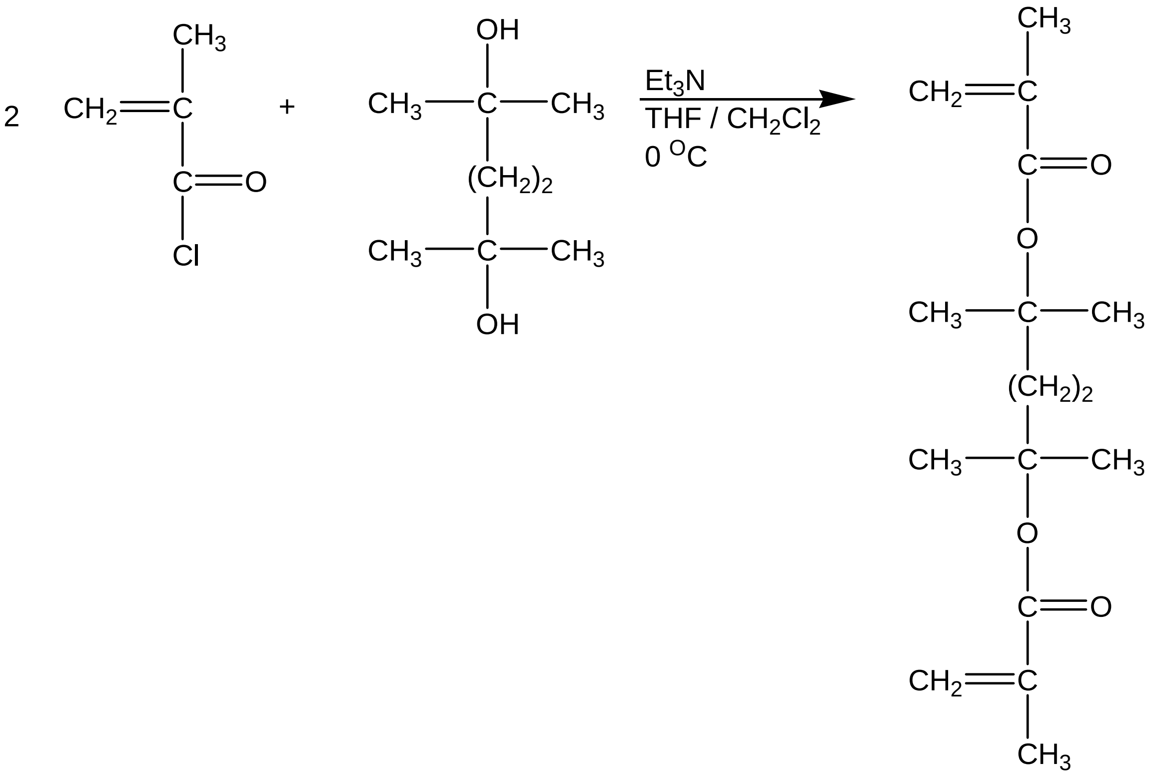
[336] K. Ogino, J.-S. Chen, and C. K. Ober, "Synthesis and Characterization of Thermally Degradable Polymer Networks." *Chem. Mater.*, **1998**, *10*(12), 3833-3838.



Scheme 5.1. Synthesis of 2,5-dimethyl-2,5-hexanediol dimethacrylate.

5.3.2 Monomer synthesis

The synthesis of DHDMA is shown in Scheme 5.1. First, 2,5-dimethyl-2,5-hexanediol (10.0 g, 0.068 mol, Aldrich, used as received) was dissolved in approximately 300 mL CH_2Cl_2 (Allied Signal, distilled from CaH_2). The reaction mixture was cooled to 0 ^{O}C and triethylamine (23.8 mL, 0.17 mol, Aldrich, used as received) was added. Methacryloyl chloride (14.5 mL, 0.15 mol, Acros, fractionally distilled) was added drop-wise via an addition funnel. The reaction was allowed to proceed for 6 hours. The product mixture was washed with basic water (pH = 9) and filtered through two silica columns, followed by one alumina column.

5.3.3 Synthesis of Star-shaped Polymers via Living Anionic Polymerization

The star-shaped polymers were synthesized via the arm-first anionic polymerization method. Both iBMA and *t*-BMA containing star-shaped polymers were synthesized in the exact same manner. The synthesis of the poly(iBMA) DHDMA star-shaped polymers consisted of three steps. Approximately 70 mL of THF (Allied signal, dried over THF) were transferred into a 100 mL round-bottom flask and the flask was cooled to –78 ^{O}C using a dry ice bath. An excess of 1,1-diphenylethylene (0.40 mL, 0.0022 mol, Aldrich, titrated with sec-butyllithium (*s*-BuLi)) was syringed into the reaction vessel, followed by the drop-wise addition of *s*-BuLi (0.35 mL, 0.20 mmol, FMC, used as received). The arm monomer isobutyl methacrylate (5.7 mL, 0.052 mol, TCI, distilled from CaH_2 and titrated with triethylaluminum)[337,338] was slowly syringed

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[337] R. D. Allen, T. E. Long, and J. E. McGrath, "Preparation of High Purity, Anionic Polymerization Grade Alkyl Methacrylate Monomers." *Polym. Bull.*, **1986**, *15*(2), 127-134.

[338] T. E. Long, "Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems." Dissertation, VA Polytech. Inst. & State Univ., 1987.

into the reaction vessel and polymerization was allowed to proceed for 30 min. DHDMA (0.30 mL, 0.0012 mol) was syringed very slowly into the reactor and the coupling reaction was terminated with 1 mL degassed methanol (Allied Signal, used as received) at 1.5 h after DHDMA addition. The star-shaped polymer was precipitated into a 9:1 methanol: water solution and dried overnight under vacuum at 65 ^{O}C. The polymers were analyzed using ^{1}H NMR (400 MHz, $CDCl_3$), gel permeation chromatography (40 ^{O}C, THF, MALLS), and DSC (N_2, 10 ^{O}C/ min.).

5.3.4 Star-shaped Polymer Hydrolysis

The hydrolysis of the star-shaped polymers was carried out by dissolving 500 mg of the star-shaped polymer sample into 40 mL THF. HCl (5 mL, 6M) was added drop-wise to this solution,. The solution refluxed at 65 ^{O}C in an oil bath for 12 hours to ensure complete hydrolysis. The hydrolysis product of the poly(iBMA) DHDMA star-shaped polymer, poly(isobutyl methacrylate)-*block*-poly(methacrylic acid), was precipitated into 400 mL methanol and filtered. The poly(methacrylic acid) arm polymers were precipitated into 400 mL hexanes and filtered. Both filtered polymers were dried under vacuum at 65 ^{O}C for 12 hours.

5.3.5 Characterization

^{1}H and ^{13}C NMR spectra were obtained using a Varian Unity spectrometer operating at 400 MHz and 100 MHz, respectively. Deuterated chloroform (Cambridge Isotope Laboratories) was used as the solvent, and spectra were obtained at 23 °C. A Waters 717plus Autosampler coupled to a Waters 2410 refractive index detector was used to determine polymer molecular weights. SEC measurements were performed in

THF at 40 °C. Absolute molecular weights were determined using a Wyatt Technology miniDAWN® static three-angle laser light scattering detector (MALLS). Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/ min under nitrogen. Glass transition temperatures are reported as the midpoints of the changes in heat capacity during the second heat. Refractive indices were obtained using a refractometer that was temperature-controlled to 18 °C. Refractive indices were normalized to 20 °C using the instrument.

5.4 Results and Discussion

5.4.1 Cleavable Monomer Synthesis

DHDMA was synthesized via the coupling of a molar equivalent of 2,5-dimethyl-2,5-hexanediol and two equivalents of methacryloyl chloride. This reaction was carried out in triethylamine, which acted as both the acid scavenger, as well as making the acid chloride more susceptible to nucleophilic attack. Although the crude yield of this reaction was very high (80-95%), it was extremely difficult to completely remove the triethylamine hydrochloride. This removal was necessary due to the ability of this salt to terminate anionic polymerization. The DHDMA monomer was purified using two silica columns to remove any water, followed by a basic alumina column to remove any methacrylic acid by-product. The extensive use of columns in the purification of the monomer resulted in low recovered yields. Due to the high molecular weight of DHDMA, distillation under reduced pressures as low as 0.03 mm Hg was not possible.

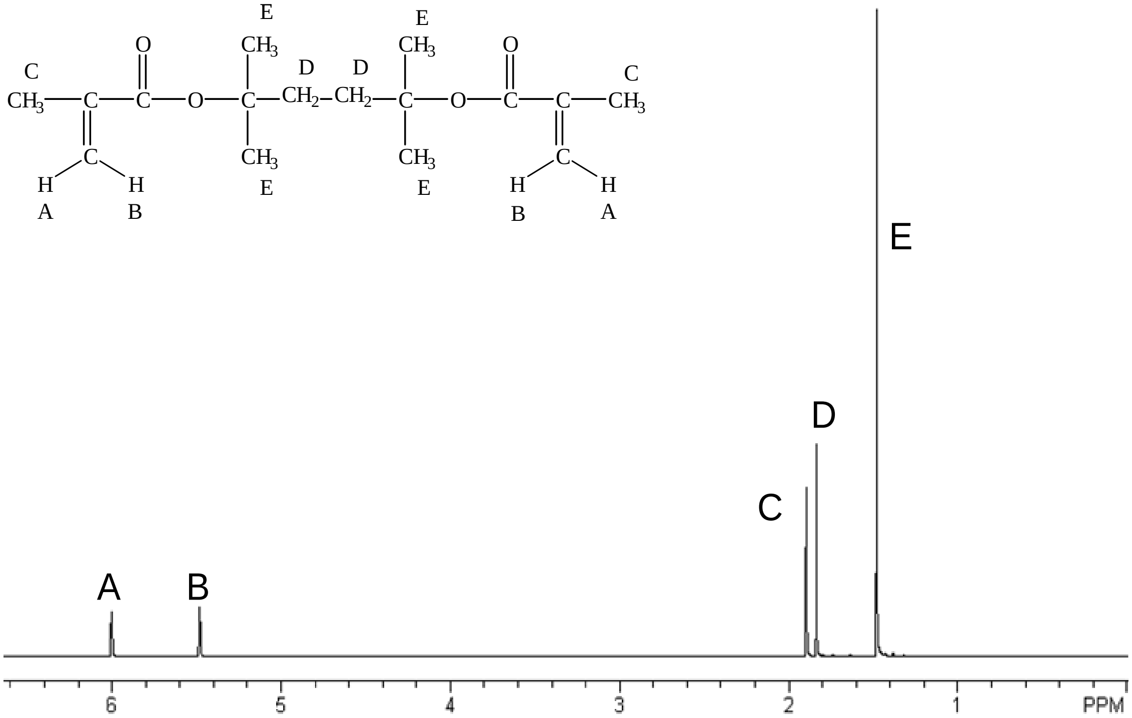


Figure 5.1: ^{1}H NMR spectrum of 2,5-dimethyl-2,5-hexanediol dimethacrylate

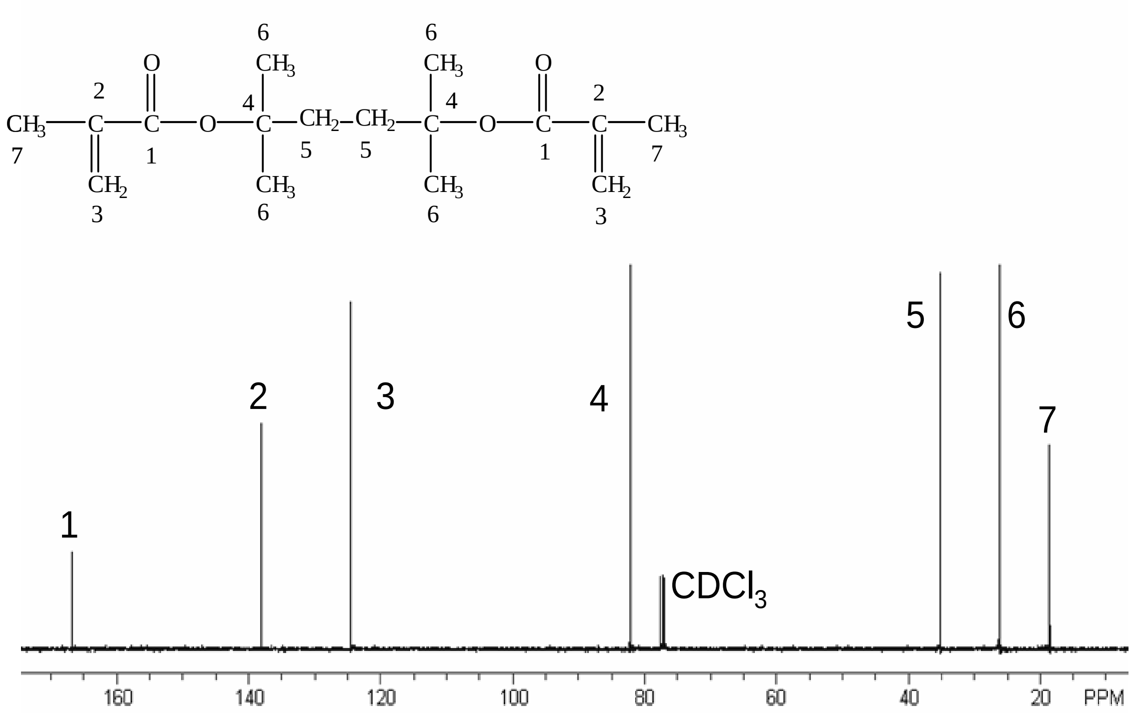
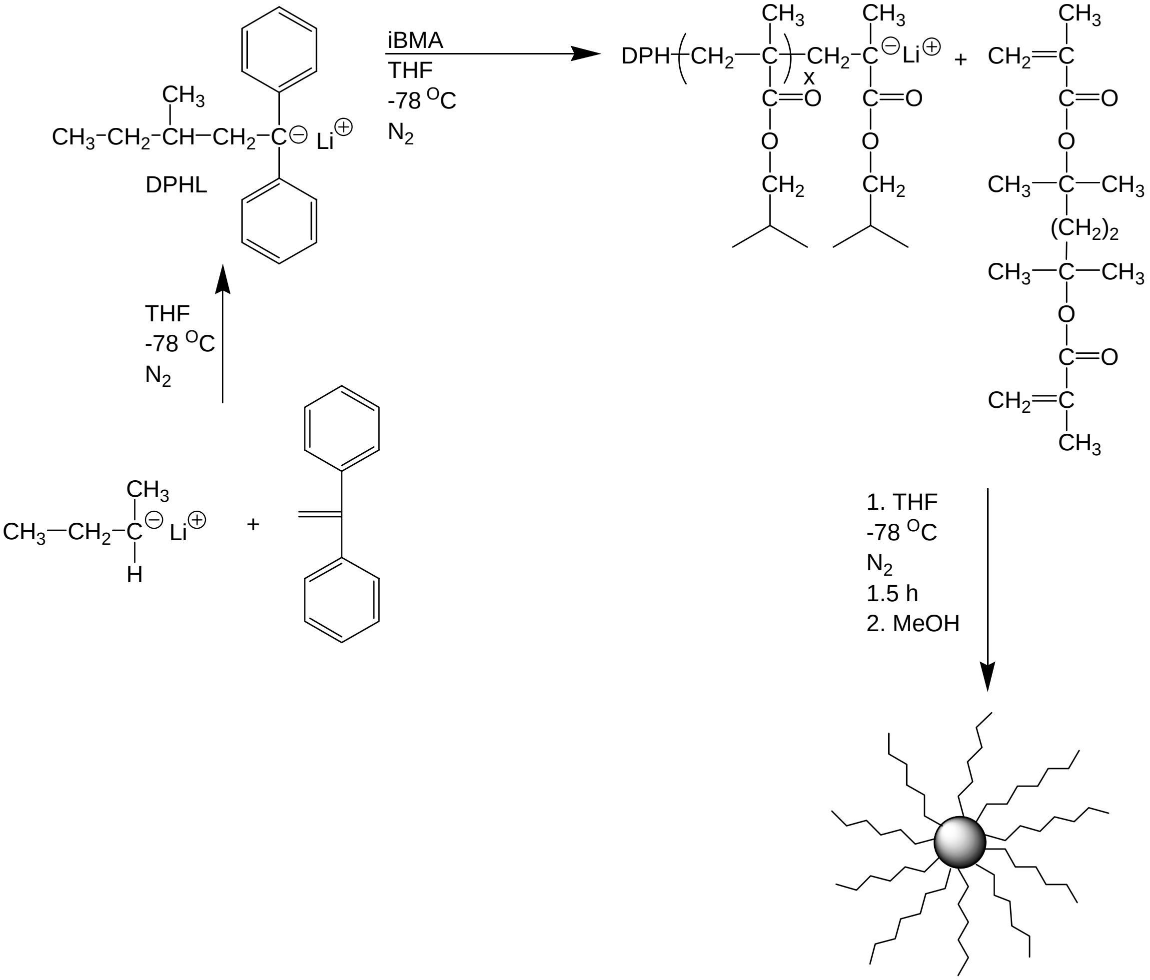


Figure 5.2: ^{13}C NMR spectrum of pure DHDMA

Although DHDMA was previously discussed in the literature, some important physical constants were not reported. The density was determined to be 1.16 g/mL and the refractive index normalized to 20 ^{O}C (n^{20}) was determined to be 1.455. The product was shown to be pure by ^{1}H NMR ($CDCl_3$): δ 6.0 (s, 2H, CH_2=), 5.5 (s, 2H, CH_2=), 1.9 (s, 4H, CH_2CH_2), 1.8 (s, 6H, $=CCH_3$), 1.5 (s, 12H, $C(CH_3)_2$). The structure was also verified using ^{13}C NMR ($CDCl_3$): δ 166 (s, 2C, OC(=O)C), 138 (s, 2C, $CH_3C(=CH_2)$), 125 (s, 2C, $CH_2=C$), 83 (s, 2C, $OC(CH_3)_2C$), 35 (s, 2C, CH_2CH_2), 26 (s, 4C, $C(CH_3)_2$), 18 (s, 2C, $CH_3C(=CH_2)$. The average recovered yield of the monomer was 35% following purification, due to the large amount of column chromatography that was required. The ^{1}H and ^{13}C NMR spectra are shown in Figures 5.1 and 5.2, respectively.

5.4.2 Synthesis of cleavable star-shaped polymers

Novel poly(isobutyl methacrylate) (iBMA) and poly(*tert*-butyl methacrylate) (*t*-BMA) star-shaped polymers containing the cleavable divinyl coupling reagent 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) were synthesized using living anionic polymerization (Scheme 5.2). High molecular weights and coupling efficiencies were observed using gel permeation chromatography. Thermal analysis indicated that the glass-transition temperatures of the star-shaped polymers were very similar to the glass-transition temperatures of the arm homopolymers.



Scheme 5.2: The arm-first star-shaped polymer polymerization of iBMA and DHDMA.

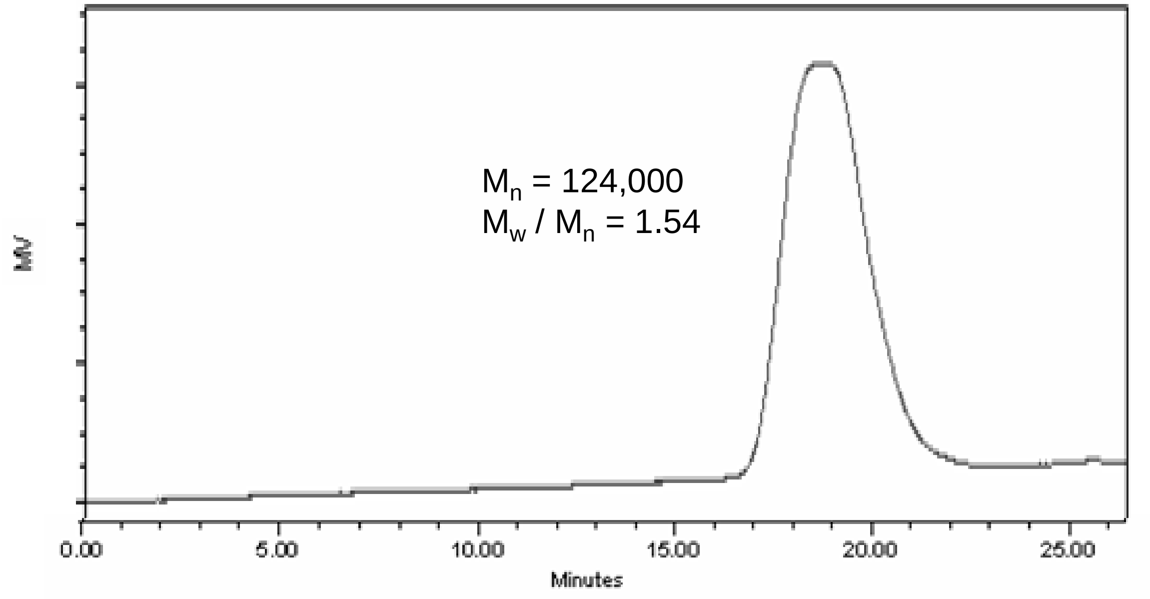


Figure 5.3: SEC chromatogram of a typical poly(*t*-BMA) DHDMA star-shaped polymer.

Two important characteristics of the star-shaped polymers were varied in order to investigate structure-property relationships of these polymers. A variety of arm molecular weights were targeted between 5,000 and 25,000 g/mol. Another variable is the molar ratio of the coupling monomer to the initiating species. Ideally, this ratio determines the core size and the average number of attached arms. Typically, higher amounts of coupling monomer relative to the number of growing chains leads to larger star cores with more arms per star, which influences properties such as star-shaped polymer diffusion.[339] Star-shaped polymers with molar ratios of 3:1, 4:1, and 6:1 were synthesized to study this effect. The molecular weight data for these products is included in Table 5.1. SEC analysis of the poly(iBMA) containing star-shaped polymers indicated that high molecular weights were achieved, relative to the target arm polymer molecular weights. The number average molecular weights of the star-shaped polymers were typically 6 to 10 times higher than the expected molecular weight of the arm polymers. In addition, SEC analysis indicated that complete coupling of the arm polymers to the star-shaped polymer cores occurred.

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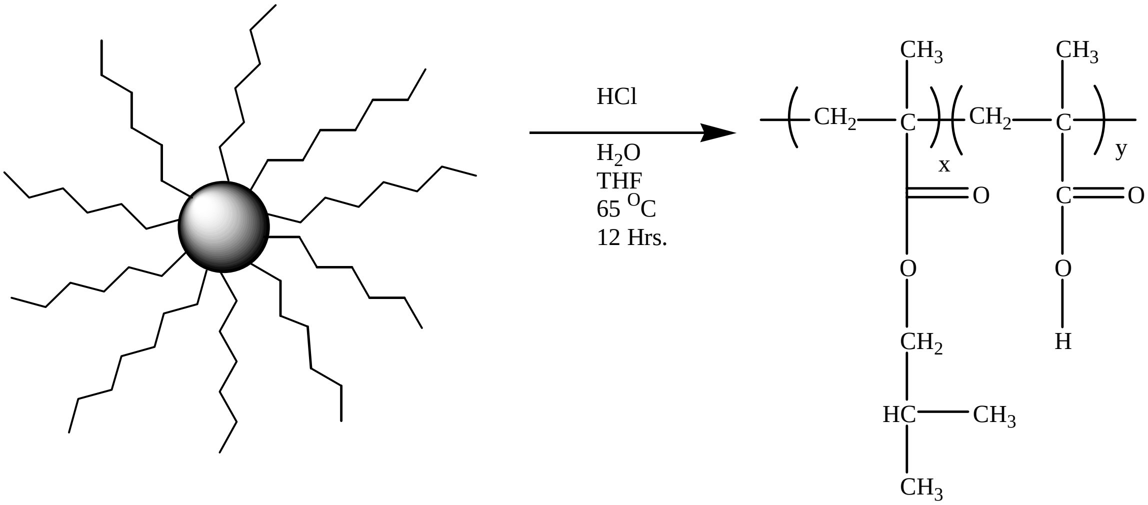
[339] K. R. Shull, E. J. Kramer, and L. J. Fetters, "Effect of Number of Arms on Diffusion of Star Polymers." *Nature,* **1990**, *345*(6278), 790-791.

Table 5.1: Molecular weight data for DHDMA star shaped polymers. Both the poly(iBMA) and poly(*t*-BMA) DHDMA star-shaped polymers exhibited high molecular weights relative to the target arm molecular weights.

Arm Polymer	Calculated Arm M_n	DHDMA: Initiator	Weight % DHDMA	Star M_n^a	Star M_w^a	Star M_w/M_n^a
iBMA	5,000	3:1	12	29,100	58,700	2.00
	5,000	4:1	20	83,800	200,000	2.43
	10,000	4:1	8	73,400	117,000	1.60
	25,000	4:1	4	48,700	93,000	1.91
t-BMA	10,000	4:1	8	128,000	252,000	1.97
	10,000	6:1	10	46,200	82,400	1.78
	25,000	4:1	4	124,000	190,000	1.54
	25,000	6:1	5	224,000	393,000	1.75

The T_g of the poly(iBMA) containing star-shaped polymers was determined to be 73 ^{O}C. The polymerization of the poly(*t*-BMA) containing star-shaped polymers resulted in three polymer samples whose molecular weight (M_n) was in excess of 100,000 g/mol. The molecular weights were 9 to 13 times higher than the expected arm molecular weights of the high molecular weight star-shaped polymers. A typical SEC chromatogram of a poly (t-BMA) DHDMA star-shaped polymer is depicted in Figure 5.3. Similar to the iBMA containing star-shaped polymers, 100 % coupling efficiency was observed in all of the samples synthesized. Poly(*t*-BMA) homopolymers of molecular weights similar to the expected arm molecular weights were shown to elute at much longer times than the elution times of the star-shaped polymers. The SEC traces indicated only a single peak that was attributed to the star-shaped polymer. No peaks due to residual lower molecular weight arm polymers were observed. A T_g of 125 ^{O}C was measured for these star-shaped polymers, which is very similar to the 123 ^{O}C that was reported earlier.[29]



Scheme 5.3: Hydrolysis of poly(iBMA) DHDMA star-shaped polymer.

5.4.3 Hydrolysis of the Star-Shaped Polymers

The poly(iBMA)-arm stars were synthesized due to the fact that the isobutyl group is hydrolytically stable. Thus, hydrolysis of the core of the star-shaped polymer would not affect the structure of the arms. The iBMA-containing star-shaped polymers were initially subjected to hydrolytic conditions at 25 ^{O}C for 24 hours. The SEC data indicated that hydrolysis did not occur at these mild conditions, since the MALLS $<M_n>$ of the sample following the acidic treatment (53,900) was very similar to the original sample (48,700).

The hydrolysis of the star-shaped poly(isobutyl methacrylate) proceeded successfully at 65 °C (Scheme 5.3). The progression of this reaction was followed using ^{1}H NMR, shown in Figure 5.4. The ^{1}H NMR spectrum of the initial star-shaped polymer showed a resonance at 1.6 ppm, corresponding to the four methyl substituents that are α to the tertiary carbons on DHDMA; this peak identified the presence of the coupling unit in the star-shaped polymer. All other protons signals that could be used to identify the coupling unit overlap with the methylene proton peaks from the polymer backbone. After hydrolysis was carried out, the methyl peak at 1.6 ppm, labeled ‘C’ in Figure 5.4, disappeared completely. This indicated that the coupling unit was no longer present and hydrolysis occurred.

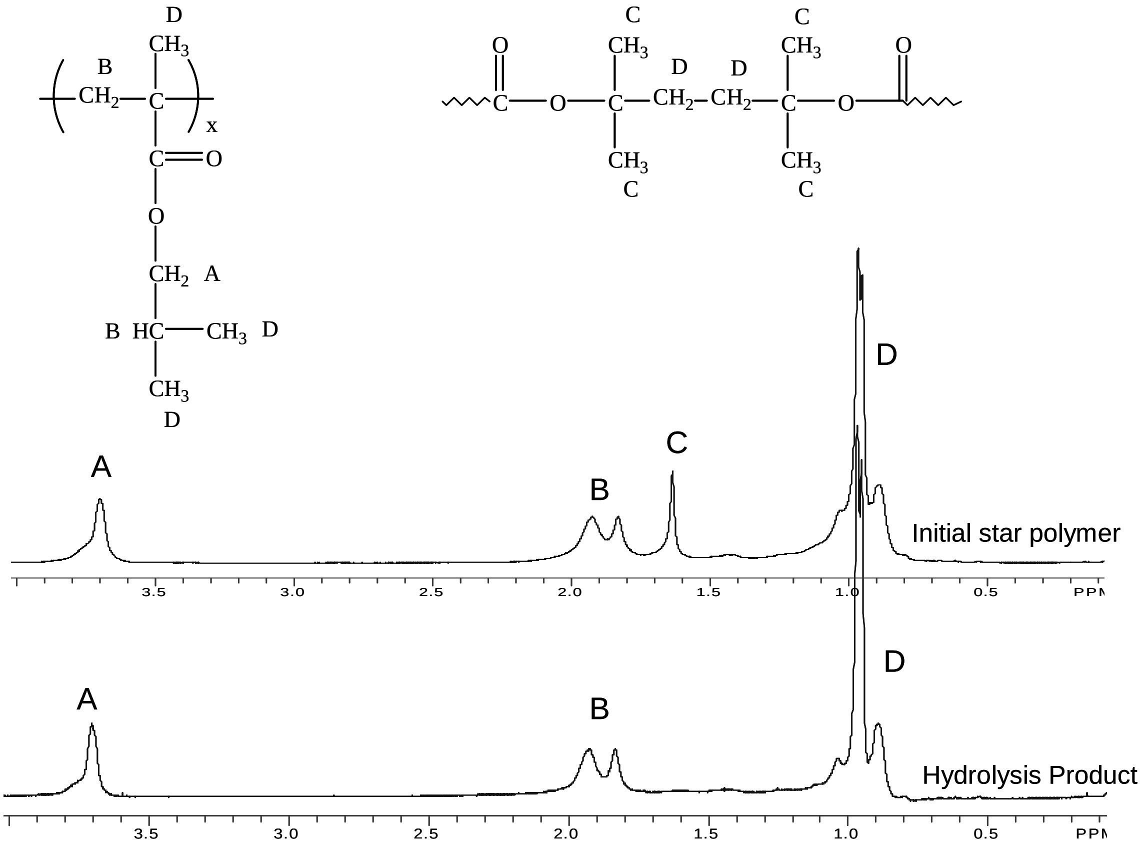


Figure 5.4: ^{1}H NMR spectra of the iBMA-containing star-shaped polymers before and after hydrolysis indicated the successful removal of the coupling group, identified by peak ‘C’.

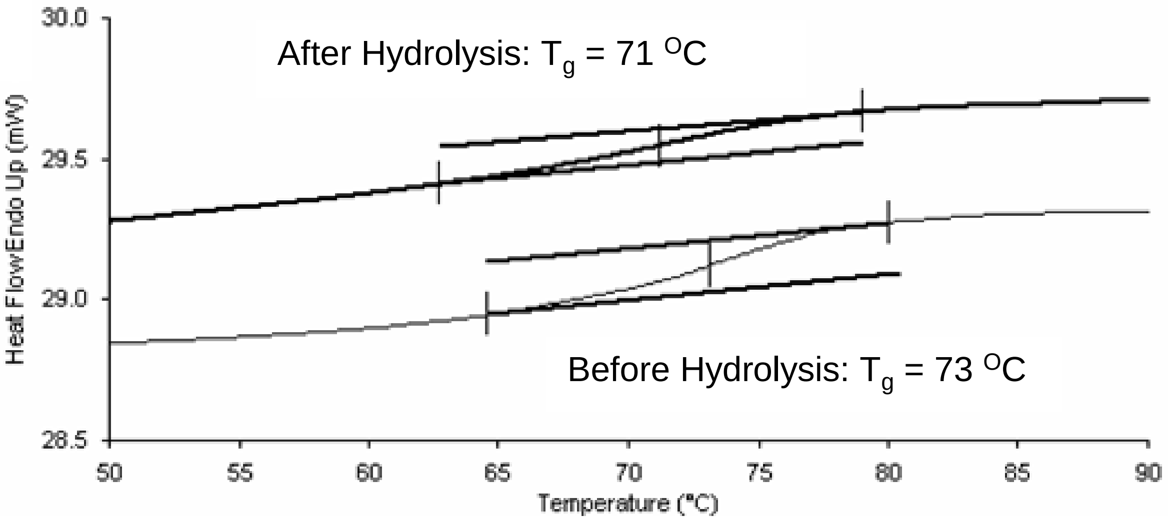


Figure 5.5: DSC trace of poly(iBMA) DMDM star-shaped polymer before and after hydrolysis.

The hydrolysis of tertiary alkyl-ester bonds in the DHDMA core occurred without affecting the hydrolytically stable isobutyl groups on the arms. The ^{1}H NMR resonance peak at 3.8 ppm, which can be used to identify the presence of iBMA, was present in both the initial star-shaped polymer and the hydrolysis product. In addition, the T_g of the polymers did not change significantly as a result of hydrolysis. The T_g of the hydrolysis product was measured to be 73 ^{O}C. Figure 5.5 shows the DSC curves of the iBMA star shaped-polymer and the hydrolysis product. The methacrylic acid block in the hydrolysis product was not large enough to produce a measurable T_g. A distinguishing feature of the *t*-BMA-containing star-shaped polymers is that they hydrolyze to form only poly(methacrylic acid), unlike star-shaped polymers that contain hydrolytically stable repeating units. This feature facilitates the identification of the hydrolysis product through ^{1}H NMR. During hydrolysis, both the *tert*-butyl and DHDMA coupling groups were cleaved. As a result, the large ^{1}H NMR peak at 1.5 ppm corresponding to the methyl protons on both the *t*-butyl and the DHDMA coupling units was absent in the hydrolysis product spectrum.

5.5 Conclusions

Novel pH- sensitive methacrylic star-shaped polymers composed of iBMA and *t*-BMA arms and acid-cleavable DHDMA cores were successfully synthesized via anionic polymerization. The monomer DHDMA was purified thoroughly enough to be used in anionic polymerization. These star-shaped polymers were polymerized in quantitative yields and very high coupling efficiencies. Very high molecular weights relative to the target arm molecular weights were observed for both types of star-shaped polymers.

Higher amounts of coupling reagents led to larger cores and molecular weights as high as 224,000 g/mol. The glass transition temperatures for the iBMA and *t*-BMA- containing star-shaped polymers of 73 and 125 °C, respectively, corresponded well with published values of the homopolymers. The alkyl-ester bonds in the DHDMA cores were shown to be hydrolytically stable at 25 °C, but hydrolysis occurred at 65 °C. The hydrolysis was demonstrated using ^{1}H NMR, indicating that the alkyl bridge contained in the DHDMA repeat-unit was completely removed upon hydrolysis. This indicates that these star-shaped polymers can be cleaved into the constituent arm polymers.

5.6 Acknowledgements

The authors gratefully acknowledge the Carilion Biomedical Institute, Virginia Tech Optical Sciences and Engineering Research (OSER) Center, and the Jeffress Memorial Trust Fund for their financial support of this project. We would also like to thank FMC Lithium Division for the generous donation of *sec*-butyllithium.

Chapter 6: Synthesis and Cleavage of Core-Labile Poly (Alkyl methacrylate) Star-Shaped Polymers

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J. Polym. Sci. A. **2003**, *41*, 3083-3093.

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6.1 Abstract

Core-cleavable star polymers were synthesized via coupling living anionic poly(alkyl methacrylate) arms with either dicumyl dimethacrylate (DCDMA) or 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA). This synthetic methodology led to the formation of star polymers that exhibited high molecular weights and relatively narrow molecular weight distributions. The labile tertiary alkyl esters in the DCDMA and DHDMA star polymer cores were readily hydrolyzed under acidic conditions. High molecular weight star polymer cleavage led to well-defined arm polymers with lower molecular weights. Hydrolysis was confirmed via ^{1}H NMR spectroscopy and gel permeation chromatography. Thermogravimetric analysis (TGA) of the star polymers demonstrated that the DCDMA and DHDMA star polymer cores also thermally degraded in the absence of acid catalysts at 185 °C and 220 °C respectively, and core cleavage temperatures were independent of the arm polymer composition. The difference in core degradation temperatures was attributed to the increased reactivity of the DCDMA derived cores. TGA-mass spectrometry (TGA-MS) detected the evolution of the diene by-product of the core degradation and confirmed the proposed degradation mechanism.

The DCDMA monomer exhibited a higher degradation rate than DHDMA under identical reaction conditions due to additional resonance stabilization of the liberated by-product, making it a more responsive cleavable coupling monomer than DHDMA.

Keywords: star polymers, anionic polymerization, degradation, alkyl methacrylate, thermal degradation

6.2 Introduction

Numerous families of macromolecules with an array of topologies, including star polymers,[340,341] were previously synthesized via living anionic polymerization.[342,343] Living polymerizations are ideal for the synthesis of tailored polymer architectures because the propagating intermediate does not undergo termination or chain-transfer,[344] which results in well-defined macromolecules. Two methods, termed *core-first* and *arm-first*, are commonly used in the synthesis of star polymers. The core-first method has utilized polyfunctional initiators,[345,346] and the number of polymer arms was dictated by the number of initiating sites. This method was only useful for the controlled synthesis of

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[342] H. L. Hsieh and R. P. Quirk, *Anionic Polymerization : Principles and Practical Applications*, New York: Marcel Dekker, 1996.

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[344] M. Maurice, *Anionic Polymerization : Principles and Practice*, New York: Academic Press, 1983.

[345] J. P. Kennedy and S. Jacob, "Cationic Polymerization Astronomy. Synthesis of Polymer Stars by Cationic Means." *Acc. Chem. Res.*, **1998**, *31*(12), 835-841.

[346] E. Cloutet, J. Fillaut, Y. Gnanou, and D. Astruc, "Hexaarm Star-Shaped Polystyrenes by Core-First Method." *J. Chem. Soc., Chem. Commun.*, **1994**, *21*, 2433-2434.

star polymers with a limited number of arms. In contrast, the arm-first method for the preparation of star polymers was performed via the preparation of the living arm macromolecule and subsequent arm coupling.[347] For example, multifunctional end-capping reagents, such as chlorosilanes,[348,349] were utilized for the synthesis of well-defined star macromolecules.

Significant research was devoted to poly(alkyl methacrylate) living polymerizations in the 1980's due to the intense interest in well-defined anionic polymerization strategies.[350,351,352] Star polymer coupling reactions were also accomplished using a range of divinyl monomers, such as ethylene glycol dimethacrylate (EGDMA)[353] under living anionic polymerization conditions. The use of divinyl reagents is widely recognized to result in stars containing small crosslinked cores.[354] EGDMA was utilized in the synthesis of poly(alkyl methacrylate) star polymers, due to the relative

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[347] M. Lazzari, T. Kitayama, M. Janco, and K. Hatada, "Synthesis of Syndiotactic Star Poly(Methyl Methacrylate)s with Controlled Number of Arms." *Macromolecules*, **2001**, *34*(17), 5734-5736.

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[350] R. D. Allen, T. E. Long, and J. E. McGrath, "Preparation of High Purity, Anionic Polymerization Grade Alkyl Methacrylate Monomers." *Polym. Bull.*, **1986**, *15*(2), 127-134.

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[352] T. E. Long, R. A. Guistina, B. A. Schell, and J. E. McGrath, "Hindered Lithium Dialkylamide Initiators for the Living Anionic-Polymerization of Methacrylic Esters." *J. Polym. Sci. A Polym. Chem.*, **1994**, *33*(13), 2425-2430.

[353] V. Efstratiadis, G. Tselikas, N. Hadjichristidis, J. W. Li, Y. Wan, and J. W. Mays, "Synthesis and Characterization of Poly(Methyl Methacrylate) Star Polymers." *Polym. Int.*, **1994**, *33*(2), 171-179.

[354] M. K. Martin, T. C. Ward, and J. E. McGrath, "The Reactivity of Polydiene Anions with Divinylbenzene," in *Anionic Polymerization: Kinetics, Mechanisms, and Synthesis*, ed. J. E. McGrath, Washington, D. C.: American Chemical Society, 1981.

reactivity of the living enolate and the coupling reagent. Most divinyl compounds such as EGDMA result in star polymers that are not susceptible to subsequent core cleavage, thus preventing the conversion of star polymers to a plurality of individual arms. However, a recent example of a cleavable star polymer involved ethylene glycol di(1-methacryloyloxy) ethyl ether, which contained two hydrolyzable esters.[355,356] This acid-sensitive divinyl compound was employed with organolithium initiators and methyl methacrylate to form star and network polymers. The star polymers were quantitatively hydrolyzed under slightly acidic conditions at ambient temperatures within a few minutes. More recently, polyacrylamine networks, crosslinked using acetal-containing divinyl compounds, were used to encapsulate fluorescent bovine serum albumin. These proteins were rapidly released when the pH was lowered from seven to five.[357] Although cleavable star and network polymers containing acetal crosslinking moieties were shown to undergo facile hydrolysis, acid-catalyzed elimination under anhydrous conditions was not observed.

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[355] E. Ruckenstein and H. Zhang, "Breakable Crosslinkers and Use for Preparation of Polymers Using Same." *US* 6,323,360, **2001**.

[356] E. Ruckenstein and H. Zhang, "A Novel Breakable Cross-Linker and pH-Responsive Star-Shaped and Gel Polymers." *Macromolecules*, **1999**, *32*(12), 3979-3983.

[357] N. Murthy, Y. X. Thng, S. Schuck, M .C. Xu, and J. M. J. Fréchet, "A Novel Strategy for Encapsulation and Release of Proteins: Hydrogels and Microgels with Acid-Labile Acetal Cross-Linkers." *J. Am. Chem. Soc.*, **2002**, *124*(42), 12398-12399.

The *tert*-butyl ester has received significant attention in our laboratories as an effective protecting group due to the labile ester-alkyl bond.[358,359,360] Several poly(*tert*-butyl methacrylate) (*t*-BMA) containing polymers were synthesized in an attempt to introduce carboxylic acids and metal carboxylates via the deprotection of the *tert*-butyl groups following polymerization.[361,362] The *t*-butyl protecting group was easily removed via acid-catalyzed processes, in the presence[363,364] or absence of water.[365] The *tert*-butyl group was also shown to be susceptible to thermal elimination, and readily hydrolyzable anhydride linkages were obtained.[366] In addition, the removal of *tert*-butyl ester protecting groups was selectively conducted in poly(*t*-BMA) containing block copolymers[367,368,369] and star polymers.[370]

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[358] E. K. Euranto, "Esterification and Ester Hydrolysis." in *The Chemistry of Carboxylic Acids and Esters*, ed. S. Patai, New York: Interscience, 1969.

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[360] E. K. Euranto, "Esterification and Ester Hydrolysis." in *The Chemistry of Carboxylic Acids and Esters*, ed. S. Patai, New York: Interscience, 1969.

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Tert-butyl esters in divinyl crosslinked networks were also shown to undergo cleavage reactions. 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) was recently used in the synthesis of acid-cleavable polymer networks.[371] Positive photoresists in microlithographic applications typically employed photoacid generators to generate sub-micron images.[372,373] Poly(DHDMA) networks have attracted commercial attention in microlithography[374] due to the highly acid-labile nature of DHDMA, and Ober et al.[375] studied the uncatalyzed thermal cleavage of poly(DHDMA) networks. Thermal ester cleavage occurred at 200 °C yielding anhydrides. Subsequent hydrolysis of the anhydride-containing polymer in the presence of sodium hydroxide led to a base-soluble polymer. The acid-catalyzed hydrolysis of DHDMA-containing thermoplastics was recently accomplished in our laboratories to induce topological reorganizations to linear polymers.[376,377]

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[372] R. D. Allen, R. Sooriyakumaran, J. Opitz, G. M. Wallraff, G. Breyta, R. A. Dipieto, D. C. Hofer, U. Okoroanyanwu, and C. G. Wilson, "Progress in 193 nm Positive Resists." *J. Photopolym. Sci. Tech.*, **1996**, *9*(3), 465-473.

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The dimethacrylate monomers 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) and dicumyl dimethacrylate (DCDMA) were used to couple living poly(alkyl methacrylate) arm polymers into novel star polymers. These stars were designed to contain cleavable cores by utilizing the acid-labile nature of DCDMA and DHDMA. Both star polymer compositions were hydrolyzed under acidic conditions and elevated temperatures to yield lower molecular weight linear polymers. DCDMA was preferred due to more facile purification and more rapid hydrolysis compared to DHDMA.

6.3 Experimental

6.3.1 Materials

Materials were used as received unless otherwise noted. 1,1-Diphenylethylene (Aldrich, 97%) was titrated using *sec*-butyllithium (FMC Lithium Division, 2.21 M) under nitrogen and vacuum distilled (0.08 mm Hg) at 65 °C. Methyl methacrylate (Aldrich, 99%), isobutyl methacrylate (TCI, 98%), and *tert*-butyl methacrylate (TCI, 98%) were dried over CaH_2 (Aldrich, 95%) and vacuum distilled (0.08 mm Hg). The monomers were then treated with triethylaluminum (Aldrich, 1.6 M) and vacuum distilled (0.08 mm Hg). THF (Burdick & Jackson, HPLC) was stirred over sodium (Aldrich, lump) and benzophenone (Aldrich, 99%), and distilled under nitrogen. Dichloromethane (HPLC, Burdick & Jackson) was stirred over CaH_2 overnight and distilled under nitrogen. Basic alumina (Aldrich, 150 mesh) was activated at 125 °C immediately prior to use.

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6.3.2 Coupling Monomer

The coupling monomers DCDMA and DHDMA were synthesized using methacryloyl chloride and the corresponding alcohol.[378,379] For the synthesis of DCDMA, dicumyl alcohol (α, α, α', α'-tetramethyl-1,4-benzenedimethanol, 15.0 g, 0.077 mol, Aldrich, 99%) and triethylamine (25.7 mL, 0.185 mol, Aldrich, 98%) were added to a clean, dry, round-bottomed flask containing dichloromethane (400 mL). The solution was cooled to 0 °C under nitrogen and methacryloyl chloride (16.4 mL, 0.169 mol, Aldrich, 98%) was added drop wise. The reaction was allowed to proceed for 8 hours. The product mixture was washed twice with basic water (pH ~ 8, 400 mL). The solvent was removed in vacuo. DCDMA was recrystallized five times from a 3:1:1 solution of methanol, ethanol, and water. The average recovered yield of anionic polymerization-grade DCDMA was 65 percent. Monomer structure was verified using ^{1}H NMR spectroscopy (CD_2Cl_2): δ 7.3 (s, 4H, -C_6H_4-), 6.0 (s, 2H, CH_2=), 5.5 (s, 2H, CH_2=), 1.8 (s, 6H, =CCH_3), 1.5 (s, 12H, $C(CH_3)_2$) and ^{13}C NMR spectroscopy (CD_2Cl_2): δ 166 (s, 2C, OC(=O)C), 145 (s, 2C, Ar) 138 (s, 2C, $CH_3C(=CH_2)$), 125 (s, 2C, CH_2=C), 124 (s, 4C, Ar), 82 (s, 2C, $OC(CH_3)_2C$), 29 (s, 4C, $C(CH_3)_2$), 18 (s, 2C, $CH_3C(=CH_2)$).

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[378] T. E. Long, L. Kilian, Z.-H. Wang, and A. R. Esker, "Synthesis and Characterization of Novel Acid-Sensitive *Tert*-Butyl Methacrylate and Isobutyl Methacrylate Containing Star-Shaped Polymers." *Proc. SPIE- Soc. Opt. Eng.*, **2001**, *4512(Complex Adaptive Structures)*, 65-74.

[379] K. Ogino, J.-S. Chen, and C. K. Ober, "Synthesis and Characterization of Thermally Degradable Polymer Networks." *Chem. Mater.*, **1998**, *10*(12), 3833-3838.

DHDMA was synthesized using 2,5-dimethyl-2,5-hexandiol in a manner identical to the DCDMA synthesis. Following solvent extraction, DHDMA was purified using two silica (Aldrich, 70-230 mesh) columns and one activated basic alumina column. Dichloromethane was the mobile phase for all three columns. Only about 40 percent of DHDMA was recovered after the necessary extensive purification steps. The structure of DHDMA was verified using ^{1}H NMR spectroscopy ($CDCl_3$): δ 6.0 (s, 2H, CH_2=), 5.5 (s, 2H, CH_2=), 1.9 (s, 4H, CH_2CH_2), 1.8 (s, 6H, $=CCH_3$), 1.5 (s, 12H, $C(CH_3)_2$) and ^{13}C NMR spectroscopy ($CDCl_3$): δ 166 (s, 2C, $OC(=O)C$), 138 (s, 2C, $CH_3C(=CH_2)$), 125 (s, 2C, $CH_2=C$), 83 (s, 2C, $OC(CH_3)_2C$), 35 (s, 2C, CH_2CH_2), 26 (s, 4C, $C(CH_3)_2$), 18 (s, 2C, $CH_3C(=CH_2)$). Thin layer chromatography of the purified monomers revealed a single spot when dichloromethane was used as the mobile phase. Due to the onset of thermal decomposition above 200 ^{O}C, neither DCDMA nor DHDMA was analyzed using gas chromatography or mass spectrometry.

6.3.3 Synthesis of Poly(MMA) star polymers

Various star polymers were synthesized using identical synthetic methodologies. The synthesis of DCDMA-coupled star polymers is shown in Scheme 6.2, and consisted of three sequential steps**.** A flame-dried, 100-mL, round-bottomed flask was pressurized with N_2 (10 psi), charged with purified THF (65 mL), and cooled to –78 °C in an isopropanol and dry ice bath. 1,1-Diphenylethylene (0.005 mol, 0.20 mL) was added to the flask using a syringe, and minor impurities were titrated using *sec*-butyllithium (< 0.1 mL). The red diphenylhexyllithium (DPHL) initiator was formed via the drop wise addition of s*ec*-butyllithium (0.001 mol, 0.45 mL). Cold methyl methacrylate (0.05 mol, 5.0 g) monomer was added drop wise to the DPHL solution, and the polymerization was allowed to proceed for 30 min. Following the quantitative conversion of the monomer, DCDMA (0.006 mol in THF) was charged, and the coupling reaction was allowed to proceed for 1.5 hours at –78 °C. The polymerization was terminated using degassed methanol (1 mL, Allied Signal, HPLC-grade) and precipitated into a 9:1 solution of methanol and deionized water (650 mL).

6.3.4 Star polymer cleavage

A star polymer sample (500 mg) was dissolved in dioxane (40 mL, Aldrich, 98%) using magnetic stirring. *para*-Toluenesulfonic acid [*p*TSA] monohydrate (100 mg, Aldrich, 98%) was added and the solution was heated to 100 °C under a nitrogen atmosphere for 12 h. The hydrolyzed star polymer was precipitated into a 9:1 methanol: water solution (400 mL) and dried at 65 °C in vacuo.

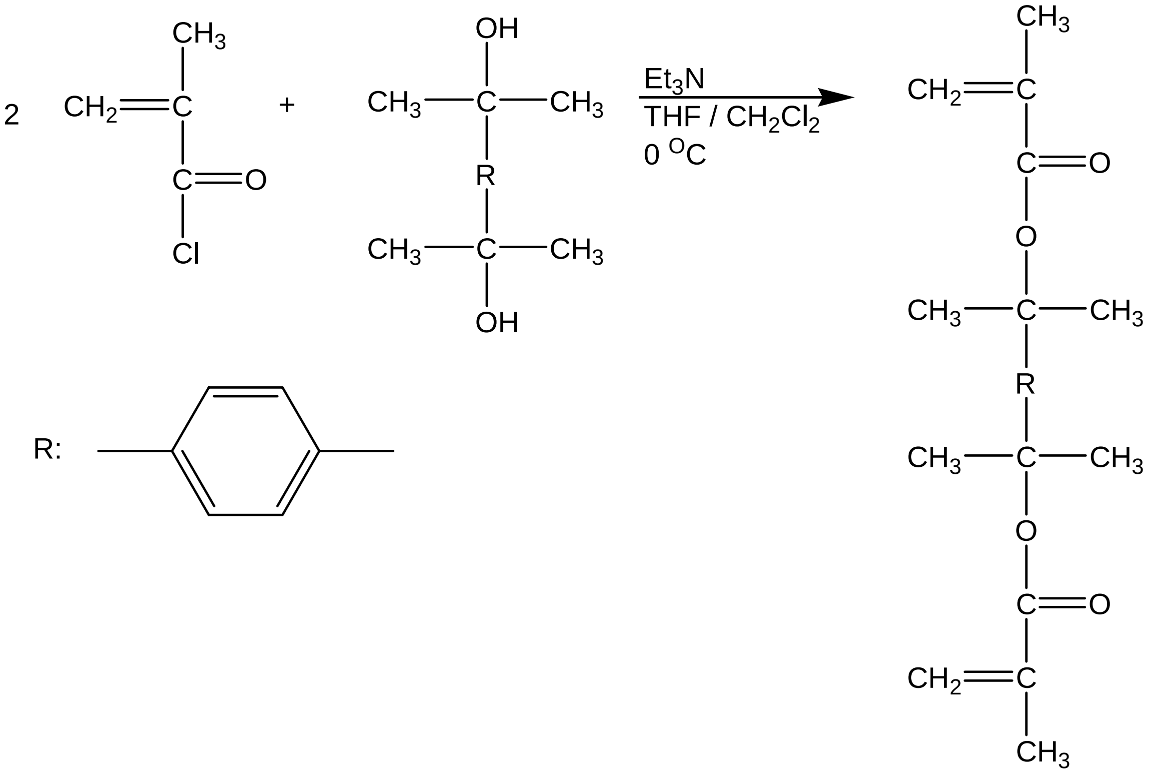
The star polymers were also cleaved at high temperatures using a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer coupled to a Balzers quadrupole mass spectrometer. The polymer samples were heated at a rate of 5 °C/min under nitrogen from 45 to 300 °C and the temperature of the capillary to the mass spectrometer was held constant at 200 °C. Weight loss was measured as a function of temperature and three mass spectrum signals characteristic of DCDMA or DHDMA thermolysis were monitored.

6.3.5 Thermal solution hydrolysis of coupling monomers

Dicumyl dimethacrylate (30 mg, 0.091 mmol) was added to a 7 mm NMR tube and dissolved in dimethyl sulfoxide $-d_6$ (1 mL, Cambridge Isotope Laboratories) and *p*TSA monohydrate (5 mg). The tube was heated at 85 °C for 5 hours. A ^{1}H NMR spectrum was obtained every 30 minutes. The same degradation experiment was performed on 2,5-dimethyl-2,5-hexanediol dimethacrylate.

6.3.6 Polymer Characterization.

^{1}H and ^{13}C NMR spectra were obtained using a Varian Unity 400 spectrometer operating at 400 MHz and 100 MHz, respectively. The polymers were dissolved in deuterated dichloromethane (Cambridge Isotope Laboratories). Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C / min under nitrogen. Glass transition temperatures are reported as the midpoints of the changes in heat capacity during the second heat. A Waters 717plus autosampler coupled to a Waters 2410 refractive index detector was used to determine polymer molecular weights. The polymer molecular weights were also determined using a Wyatt Technology MiniDAWN static three-angle laser light scattering detector (MALLS), which provided absolute weight average molecular weights. SEC measurements were performed at 40 °C in THF at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.



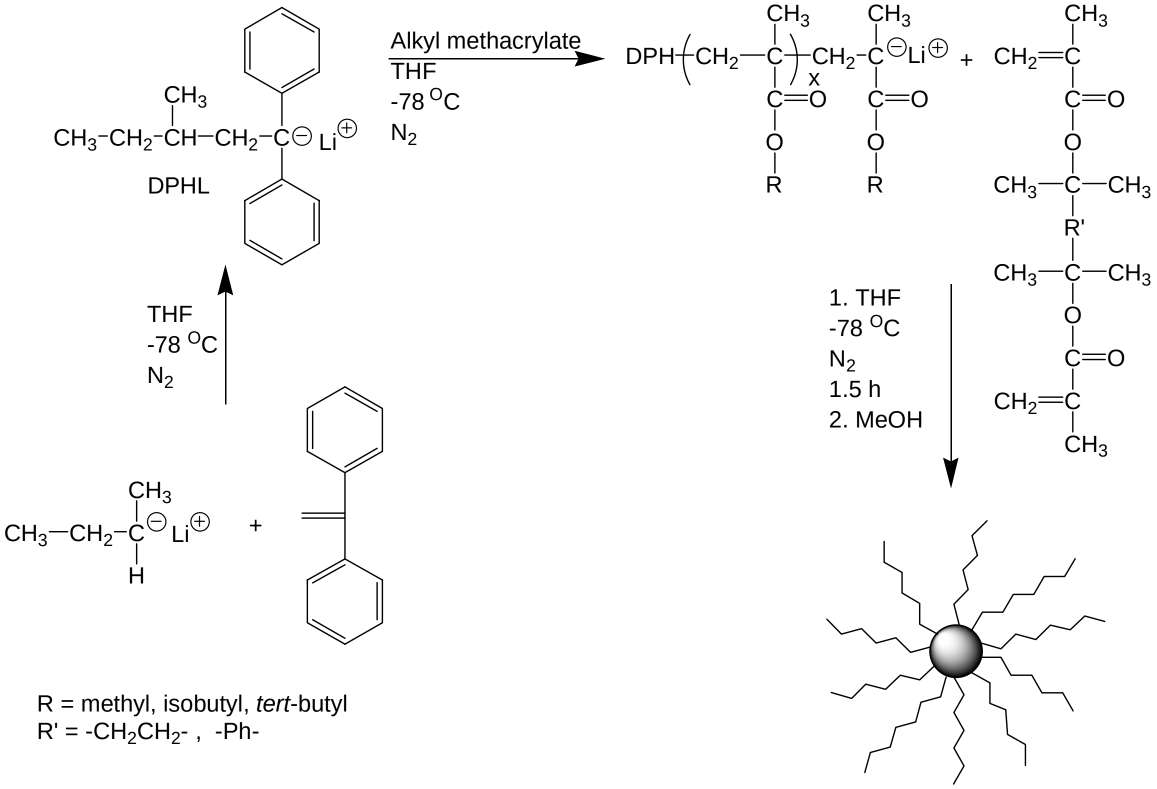
Scheme 6.1: DCDMA was synthesized in very high yields using acid chloride chemistry

6.4 Results and Discussion

6.4.1 Coupling Monomer Synthesis and Purification

Both divinyl linking agents, 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) and dicumyl dimethacrylate (DCDMA), were synthesized using two molar equivalents of methacryloyl chloride and one equivalent of either 2,5-dimethyl-2,5 hexanediol or dicumyl alcohol. Although the reactions proceeded in moderately high yields of crude product, numerous subsequent purification steps decreased the recovered yield drastically. The ^{1}H NMR spectral assignments were based on spectral assignments of *tert*-butyl methacrylate and the corresponding diols. In the DCDMA spectrum, a singlet at 7.3 ppm was assigned to the four phenyl protons. The olefin protons trans and cis to the ester were observed at 6.1 and 5.6 ppm, respectively. The methacrylate methyl protons appeared at 1.9 ppm and the twelve methyl protons adjacent to the tertiary carbons appeared at 1.6 ppm.

High purities of DHDMA and DCDMA were required in order to carry out the star polymer coupling reactions. Purification of DHDMA was difficult to achieve due to premature polymerization during vacuum distillation (0.06 mm Hg) at elevated temperatures (60 °C). Thus, DHDMA purification strategies resulted in low recovered yields and motivated the synthesis of alternate divinyl compounds such as DCDMA. The crystalline DCDMA monomer was recrystallized from a solution of methanol, ethanol, and water. Typically, multiple recrystallization steps were required to provide anionic polymerization grade monomer. Since flash chromatography and high-temperature vacuum distillations were not required in the purification of DCDMA, the isolated yield was much higher (65 %) than DHDMA.



Scheme 6.2: Synthesis of poly(methyl methacrylate) DCDMA star polymers via arm-first anionic polymerization with dimethacrylate coupling.

6.4.2 Star Polymer Synthesis

The coupling of living poly (alkyl methacrylate) arm polymers with ultrapure DHDMA or DCDMA was utilized for the synthesis of core-cleavable star polymers. The synthetic steps used in the synthesis of DCDMA-coupled star polymers are shown in Scheme 6.2. A variety of arm molecular weights between 5000 and 25000 g/ mol were targeted. The star polymer molecular weights were significantly higher than the calculated arm polymer molecular weights, and very limited success in controlling arm polymer molecular weight was achieved. In addition to arm and star molecular weight, the molar ratio of divinyl coupling reagent to initiator concentration was investigated, because this ratio was shown earlier to determine the star polymer core size and the average number of attached arms.[380] Typically, higher amounts of coupling monomer relative to living anion concentration lead to larger star cores with more attached arms, which influenced properties such as solution viscosity, melt rheology, and star polymer diffusion.[381] In this study, 3:1 to 6:1 molar ratios, which are common levels for divinyl coupling, were employed in the preparation of the star polymers.

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[380] J. W. Mays, N. Hadjichristidis, and L. J. Fetters, "Star Branched Polystyrenes: An Evaluation of Solvent and Temperature Influences on Unperturbed Chain Dimensions," *Polymer,* **1988**, *29*(4), 680-685.

[381] K. R. Shull, E. J. Kramer, and L. J. Fetters, "Effect of Number of Arms on Diffusion of Star Polymers," *Nature,* **1990**, *345*(6278), 790-791.

Table 6.1: Molecular weight data of DHDMA star polymers containing different arm compositions.

Arm Polymer	DHDMA: Initiator	Weight % DHDMA	Star M_n[a]	Star M_w[a]	Star M_w/M_n[a]
iBMA	3:1	12	29100	58200	2.00
	4:1	20	83800	200000	2.43
	4:1	8	73400	117000	1.60
	6:1	9	189000	386000	2.04
t-BMA	4:1	8	128000	252000	1.97
	4:1	4	124000	190000	1.54
	6:1	5	224000	393000	1.75
MMA	3:1	12	19400	27000	1.39
	4:1	8	42300	86700	2.05

[a] SEC conditions: 40 °C, THF, 1 mL/ min, MALLS

The DHDMA containing star polymers exhibited high molecular weights and bimodal molecular weight distributions (Table 6.1). The DHDMA star polymer number-average molecular weights ranged between 25000 and 225000 g/ mol. The broad molecular weight distributions were due to uncoupled arms that were not fractionated from the star polymers. Previous fractionated star polymers comprising Poly(MMA) arms coupled to ethylene glycol dimethacrylate (EGDMA) cores exhibited molecular weight distributions as high as 1.82.[382] The DHDMA star and arm polymers overlapped significantly, resulting in a single, broad peak in the SEC chromatogram. Star polymers synthesized with higher DHDMA to arm ratios often displayed higher molecular weights. However, the coupling efficiencies were lower, presumably due to more termination of the arm polymers by impurities in DHDMA when larger concentrations were used. Lower molecular weight distributions were also often observed in star polymer samples containing lower amounts of DHDMA. As expected, the star polymer glass transition temperatures were similar to the homopolymers. Differential scanning calorimetry was used to determine a T_g of 73 °C for the poly(iBMA) DHDMA star polymers. A T_g of 125 °C was measured for the poly(t-BMA) DHDMA star polymers, which is very similar to the 123 °C that was reported earlier for poly(t-BMA) homopolymers.[383]

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[382] P. Lang, W. Burchard, M. S. Wolfe, H. J. Spinelli, and L. Page, "Structure of Pmma/Egdma Star-Branched Microgels," *Macromolecules*, **1991**, *24*(6), 1306-1314.

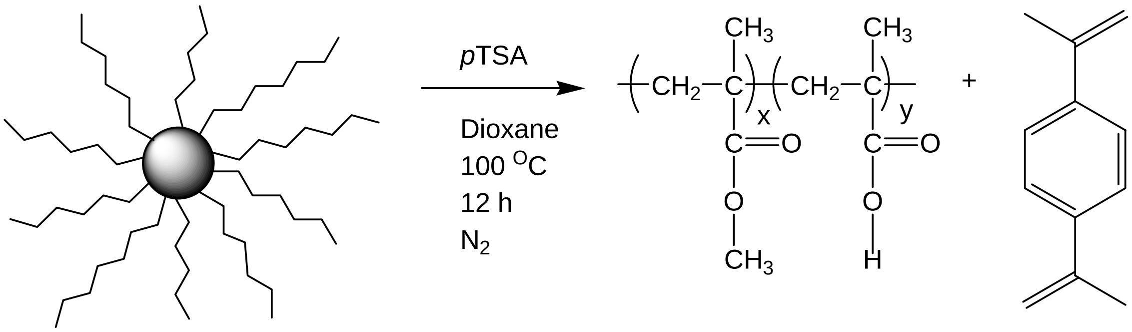
[383] T. E. Long, "Anionic Synthesis and Characterization of Alkyl Methacrylate Containing Polymeric Systems" (Dissertation, VA Polytech. Inst. & State Univ., 1987).

Table 6.2: Molecular weight data of Poly(MMA) DCDMA star polymers.

Arm Type	DCDMA: Initiator	Arm[a] M_n[b]	Arm[a] M_w / M_n [b]	Star M_n[b]	Star M_w / M_n[b]
PMMA	4:1	15500	1.07	160000	1.57
PMMA	6:1	50000	1.05	229000	1.33

[a] Uncoupled arm polymer
[b] SEC conditions: 40 °C, THF, MALLS detector

The DCDMA containing star polymers generally exhibited much greater molecular weights relative to the uncoupled arm polymers, although residual arm was typically present at low levels. Star and uncoupled arm polymer molecular weights were determined separately (Table 6.2) due to the more well-defined star and arm peaks in the bimodal DCDMA star polymer chromatogram. Higher coupling efficiencies were observed when lower molecular weight arm polymers were targeted, presumably due to a constant low level of protic impurities.



Scheme 6.3: Acid-catalyzed hydrolysis of Poly(MMA) DCDMA star polymers resulted in the formation of lower molecular weight linear polymers.

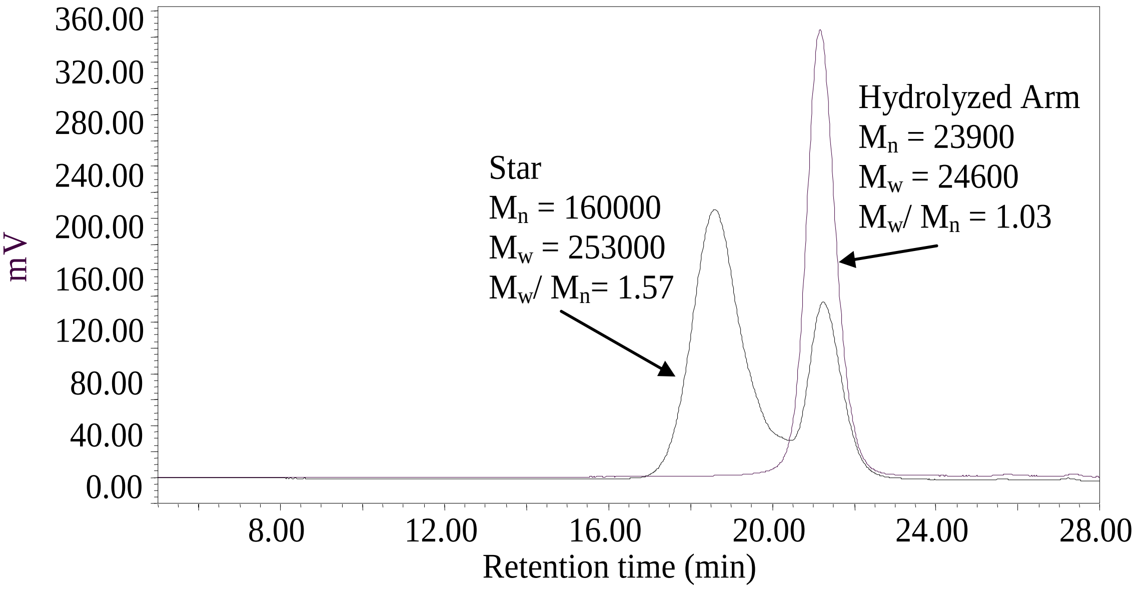


Figure 6.1: The overlay of the SEC traces from the PMMA DCDMA star polymer sample and the hydrolyzed arm polymer indicated that the star polymer reverted to the arm polymer.

6.4.3 Star polymer hydrolysis

The DHDMA star shaped polymers were hydrolyzed under several different conditions in order to determine the effect of temperature. The star polymers were hydrolytically stable when stirred in a solution of 2% HCl in THF at 25 °C for 48 h. DHDMA-coupled star polymers were also hydrolytically stable at 65 °C for 8 h in dilute acid. In contrast, the DCDMA star polymers underwent hydrolysis under these conditions. The star polymers were also subjected to hydrolytic conditions (100 °C, 2% *para*-toluenesulfonic acid monohydrate) that ensured complete hydrolysis (Scheme 6.3). The hydrolysis of the DCDMA star polymers led to the formation of arm polymers only. This conclusion was based on a single peak in the SEC chromatogram. The chromatogram of the original star polymer sample indicated that there were residual uncoupled arms (<15 wt. %, estimated using the DRI peak) at the expected lower molecular weight. After hydrolysis, the star polymer peak disappeared completely, and only a large single peak that was consistent with the residual arm peak in the original chromatogram was observed (Figure 6.1). Table 6.3 summarizes the molecular weight changes that occurred during the hydrolysis of the Poly(MMA) DCDMA star polymers. In a similar fashion, DHDMA star polymers also underwent a reduction in molecular weight upon hydrolysis. For example, a Poly(iBMA) DHDMA star polymer exhibited an original M_n of 83800 g/ mol, and after hydrolysis, the M_n decreased to 23500 g/ mol, accompanied by a decrease in the molecular weight distribution.

Table 6.3: Comparison between the molecular weights of the star polymers and the hydrolyzed arm polymers indicates a drastic reduction in the molecular weight.

Coupling Reagent	Arm Type	Coupling: Initiator Molar Ratio	M_n Star [a]	M_w / M_n Star	M_n Arms [a,b]	M_w / M_n Arms [a,b]
DCDMA	PMMA	4:1	160000	1.57	23900	1.03
DCDMA	PMMA	4:1	229000	1.33	69400	1.04
DHDMA	PiBMA	6:1	189000	2.04	21900	1.40
DHDMA	PiBMA	4:1	83800	2.43	23500	1.82

[a] SEC conditions: 40 °C, THF, MALLS detector
[b] Hydrolyzed arm polymer

A comparison between the ^{1}H NMR spectra of the Poly(iBMA) DHDMA star polymer before and after hydrolysis indicated quantitative degradation of the DHDMA star polymer cores. The spectrum of the initial star polymer revealed a resonance at 1.6 ppm, which corresponded to the four methyl groups in the DHDMA units. This peak confirmed the presence of the coupling unit in the star polymer, and all other resonances that were associated with the coupling unit overlapped with the backbone methylenes. After hydrolysis, the methyl peak at 1.6 ppm (labeled 'C' in Figure 6.2), disappeared completely, which confirmed quantitative core cleavage. ^{1}H NMR was also used to confirm the degradation of the Poly(MMA) DCDMA star polymer cores. A small ^{1}H NMR resonance was observed at 7.3 ppm, indicating the presence of DCDMA.

However, after hydrolysis, this resonance completely disappeared, indicating that complete removal of the crosslinking unit had occurred. The glass transition temperatures of the Poly(iBMA) DHDMA star polymers and the Poly(MMA) DCDMA star polymers did not change following star cleavage.

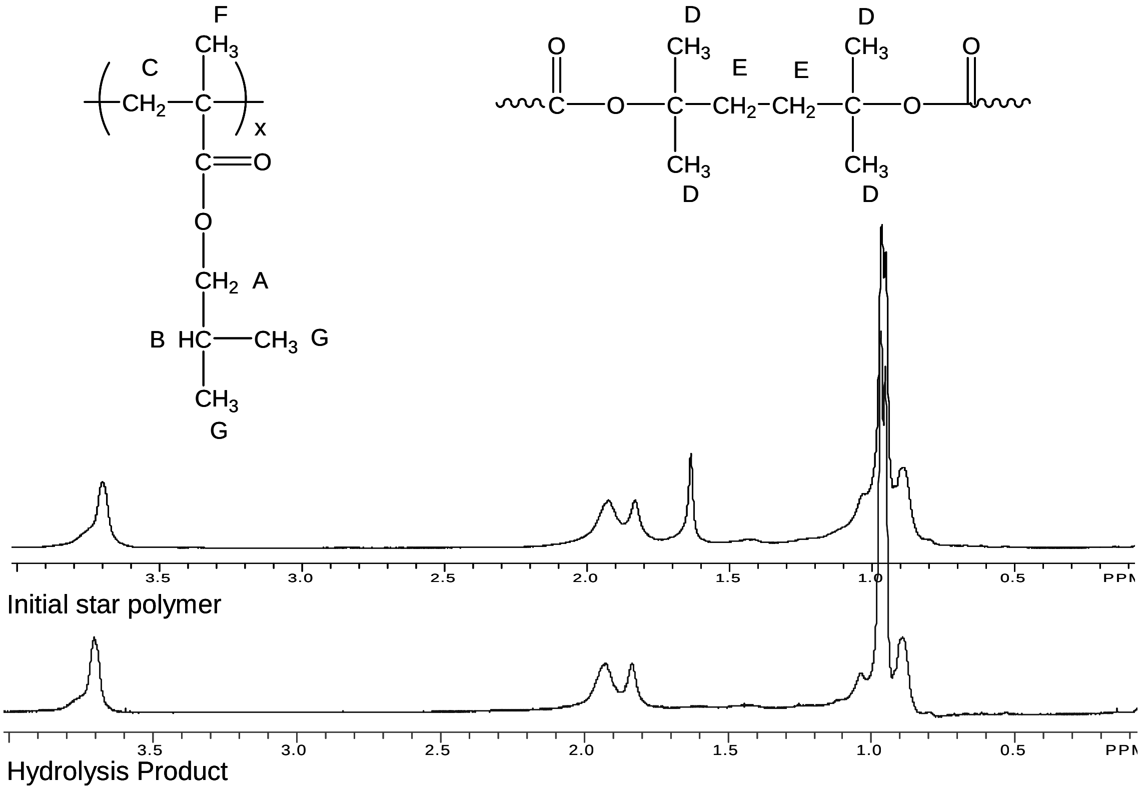
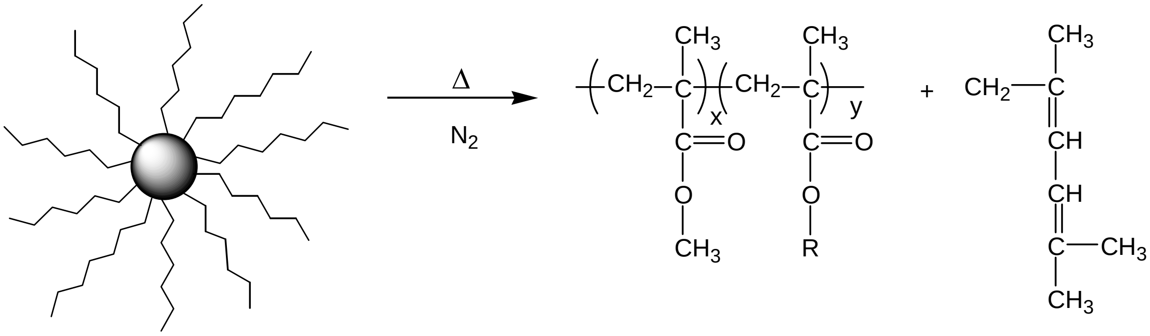


Figure 6.2: A comparison between the ^{1}H NMR spectra of the PiBMA DHDMA star polymer and the hydrolysis product indicated the absence of the star core in the product spectrum.



Scheme 6.4: The degradation of the DHDMA monomer resulted in the formation of the diene 2,5-dimethyl-2,4-hexadiene.

6.4.4 Thermolysis of Star Polymers

The star polymer cores were thermally labile in the absence of acid catalysts at elevated temperatures. The DHDMA and DCDMA containing star polymers degraded in a TGA-MS experiment via the elimination of the labile bridging alkyls. The DHDMA star polymer cores exhibited an onset of thermal weight loss at 220 ^{O}C, eliminating 2,5-dimethyl-2,4-hexadiene (Scheme 6.4). A 5% weight loss (Figure 5) was observed at 239 °C, which was significantly lower than 271 °C that was reported earlier for ethylene glycol dimethacrylate coupled poly(alkyl methacrylate) star polymers.[39] At the completion of the core degradation step, a 9% weight loss was observed. This loss corresponded well to the 8% weight loss that was expected based on ^{1}H NMR spectroscopic analysis and the charged DHDMA weight percent in the star polymer composition. The degradation mechanism of the Poly(iBMA) DHDMA star polymer cores was also confirmed using TGA-MS. The cleavage of the DHDMA alkyl esters led to the generation of the by-product 2,5-dimethyl-2,4-hexadiene (Scheme 6.4).

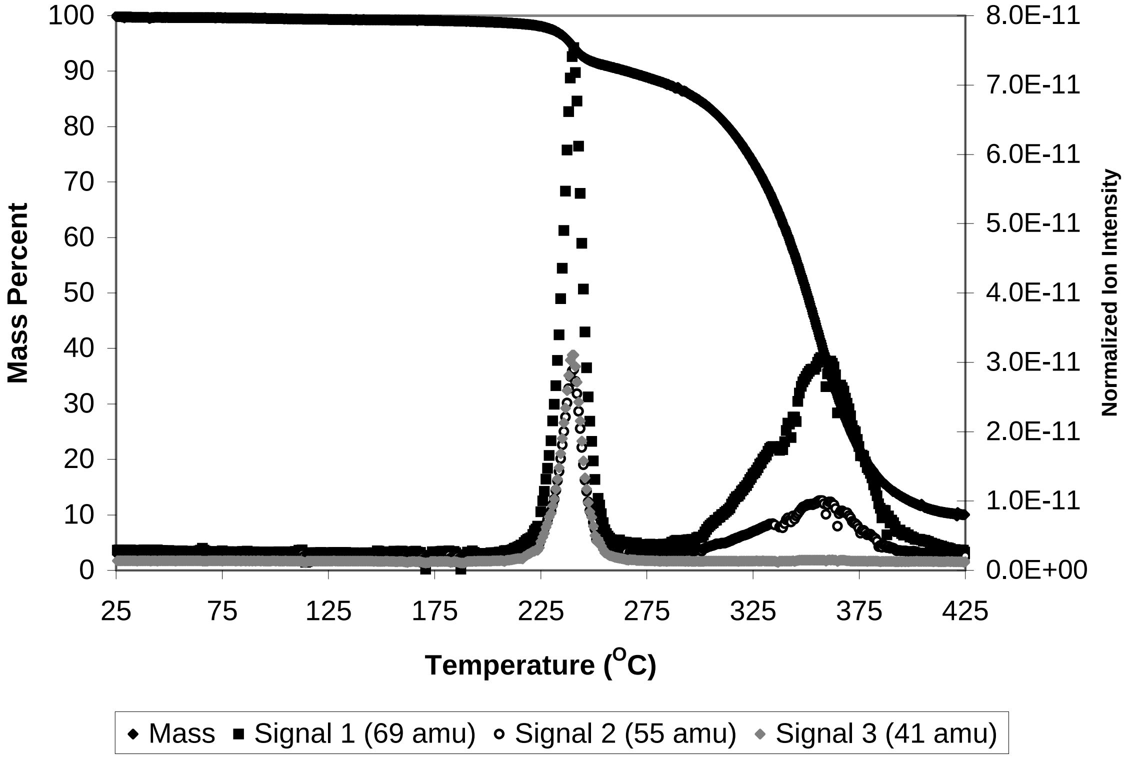


Figure 6.3: TGA-MS analysis of the thermal degradation of PiBMA DHDMA confirmed the evolution of 2,4-dimethyl-1,3-hexadiene as the star polymer underwent degradation.

Using a reference spectrum of this compound obtained from the NIST Chemistry Web Book, three molecular mass peaks were selected based on their relatively high intensities in the spectrum.[384] These three molecular weight signals were monitored using the mass spectrometer during the TGA experiment. The simultaneous evolution of the molecular weight fragments at 41, 55, and 69 amu confirmed core thermolysis in the Poly(iBMA) DHDMA star polymers (Figure 6.3). All three mass signals rose substantially at the onset of degradation at 220 °C, reaching a peak at 245 °C. The signals decreased to baseline strength when core degradation was complete at 260 °C. Further arm polymer degradation at higher temperatures was not accompanied by a simultaneous change in all three mass signals.

The degradation temperature and mechanism of the Poly(MMA) DCDMA star polymers was also confirmed using TGA-MS. The mass spectrometer monitored molecular ions with masses of 143, 117, and 77 amu. The monitored molecular weight signals were chosen based on the mass spectrum of the expected degradation by-product *p*-diisopropenylbenzene, which indicated that these were the primary fragmentation peaks. The TGA-MS of the Poly(MMA) DCDMA star polymers resulted in the detection of *p*-diisopropenylbenzene at 180 °C. The DCDMA core degradation was 50 °C lower than DHDMA star polymers. This observation was consistent with the expectation that DCDMA would degrade more readily than DHDMA due to additional resonance stabilization in the elimination product. The actual onset of degradation may be lower than the value that was measured via the TGA-MS. It is possible that the onset of

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[384] NIST Chemistry WebBook http://webbook.nist.gov/chemistry/

degradation occurred at a lower temperature, but that *p*-diisopropenylbenzene was not sufficiently volatile until higher temperatures.

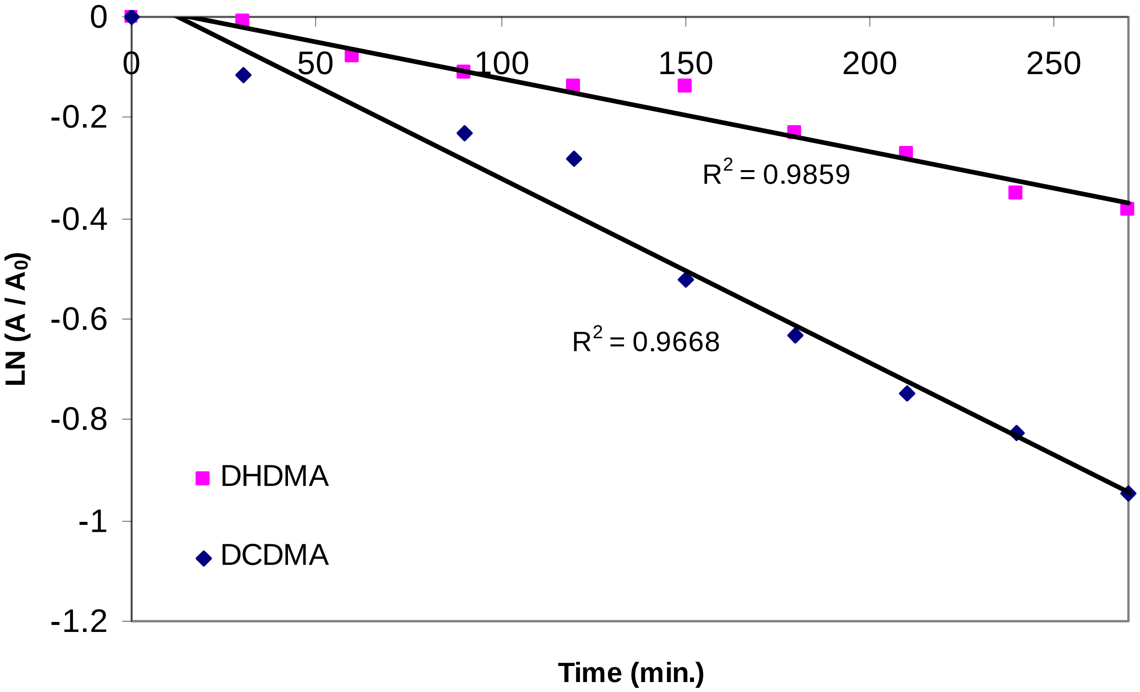

Figure 6.4: The reaction kinetics of the DHDMA and DCDMA degradation, measured by the disappearance of the olefinic ^{1}H NMR resonances, showed the faster rate of DCDMA degradation.

6.4.5 Relative Rates of Monomer Degradation

Although both *t*-BMA and DHDMA cleave to form methacrylic acid, their rates of degradation are much slower than other methacrylic acid protecting groups. Tertiary alkyl-ester bonds degrade via the $A_{AL}1$ mechanism, resulting in the formation of a tertiary carbocation.[17] In the case of DCDMA cleavage, the carbocation intermediate is highly resonance stabilized, presumably resulting in an increased reaction rate. The diene formed in the elimination, *p*-diisopropenylbenzene is also more conjugated than 2,5-dimethyl-2,4-hexadiene. In order to directly compare the rates of catalyzed degradation, DHDMA and DCDMA were degraded at 85 °C and monitored using ^{1}H NMR spectroscopy. Scheme 6.4 shows the DCDMA degradation reaction. Both DCDMA and DHDMA ^{1}H NMR spectra contained several resonances that were suitable to quantify degradation rates. The methacrylate monomer olefinic peaks (5.9 ppm and 5.5 ppm) shifted during degradation since methacrylic acid exhibited olefinic peaks that occurred at slightly higher chemical shifts (6.0 and 5.6 ppm). During DCDMA degradation, another set of olefinic peaks (5.1 and 5.4 ppm) arose due to the formation of the *p*-diisopropenylbenzene by-product, and these peaks were also monitored. DCDMA showed a faster rate of degradation than DHDMA. Both reactions showed a constant divinyl monomer decrease and an expected increase in the diene resonances, suggesting that unexpected side reactions were not occurring. Figure 6.4 shows the decrease in the normalized olefinic peaks of DCDMA and DHDMA as a function of degradation time. The ^{1}H NMR spectroscopic experiment indicated that after 4.5 hours, 60 % of the DCDMA had degraded, compared to 32% DHDMA degradation. The faster degradation kinetics of DCDMA indicated that the use of this coupling monomer would lead to more readily cleavable polymers.

6.5 Conclusions

Core cleavable poly (alkyl methacrylate) star polymers, synthesized via living anionic polymerization, were quantitatively hydrolyzed into arm polymers. The novel divinyl linking monomer dicumyl dimethacrylate (DCDMA) was synthesized in high yields. DCDMA was rigorously purified and served as an efficient coupling monomer for anionic polymerization. This monomer was utilized to synthesize cleavable star polymers comprised of Poly(MMA) arms and DCDMA cores. These star polymers had higher coupling efficiencies relative to those coupled with 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA). DHDMA was also successfully used to couple several different poly(alkyl methacrylate) arm types to form cleavable star polymers.

DCDMA containing star polymers exhibited improved acid-catalyzed cleavage efficiency over DHDMA star polymers under identical conditions. *Para*-toluenesulfonic acid-catalyzed hydrolysis of DCDMA star polymers was quantitative in less than 6 hours at 100 °C in dioxane. In comparison, DHDMA star polymers required more than 10 hours to hydrolyze completely under identical conditions. The onset of uncatalyzed thermal degradation for DCDMA stars (180 °C) was substantially lower than the temperature observed for DHDMA star polymers (230 °C). The mechanism of thermal degradation was confirmed utilizing mass spectrometry. The DCDMA monomer was also shown to cleave much more rapidly than DHDMA in an acidic environment at elevated temperatures.

6.6 Acknowledgements

The authors would like to thank the Carilion Biomedical Institute, the Virginia Tech OSER Center, and the Petroleum Research Fund (35190-AC7) for financial assistance. This material is based upon work supported in part by the U.S. Army Research Laboratory and the U.S. Army Research Office under contract/grand number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. We also gratefully acknowledge the generous donation of *sec*-butyllithium from FMC Lithium Division.

Chapter 7 : Synthesis of Cleavable Branched Poly (2-Ethylhexyl Acrylate) and Use as Deactivatable Adhesive

Taken From:
J. Adhes. **2004**, in progress.

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7.1 Abstract

Branched poly(2-ethylhexyl acrylate) [EHA] pressure-sensitive adhesive polymers were synthesized containing the acid-cleavable branching comonomer dicumyl dimethacrylate (DCDMA). These copolymers exhibited very high weight-average molecular weights and 180° peel strengths, relative to the EHA homopolymers. Increasing the dimethacrylate monomer amounts charged into the reactions raised both weight-average molecular weights and peel strengths drastically. Polymer crosslinking occurred when 4.5 weight percent or more DCDMA was charged into the reaction. Crosslinking was observed at significantly lower amounts of DCDMA when it was copolymerized with methyl methacrylate. Branched terpolymers containing EHA, DCDMA, and methyl methacrylate exhibited greater peel strengths relative to the copolymers lacking MMA, due to the greater molecular weight present in these adhesives. Following exposure of the adhesive polymer to acidic conditions, the DCDMA branching points cleaved. The hydrolysis of the branching points was verified using ^{1}H NMR spectroscopy. The 180° peel strengths of the PSAs consequently decreased 75 to 90 percent. Higher molecular weight adhesives with greater peel strengths exhibited greater adhesion upon hydrolysis, presumably due to higher

molecular weights between branch points. Copolymer adhesives comprised of 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) and EHA were also deactivated hydrolytically. The adhesive deactivation behavior was independent of the type of branching reagent used.

Keywords: free-radical copolymerization, crosslinking, degradation, branched, cleavable polymers, acrylate

7.2 Introduction

Numerous linear and branched polymers were synthesized previously that were designed to dissociate into linear oligomers either reversibly or irreversibly. Strongly associating polymers containing telechelic self-complementary multiple hydrogen bonding (MHB) groups aggregated reversibly, while behaving like low molecular weight polymers at higher processing temperatures.[385] Due to the hydrogen bonding interactions, these telechelic MHB-containing polymers exhibited similar melt rheological behavior as much higher molecular weight polymers below the dissociation temperature of 80 °C.[386,387] At higher temperatures, the MHB interactions were disrupted and the MHB polymer viscosities were similar to non-MHB polymers. This effect was

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[385] B. J. B. Folmer, R. P. Sijbesma, and E. W. Meijer, "Unexpected Entropy-Driven Ring-Opening Polymerization in a Reversible Supramolecular System." *J. Am. Chem. Soc.*, **2001**, *124*(43), 2093-2094.

[386] K. Yamauchi, J. R. Lizotte, and T. E. Long, "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules Via a Michael Addition." *Macromolecules*, **2002**, *35*(23), 8745-8750.

[387] K. Yamauchi, J. R. Lizotte, D. M. Hercules, M. J. Vergne, and T. E. Long, "Combinations of Microphase Separation and Terminal Multiple Hydrogen Bonding in Novel Macromolecules." *J. Am. Chem. Soc.*, **2002**, *124*(29), 8599-8604.

also observed in random poly(alkyl methacrylate) copolymers containing a low percentage of self-complementary MHB functionalities.[388]

Stimuli-responsive star and network polymers were developed that were designed to undergo topological reorganization, irreversibly cleaving to linear polymers. Polymer networks containing acetal crosslinking points were synthesized previously. Due to the reactivity of the acetal crosslinking functional groups, these networks were highly pH responsive; rapid degradation of these networks occurred below pH = 5, releasing an embedded fluorescent bovine serum albumin derivative.[389] The delivery of embedded drug molecules was proposed as an application of these responsive networks. The diacetal ethylene glycol di(1-methacryloyloxy)ethyl ether was used to synthesize cleavable star polymers via anionic polymerization.[390] Both star and network polymers containing this crosslinking reagent hydrolyzed completely in the presence of aqueous acid at room temperature. pH-responsive star polymers containing tertiary-alkyl ester linkages were also synthesized in our laboratories via living anionic polymerization, yielding high molecular weight star polymers exhibiting relatively narrow molecular weight distributions. These star polymers were cleaved under either acidic or high-temperature conditions.[391,392] Cleavage of the dicumyl dimethacrylate or 2,5-dimethyl-

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[388] K. Yamauchi and T. E. Long, "Thermoreversible Poly(Alkyl Acrylates) Consisting of Self-Complementary Multiple Hydrogen Bonding." *Macromolecules*, **2003**, *36*(4), 1083-1088.

[389] N. Murthy, Y. X. Thng, S. Schuck, M .C. Xu, and J. M. J. Frechet, "A Novel Strategy for Encapsulation and Release of Proteins: Hydrogels and Microgels with Acid-Labile Acetal Cross-Linkers." *J. Am. Chem. Soc.*, **2002**, *124*(42), 12398-12399.

[390] E. Ruckenstein and H. Zhang, "A Novel Breakable Cross-Linker and pH-Responsive Star-Shaped and Gel Polymers." *Macromolecules*, **1999**, *32*(12), 3979-3983.

[391] L. Kilian, Z.-H. Wang, A. R. Esker, and T. E. Long, "Topological Reorganization of Star-Shaped Polymers." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **2002**, *43*(1), 332-333.

2,5-hexanediol dimethacrylate star cores led to topological reorganization of the star polymers to linear polymers. Reductions in number average molecular weights as high as 90 percent were observed following hydrolysis. Star polymers containing base-hydrolysable cores were also synthesized via core-first SFRP and cleaved.[393]

Adhesives comprised of crosslinked network polymers provide extremely strong permanent bonds. However, these adhesives cannot be readily removed at a later time; this limitation is an obstacle for applications that require strong, but temporary, scaffolding adhesives. Several network adhesive polymers were developed that contained functional group(s) that cleaved under controlled conditions. Thermally reversible epoxy[394,395] and urethane[396] adhesives were synthesized that could be cleaved back into linear polymers utilizing retro-Diels Alder chemistry. These polymers contained maleimide and furan functional groups in the backbone, which cleaved upon exposure to high temperatures. Diels-Alder dimerization occurred when the temperature of the adhesive was subsequently reduced below 40 °C. Controlled-release[397] and self-

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[392] L. Kilian, Z.-H. Wang, and T. E. Long, "Synthesis and Cleavage of Core-Labile Poly(Alkyl Methacrylate) Star Polymers." *J. Polym. Sci. A Polym. Chem.*, **2003**, *41*(19), 3083-3093.

[393] C. J. Hawker, "Architectural Control in "Living" Free Radical Polymerizations: Preparation of Star and Graft Polymers." *Angew. Chem. Int. Ed. Engl.*, **1995**, *4*(13/14), 1456-1459.

[394] J. R. McElhanon, E. M. Russick, D. R. Wheeler, D. A. Loy, and J. H. Aubert, "Removable Foams Based on an Epoxy Resin Incorporating Reversible Diels-Alder Adducts." *J. Appl. Polym. Sci.*, **2002**, *85*(7), 1496-1502.

[395] D. A. Loy, D. R. Wheeler, E. M. Russick, J. R. McElhanon, and R. S. Saunders, "Method of Making Thermally Removable Epoxies." *US* 6,337,384, **2002**.

[396] D. A. Loy, D. R. Wheeler, J. R. McElhanon, R. S. Saunders, and M. L. Durbin-Voss, "Method of Making Thermally Removable Polyurethanes." *US* 6,403,753, **2002**.

[397] J. H. Small, D. A. Loy, D. R. Wheeler, J. R. McElhanon, and R. S. Saunders, "Method of Making Thermally Removable Polymeric Encapsulants." *US* 6,271,335, **2001**.

healing[398] materials based on the retro-Diels Alder cleavage of similar networks were also developed.

Polymer storage moduli influence the interfacial performance of pressure-sensitive adhesives (PSAs) significantly. Adhesive deactivation was previously achieved via photoinduced crosslinking to produce high-modulus (G') networks with little adhesive character.[399,400,401] The modification of a functionalized 2-ethylhexyl acrylate-based PSA with acrylate or methacrylate functional groups enabled photocrosslinking in the presence of a free-radical photoinitiator. Examples of cinnamate-containing PSAs that crosslinked under UV light have also been reported.[402] The extents of adhesive deactivation were sensitive to polymer molecular weights and the level of long chain branching.

Pressure-sensitive adhesive deactivation resulting from polymer cleavage has not been reported by other researchers. Such cleavage is expected to reduce polymer entanglement, subsequently weakening cohesive strength significantly. Using the acid-labile divinyl branching comonomer dicumyl dimethacrylate (DCDMA), branched adhesive polymers were synthesized and characterized. Branched PSAs based on the more hydrolytically stable monomer 2,5-dimethyl-2,5-hexanediol dimethacrylate was

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[398] X. Chen, F. Wudl, A. K. Mal, H. Shen, and S. R. Nutt, "New Thermally Remendable Highly Cross-Linked Polymeric Materials." *Macromolecules*, **2003**, *36*(6), 1802-1807.

[399] I. Webster, "Adhesives." *US* 6,184,264, **2001**.

[400] I. Webster, "Adhesives." *WO* 9918136, **1999**.

[401] I. Webster, "The Development of a Pressure-Sensitive Adhesive for Trauma-Free Removal." *Int. J. Adhes. Adhesiv.*, **1999**, *19*(1), 29-34.

[402] L. Kilian, V. Sinani, and T. E. Long, "Effect of Molecular Weight on the Induced Deactivation of Poly(2-Ethylhexyl Acrylate) PSAs Bearing Photocrosslinkable Groups." *J. Adhes.*, **2004**, submitted.

also synthesized to examine the effect of the branching reagent structure on adhesive properties. The 180° peel strengths of these PSAs were drastically reduced upon acid-catalyzed hydrolysis of the branch points.

7.3 Experimental

7.3.1 Materials

Reagents were used without further purification, unless stated. 2-Ethylhexyl acrylate (TCI, 98%) and methyl methacrylate (Aldrich, 99%) were passed through an activated basic alumina (Aldrich, 150 mesh) column to remove the inhibitors and used without further purification. Dicumyl dimethacrylate (DCDMA) and 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) were synthesized using a previously reported procedure[403,404,405] utilizing methacryloyl chloride (Aldrich, 98%) and either dicumyl alcohol (Aldrich, 99%) or 2,5-dimethyl-2,5 hexanediol dimethacrylate (Aldrich, 99%) in the presence of triethylamine (Aldrich, 99.8%, distilled under N_2) and dichloromethane (Burdick & Jackson, HPLC, distilled from CaH_2). DCDMA was purified via recrystallization from a 1:1:3 ethanol, methanol, and water solution and DHDMA was purified using silica column chromatography utilizing dichloromethane as the stationary phase.

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[403] L. Kilian, Z.-H. Wang, and T. E. Long, "Synthesis and Cleavage of Core-Labile Poly(Alkyl Methacrylate) Star Polymers." *J. Polym. Sci. A Polym. Chem.*, **2003**, *41*(19), 3083-3093.

[404] T. E. Long, L. Kilian, Z.-H. Wang, and A. R. Esker, "Synthesis and Characterization of Novel Acid-Sensitive *Tert*-Butyl Methacrylate and Isobutyl Methacrylate Containing Star-Shaped Polymers." *Proc. SPIE- Soc. Opt. Eng.*, **2001**, *4512*, 65-74.

[405] K. Ogino, J.-S. Chen, and C. K. Ober, "Synthesis and Characterization of Thermally Degradable Polymer Networks." *Chem. Mater.*, **1998**, *10*(12), 3833-3838.

7.3.2 Instrumentation

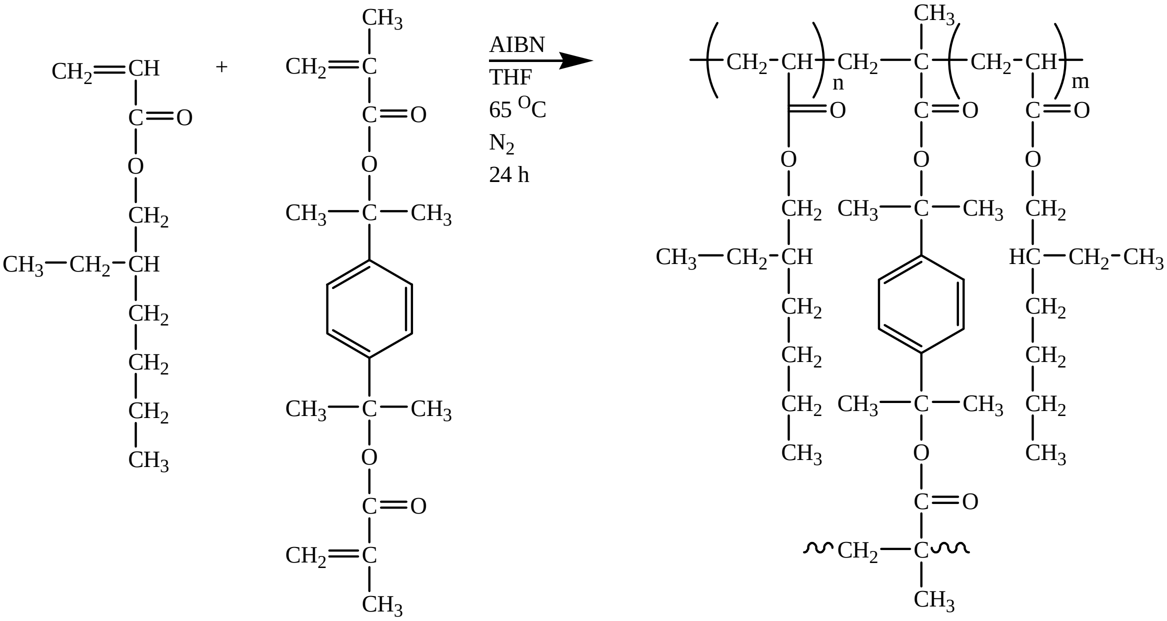
^{1}H NMR spectra were obtained using a Varian Unity 400 spectrometer and CD_2Cl_2 (Cambridge Isotope Laboratories) was used as the solvent. A Waters 717plus Autosampler coupled to a Waters 2410 refractive index detector was used to determine polymer molecular weights in THF at 40 ^{O}C. Absolute molecular weights were determined using a Wyatt Technology miniDAWN® static three-angle laser light scattering detector (MALLS). Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/ min under nitrogen. Glass transition temperatures are reported as the midpoints of the changes in heat capacity during the second heat. The 180° peel test (ASTM #D903) was performed using an Instron Universal Testing Rig (Model 4411). Peel test samples were prepared by placing a 1” X 8” PET film (Mylar®, 0.002 in. thick) strip onto the PSA film (0.2 mm PSA film on glass slide). The PSA film was applied onto clean glass slides (1” X 2”) to a thickness of 0.2 mm using a BYK “Gardner” film-casting knife with a Mitutoyo Corporation adjustable elevation device. The PET film was debonded at a rate of 5 in. / min. The peel strength was determined as the average peak force versus displacement. The peel strength was reported as an average of five samples. Dynamic mechanical analysis (DMA) was performed using a Perkin Elmer DMA-7e. Measurements were performed using a penetration probe running at 1 Hz. The temperature was increased at a rate of 1 °C / min., and the data was collected on the second heating.

7.3.3 Synthesis of Poly(2-ethylhexyl acrylate-*co*-DCDMA)

The branched poly(2-ethylhexyl acrylate-*co*-DCDMA) PSAs were synthesized via solution free radical polymerization. 2-ethylhexyl acrylate and dicumyl dimethacrylate were dissolved in cyclohexane and de-gassed for 20 min using a nitrogen purge. In some polymerizations, 3 or 4 weight percent of methyl methacrylate was added prior to purging with N_2. The sealed reactor was immersed in a temperature-controlled mineral oil bath for 15 min, and AIBN, dissolved in de-gassed cyclohexane, was syringed into the reactor. The reaction proceeded for 24 h at 65 °C. The solvent was removed via rotary evaporation and the adhesive was re-dissolved in THF. The polymers were precipitated in a dry-ice cooled 9:1 mixture of methanol and water and dried under vacuum at 25 °C upon recovery. DHDMA-branched PSAs were synthesized in an identical manner.

7.3.4 Hydrolysis of Poly(2-ethylhexyl acrylate-*co*-DCDMA)

The adhesive hydrolysis was conducted in a 50 mL round-bottomed flask containing 40 mL dioxane (Aldrich, 98%). *para*-Toluenesulfonic acid monohydrate (Aldrich, 99%) and 2 g poly(2-ethylhexyl acrylate-*co*-DCDMA) was added. The round-bottomed flask was fitted with a reflux condenser and the reaction was conducted under a nitrogen atmosphere. The flask was then heated to 100 °C for 12 hours. The hydrolyzed polymer was precipitated into a dry-ice cooled 9:1 mixture of methanol and water. The identical procedure was also used for the hydrolysis of the DHDMA-branched PSAs.



Scheme 7.1: Synthesis of DCDMA-branched poly(2-ethylhexyl acrylate) branched polymers.

7.4 Results and Discussion

7.4.1 Cleavable Branched Adhesive Synthesis

The poly(EHA-*co*-DCDMA) branched adhesive polymers were synthesized using relatively high amounts of the dimethacrylate branching monomer DCDMA (Scheme 7.1). Very high weight-average molecular weights, greater than 2,000,000 g/mol were achieved when four weight percent of DCDMA was charged to the polymerization. The actual molecular weights of the very high molecular weight PSAs were believed to be higher than 2,000,000; however, these polymers fell outside of the SEC column exclusion limit. Although networks are typically formed when divinyl comonomers are employed in free-radical copolymerization, branched polymers were synthesized previously when chain transfer[406] or free-radical scavenging reagents[407] were used in the polymerization. In the polymerization of the branched adhesives, the lack of crosslinking in the presence of such high amounts of dimethacrylate, was attributed to the high occurrence of chain transfer during free-radical polymerization of 2-ethylhexyl acrylate.[408] The degree of branching, which was reflected in the broadening of molecular weight distributions, was raised by increasing amounts of DCDMA. The branching reagent 2,5-dimethyl-2,5-hexanediol dimethacrylate (DHDMA) was also used to synthesize high molecular weight branched PSAs. Branched polymers charged with this slightly more hydrolytically stable

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[406] C. M. Crowe, "Copolymerization of Methyl Methacrylate/Ethylene Glycol Dimethacrylate - Long-Chain Branching and Crosslinking." *Poly. Mat. Sci. Eng.*, **1988**, *58*, 756-760.

[407] V. Lesturgeon, D. Durand, and T. Nicolai, "Characterization of the Structure and the Size Distribution of Branched Polymers Formed by Copolymerization of MMA and EGDMA." *Eur. Phys. J. B*, **1999**, *9*(1), 83-91.

[408] F. Heatley, P. A. Lovell, and Y. Tsuyoshi, "Chain Transfer to Polymer in Free-Radical Solution Polymerization of 2-Ethylhexyl Acrylate Studied by NMR." *Macromolecules*, **2001**, *34*(22), 7636-7641.

branching monomer exhibited similar molecular weights as the DCDMA containing PSAs.

Table 7.1: Molecular weight data of poly(2-ethylhexyl acrylate-*co*-DCDMA) and poly(2-ethylhexyl acrylate-*co*-DHDMA).

Cross-linker (XL)	Wt. % XL	Topology	$\langle M_n \rangle$	$\langle M_w \rangle$	$\langle M_w \rangle$ / $\langle M_n \rangle$	Peel Strength (N/m)
None	0	Lightly branched	61,000	156,000	2.56	0.8
DCDMA	1	Branched	44,000	195,000	4.43	1.2
DCDMA	2	Branched	68,400	178,000	2.60	1.2
DCDMA	3	Branched	85,800	314,000	3.66	2.7
DHDMA	3	Branched	68,000	192,000	2.82	7
DCDMA	4	Branched	61,600	1,800,000	29.2	94
DCDMA	4	Branched	160,000	1,480,000	9.25	82
DHDMA	4	Branched	145,000	991,000	6.83	124
DCDMA	4.5	Network	N/A	N/A	N/A	N/D
DHDMA	4.5	Network	N/A	N/A	N/A	N/D

The polymerization conditions were chosen to maximize the reproducibility of the reaction. In all cases, only 15 weight percent solids were used in the polymerization to prevent very high viscosities from impacting the polymerization. Moderate amounts of initiator (0.2 weight percent) were used to prevent the attainment of molecular weights that were considered to be too high. The polymerizing solvent was cyclohexane, which is known to exhibit a very low incidence of chain transfer during free-radical polymerization.[409] The maximum amount of DCDMA charged to reaction that resulted

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[409] R. A. Gregg and F. R. Mayo, "Chain Transfer in the Polymerization of Styrene. III. Reactivities of Hydrocarbons toward the Styrene Radical." *Disc. Faraday Soc.*, **1947**, *2*, 328-337.

in branched polymers was 4 weight percent, which corresponded to 3.3 mole percent. In comparison, MMA, which undergoes very low amounts of chain transfer,[410] underwent crosslinking when copolymerized with 0.5 weight percent DCDMA (Scheme 7.2). Polymers containing 4.5 weight percent DCDMA, or greater, crosslinked within 24 hours of the polymerization initiation. The weight-average molecular weights of the branched copolymers increased drastically when greater amounts of DCDMA were charged, while number-average molecular weight did not undergo significant change.

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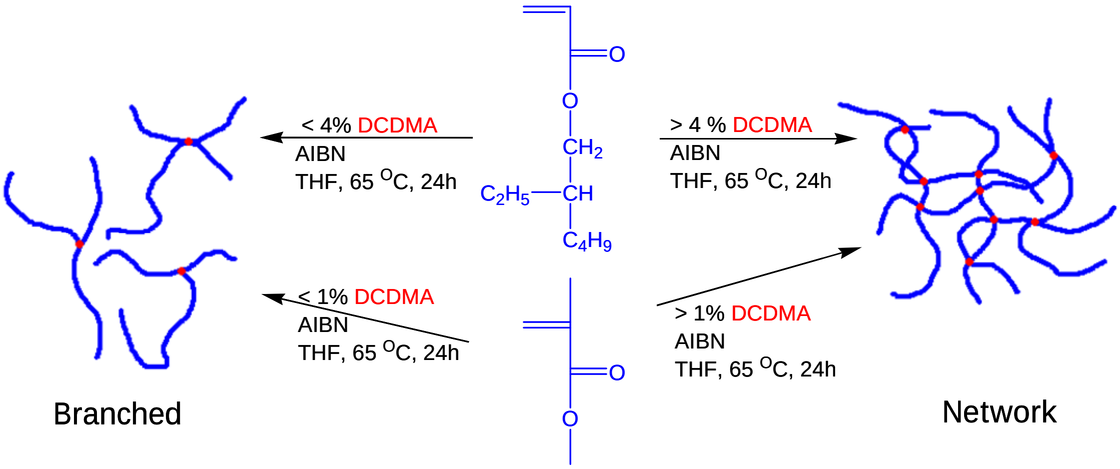
[410] J. Brandup, E. H. Immergut, and E. A. Grulke, *Polymer Handbook*, 3rd ed., New York: John Wiley and Sons, 1975.



Scheme 7.2: Effect of monomer on the polymer topology produced by free-radical copolymerizations with DCDMA.

Table 7.2: Molecular weight data of cleavable branched PSA terpolymers containing methyl methacrylate.

Weight % DCDMA	Wt. % MMA	M_n	M_w	M_w / M_n	Peel Strength
3	0	85,800	314,000	3.66	6.7
3	3	202,000	981,000	4.86	90
4	0	160,000	1,480,000	9.25	210
4	3	720,000	>2,000,000	>2.78	320

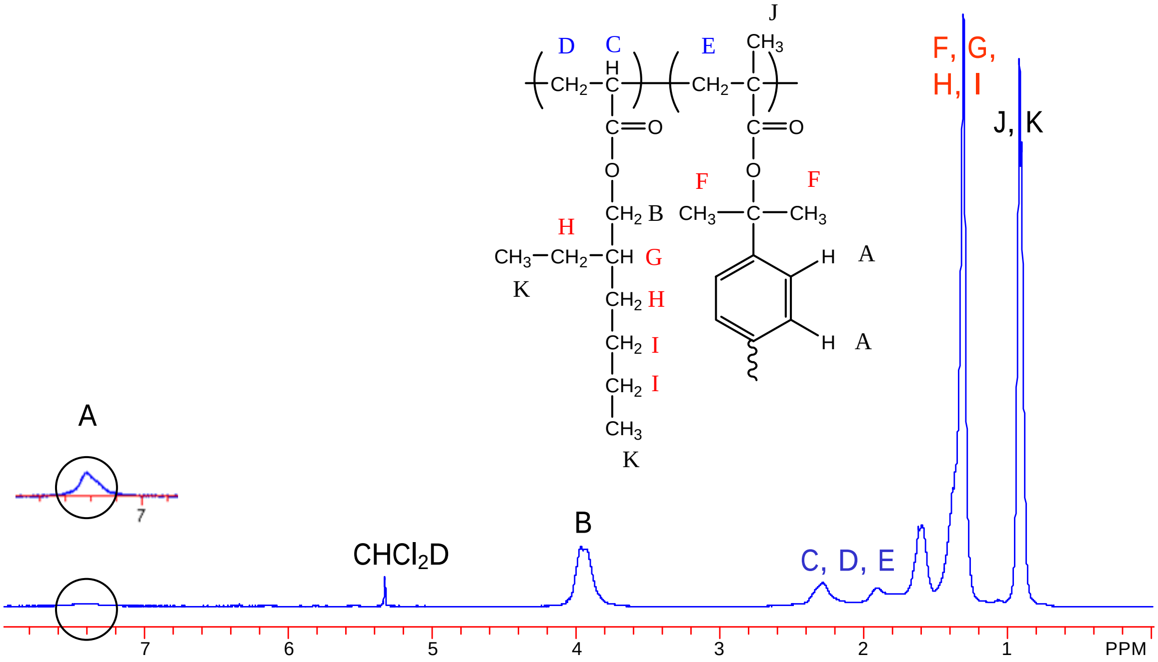


Figure 7.1: ^{1}H NMR spectroscopy of the PSA indicated the presence of DCDMA branching units in poly(EHA-*co*-DCDMA).

^{1}H NMR was used to verify the incorporation of DCDMA into the poly(EHA-*co*-DCDMA) PSA copolymer. The resonances associated with the phenyl protons of DCDMA at 7.4 ppm were used to quantify the level of DCDMA in the branched polymers. The integration of this resonance was normalized and compared to the resonance of the EHA methylene proton at 3.8 ppm. A typical polymerization that was charged with 3.3 mole percent DCDMA led to branched polymers containing 3.3 mole percent DCDMA (Figure 7.1), representing quantitative incorporation of the branching monomer. DHDMA incorporation could not be verified via ^{1}H NMR due to the overlap of the methyl resonances with those of the 2-ethylhexyl groups on the backbone. Adhesives containing low amounts (1.0-2.0 weight percent) of DCDMA exhibited low molecular weight distributions and a T_g of -67 °C was detected using DSC; this T_g was identical to poly(2-ethylhexyl acrylate) homopolymers. A T_g could not be detected via DSC in highly branched adhesive polymers (3.0-4.0 weight percent) exhibiting broad molecular weight distributions.

Low levels of the comonomer methyl methacrylate (MMA) were added to some polymerizations in order to assess an effect on adhesive performance. The molecular weights of these MMA terpolymers were found to be higher than the branched copolymers containing identical amounts of only DCDMA and EHA. The higher molecular weights of the MMA-containing terpolymers (Table 7.2) were primarily attributed to the uncontrollability of the polymerization; however, MMA radicals are known to terminate via disproportionation,[411] leading to an unsaturation at the end of the chain. This unsaturation was shown to participate in free-radical copolymerization, leading to the incorporation of graft chains,[412] and subsequent increase in molecular weight. Although the purpose of the MMA comonomer was to raise T_g, the broad molecular weight distributions prevented the determination of T_g for these terpolymers via DSC. Typical molecular weights of copolymers are summarized in Table 7.1.

7.4.2 Effect of composition on adhesive performance

Previous work indicated that the peel strength of poly(2-ethylhexyl acrylate) PSAs is strongly dependent on molecular weight.[413] A similar trend in peel strengths was observed for the DCDMA-branched poly(2-ethylhexyl acrylate) copolymers. The branched PSAs containing 3% DCDMA exhibited a low peel strength of 2.7 N/m, while two different samples containing 4% DCDMA showed peel strengths of 67 and 94 N/m. Cohesive failure was observed in all samples, and the average margin of error between identical samples was 15%. The peel strength showed a stronger dependence on $<M_w>$ rather than $<M_n>$ for these adhesives.

Polyacrylate pressure sensitive adhesive polymers typically contain several co-monomers in addition to 2-ethlyhexyl acrylate. The most common comonomers, methyl methacrylate and 2-hydroxyethyl methacrylate raise the T_g and storage modulus of PSA polymers when copolymerized in low quantities. Several branched PEHA-*co*-DCDMA

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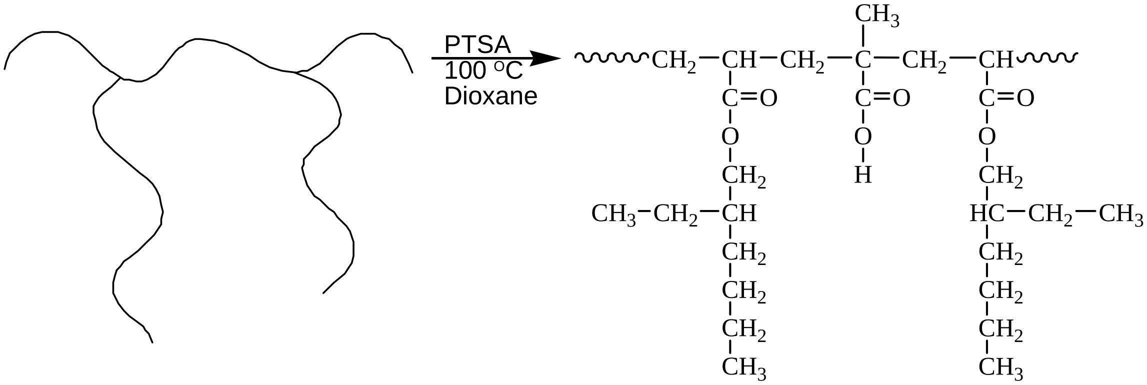
[411] T. G. Fox, J. B. Kinsinger, H. F. Mason, and E. M. Schuele, "Properties of Dilute Polymer Solutions. I. Osmotic and Viscometric Properties of Solutions of Conventional Poly(Methyl Methacrylate)." *Polymer*, **1962**, *3*(1), 71-95.

[412] C. H. Bamford and E. F. T. White, "Preparation of Block Copolymers by the Tertiary Base Method." *Trans. Faraday Soc.*, **1958**, *54*, 268-277.

[413] L. Kilian and T. E. Long, **2002**, unpublished results.

were synthesized using 3 to 4 weight percent of MMA to examine the effect of high T_g comonomers on DCDMA-branched PSAs. Due to the broad molecular weight distributions of these branched polymers, no T_g could be detected via DSC. PSAs containing 3% and 4% DCDMA exhibited increased peel strengths of 36 and 126 N/m when 3 weight percent MMA was used in the polymerization. These copolymers exhibited much higher $<M_w>$ values than similar poly(EHA-*co*-DCDMA) copolymers; the 3 weight percent DCDMA copolymer $<M_w>$ was 314,000 while the terpolymer containing 3% of both DCDMA and MMA had a weight-average molecular weight of 981,000. The molecular weight difference was attributed as the cause of the higher peel strengths. The greater molecular weight was believed to be a random event, since too little MMA was present in the reaction to effect the polymerization.



Scheme 7.3: Cleavage of PSA branching points via acid-catalyzed hydrolysis.

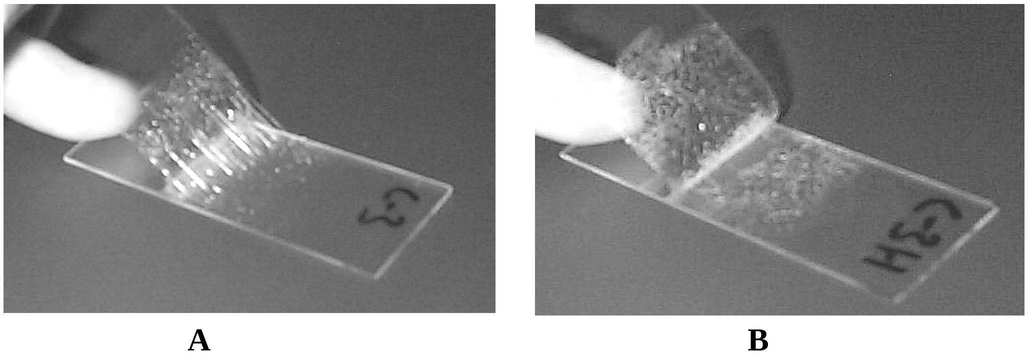


Figure 7.2: Visual evidence of branched PSA deactivation following hydrolysis. The peel strength of the poly(EHA-*co*-DCDMA) polymer decreased from 6.3 to 1.6 N/m.

7.4.3 Hydrolytic deactivation of branched PSAs

Acid-catalyzed hydrolysis of the DCDMA-containing adhesive polymers (Scheme 7.3) led to cleavage of the branching sites and significant reductions of peel strengths. This deactivation could be confirmed visually (Figure 7.2). The starting material was drawn into tendrils when the PET substrate was pulled away. Conversely, the hydrolyzed polymer broke apart rapidly when the bond was broken. This indicated a loss of cohesive strength. A comparison between the ^{1}H NMR spectra of the branched polymer and the hydrolysis product indicated that the resonance attributed to the phenyl protons present in DCDMA at 7.4 ppm was absent in the hydrolysis product. This spectral difference indicated complete removal of the DCDMA-based branch points and liberation of the diene by-product. The peel strengths of the hydrolyzed polymers were typically four to five times less than the starting materials (Figure 7.3). The hydrolysis of each molar equivalent of DCDMA led to two equivalents of methacrylic acid in the product polymer. Due to the high molar content of the methacrylic acid in the hydrolyzed polymer (expected 7 to 10 mole percent), reproducible SEC data could not be obtained from the hydrolyzed polymer when using either THF or $CHCl_3$ as the eluent.

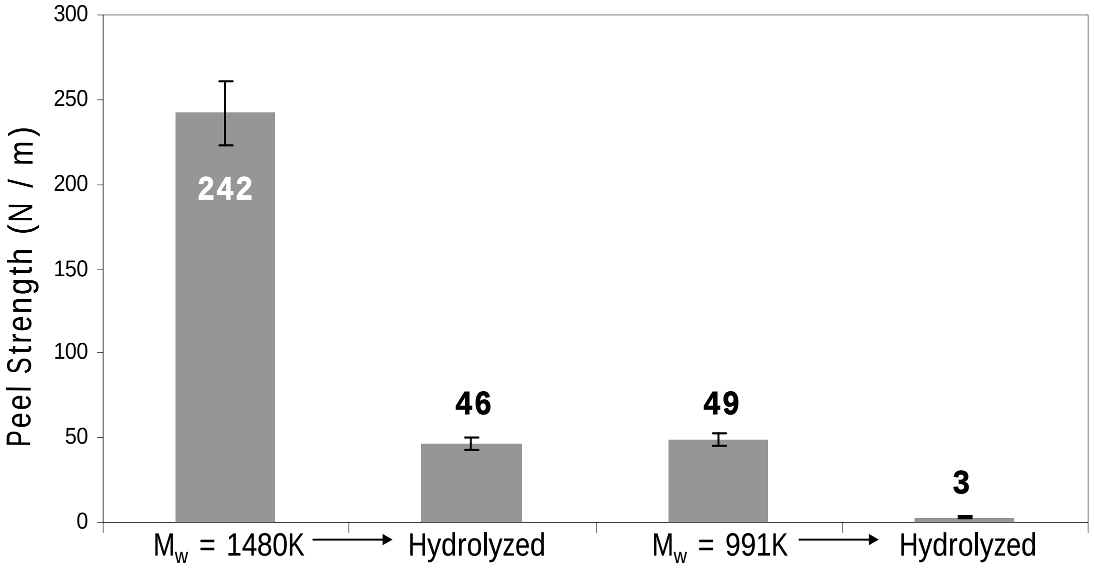


Figure 7.3: Hydrolytic cleavage of the branching points in both DCDMA and DHDMA branched polymers led to drastic reductions in 180° peel strengths.

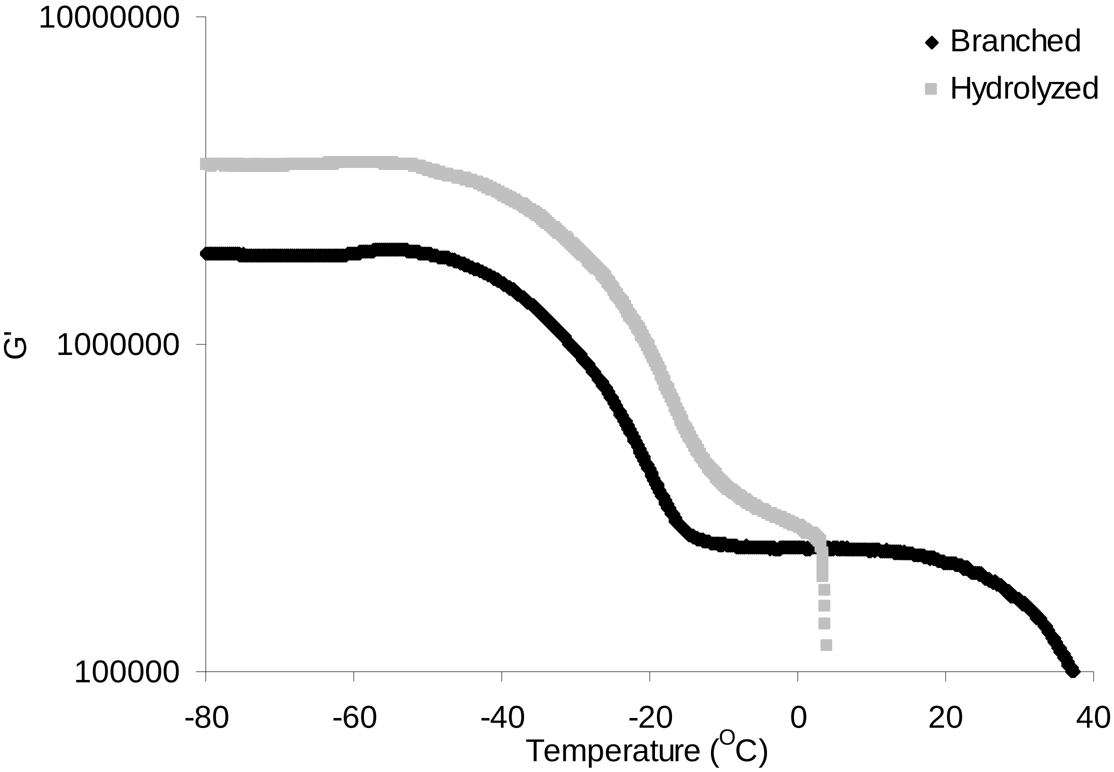


Figure 7.4: Cryogenic DMA of the poly(EHA-*co*-DCDMA) adhesive before and after hydrolysis indicated that the plateau modulus exhibited by the branched adhesive was lost upon hydrolysis.

The melt rheology of the cleavable branched poly(EHA-*co*-DCDMA) adhesive was examined using DMA (Figure 7.5). The PSA exhibited a T_g of approximately -35 °C, based on the maximum of the tan δ curve, and a plateau modulus was present from -20 to 30 °C. Although the plateau modulus (G'), which averaged 5×10^4 Pa, was substantially lower than the 1×10^5 Pa stated in the Dahlquist criterion, these PSAs exhibited excellent adhesion. Upon hydrolysis, the behavior of the cleaved polymer changed drastically at temperatures above 5 °C. The hydrolyzed polymer exhibited no plateau modulus. Instead, the modulus dropped rapidly to extremely low values ($< 5 \times 10^3$ Pa), and the PSA character was mostly lost. Due to the rigidity imposed by the methacrylic acid groups in the product polymer, the T_g rose to -30 °C and the modulus of the glassy polymer at extremely low temperatures was substantially higher.

7.5 Conclusions

Branched poly(2-ethylhexyl acrylate)s, copolymerized with relatively high amounts of the acid-cleavable comonomer dicumyl dimethacrylate, were synthesized without crosslinking. High amounts of the cleavable dimethacrylate monomer could be copolymerized due to the molecular weight-limiting effect of the chain transfer side reactions inherent to EHA free-radical polymerizations. Quantitative incorporation of DCDMA was observed for all polymerizations. These copolymers exhibited increasing weight-average molecular weights as the charged amounts of DCDMA increased. As expected, higher levels of branching reagents increased the molecular weight distributions significantly due to the increased incidence of long chain branching. These polymers served as relatively strong pressure sensitive adhesives, and 180° peel strengths indicated a strong dependence on the adhesive weight-average molecular weights.

Acid-catalyzed hydrolysis led to the selective scission of the DCDMA branch points, as evidenced by ^{1}H NMR spectroscopy. The peel strengths of the PSAs decreased between 70 and 80 percent as a result of hydrolysis. Weakening of the cohesive strength as a result of hydrolysis was observed visually. Comparable copolymer adhesives synthesized using 2,5-dimethyl-2,5-hexanediol dimethacrylate were synthesized and hydrolyzed. These PSAs exhibited a strong response to acid-catalyzed hydrolysis, leading to adhesive deactivation that was similar to DCDMA-containing PSAs.

7.6 Acknowledgements

The authors would like to thank the Carilion Biomedical Institute, Virginia Tech Optical Science and Engineering Research Center for financial assistance. This material is based upon work supported in part by the U.S. Army Research Laboratory and the U.S. Army Research Office under contract/grand number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors also acknowledge the Virginia Tech Department of Physics for the donation of Mylar® PET film. Dr. Michael Sumner is thanked for his work on the DMA instrument.

Chapter 8 : Effect of Branching on the Photo-Induced Deactivation of Cinnamate and Acrylate Modified Poly(2-ethylhexyl acrylate) PSAs

Taken From:
J. Adhes. **2004**, in progress.

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8.1 Abstract

Photodeactivatable pressure-sensitive adhesives (PSAs) were synthesized via the modification of poly(2-ethylhexyl acrylate-*co*-hydroxyethyl methacrylate) (Poly(EHA-*co*-HEMA) with acid chlorides containing either cinnamate or acrylate functional groups. Highly branched PSA terpolymers were also synthesized using EHA, HEMA, and ethylene glycol dimethacrylate (EGDMA), and were similarly modified to yield higher molecular weight adhesives containing photo-reactive groups. The introduction of these bulky functionalities to the PSAs increased glass transition temperatures and led to dramatic increases in peel strengths. The photo-active PSAs were deactivated when the cinnamate groups photocrosslinked upon exposure to UV light (λ_{max} = 320 nm). The resulting networks resulted in significant reductions in 180° peel strengths, and the adhesive failure mode changed from cohesive to adhesive. Highly branched PSAs of high molecular weights underwent significantly greater degrees of deactivation than corresponding lightly branched copolymers lacking EGDMA under similar conditions. The rates and extents of PSA deactivation were also dependent on the concentration of photoreactive groups. PSAs containing pendent acrylate groups were mixed with camphorquinone and the co-initiator dimethylaminoethyl methacrylate, and were photodeactivated using visible light. The PSAs with pendent acrylate groups deactivated more rapidly than the cinnamate-containing PSAs and lower pendent acrylate concentrations relative to cinnamate were sufficient to induce adhesive photodeactivation.

Keywords: pressure sensitive adhesive, acrylate, cinnamate, photocrosslinking, deactivation

8.2 Introduction

Light-sensitive adhesives and sealants are used in numerous medical applications, including wound solders[414] and dental fillings.[415,416] However, the force required for the removal of conventional bandaging pressure-sensitive adhesives (PSA) often causes discomfort and tissue damage, and research is currently directed toward the development of PSAs that are deactivated via crosslinking. For example, the peel strength of poly(dimethylsiloxane) [PDMS] containing adhesives was affected by radiation-induced crosslinking,[417] and peel strength reached a maximum when lightly crosslinked networks were formed. Further crosslinking led to rapid decreases in peel strengths as the modulus at room temperature increased outside the range of the Dahlquist criterion for PSA

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tack.[418] An alternative method for adhesive deactivation was the reduction of molecular weight via thermal retro-Diels Alder cleavage of adhesive polymer main chains[419] or hydrolytic cleavage of PSA polymer branching points.[420]

UV-Visible light is a well-established means for polymer crosslinking via free-radical mechanisms. For example, benzophenone-containing PSAs were photocrosslinked via exposure to UV light, which resulted in a significant peel strength reduction.[421] Several types of deactivatable adhesives that contain pendent methacrylate groups were also reported in the patent literature. Pendent methacrylate moieties were introduced as a result of either ring-opening metathesis copolymerization of endo,exo-5,6-bis(2-methacryloxyethoxycarbonyl)norborn-2-ene[422] or the post-free radical polymerization modification of methacrylic anhydride functional groups in poly(2-ethylhexyl acrylate).[423] The PSAs containing the methacrylate groups crosslinked and increased in modulus in the presence of Irgacure® photoinitiators upon exposure to visible light.[424,425] The crosslinked polymer networks exhibited relatively low peel strengths compared to the uncrosslinked PSAs, and the rate of crosslinking was

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dependent on the concentration of photoinitiator and methacrylate groups. Polyurethane PSAs[426] containing methacrylate functional groups were also synthesized, and high molecular weight polyurethane PSAs containing a photoinitiator deactivated upon visible light-induced photocrosslinking. [427,428]

Photodimerization is also an effective method for crosslinking polymers of various topologies. Photodimerizable groups are typically conjugated aromatic functional groups that absorb longer wavelength UV light (300-375 nm). For example, star polymers containing photodimerizable anthryl groups at the termini of the arms were photocrosslinked using 366 nm light to form model network polymers.[429] PET copolymers containing 2,6-anthracenedicarboxylate were also crosslinked using photo-irradiation.[430] The coumarin functional group readily undergoes photodimerization upon exposure to long-wavelength UV light, and the resulting dimer was cleaved back into the initial monomers using 254 nm light. The photoreversibility of coumarin makes this group an interesting choice, and coumarin-terminal four-armed poly(ε-caprolactone) star

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polymers,[431,432] coumarin-containing polyesters[433] and telechelic poly(ethylene glycol)s[434,435] were synthesized and photocrosslinked.

The chalcone[436] and cinnamate[437] functional groups also undergo photodimerization via the [2+2] cycloaddition mechanism. Unlike cinnamate dimerizations, these dimers are not photoreversible. Multiple dimerization reactions between cinnamate moieties on different chains lead to network formation. This “on-demand” network synthesis was used to lock the cylindrical microphase- separated morphology of poly(*t*-BMA) blocks into the poly(2-cinnamoylethyl methacrylate) phase.[438] Cinnamate photocoupling was also used to crosslink the outer shells of micelles comprised of diblock copolymers, which resulted in the synthesis of well-controlled nanospheres.[439]

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The photodimerization of cinnamate moieties in highly branched polymers is proposed as a more efficient means to improve the reduction of peel strength of switchable PSAs. The cinnamate-moiety is an excellent choice for deactivatable medical PSAs, since deactivatable medical PSAs[440] must not contain any harmful compounds that can diffuse from the adhesive into the surrounding body tissues. In this study, both lightly and highly branched poly(2-ethylhexyl acrylate-*co*-cinnamoylethyl methacrylate) photodeactivatable PSAs were synthesized. Light chain branching occurred during polymerization due to the chain transfer side reactions inherent to the free-radical polymerization of 2-ethylhexyl acrylate.[441] Very small amounts of the comonomer ethylene glycol dimethacrylate were copolymerized in some reactions in order to introduce heavier levels of branching. Similar lightly and heavily branched acrylate-containing PSAs were also synthesized and deactivated in the presence of a photoinitiator to serve as a comparison to the cinnamate-containing adhesive. The level of branching and the concentrations of the pendent photocrosslinkable groups had dramatic effects on both the rates and extents of PSA photodeactivation.

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8.3 Experimental

8.3.1 Materials

The monomers 2-ethylhexyl acrylate (Aldrich, 98%), hydroxyethyl methacrylate (Aldrich, 99%), ethylene glycol dimethacrylate (Aldrich, 98%), and dimethylaminoethyl methacrylate (Aldrich, 98%) were filtered through an activated basic alumina column (Aldrich, 150 Mesh) to remove the inhibitors. The reagents cinnamoyl chloride (Aldrich, 98%), AIBN (Aldrich, 98%), dimethylaminoethyl methacrylate (Aldrich, 99%) and camphorquinone (Aldrich, 99%) were used as received. Triethylamine (Sigma, 99%) and acryloyl chloride (Aldrich, 98%) were distilled under N_2 prior to use.

8.3.2 Synthesis of Poly(2-ethylhexyl acrylate-*co*-hydroxyethyl methacrylate) PSA

A solution of 2-ethylhexyl acrylate (34 g, 0.18 mol), hydroxyethyl methacrylate (6.0 g, 0.046 mol), and ethyl acetate (180 mL) was prepared in a 250 mL round-bottomed flask. In the polymerization of branched poly(2-ethylhexyl acrylate-*co*-hydroxyethyl methacrylate), 0.125 to 0.5 wt. % of the commoner ethylene glycol dimethacrylate (EGDMA) was also added to the reaction flask. The polymerizations were carried out at 20 percent solids. The polymerization solution was purged with nitrogen for 10 minutes and heated to 65 °C. After 10 minutes, an AIBN solution (5 mg, 0.0125 weight percent) was injected into the reaction. The polymerization proceeded for 24 h, and the polymer was subsequently precipitated into a 10-fold excess of cold methanol. The recovered polymer was dried in vacuo at 65 °C overnight.

8.3.3 Synthesis of Photodeactivatable Poly(2-ethylhexyl acrylate-co-2-cinnamoylethylhexyl methacrylate) PSA

Poly(2-ethylhexyl acrylate-*co*-hydroxyethyl methacrylate) (5.7 g) was dissolved in tetrahydrofuran (THF, ~60 mL, Burdick & Jackson, HPLC) in a 100 mL round-bottomed flask and cooled to 0 °C. Triethylamine (3.3 g, 0.032 mol) was added to the solution, and an addition funnel was fitted to the flask. A solution of cinnamoyl chloride and THF (40 mL, 0.82 M), comprising an 10:1 molar excess relative to HEMA, was added drop wise under an argon atmosphere and the reaction was allowed to proceed for 24 h at 0 °C. The product polymer was precipitated into cold methanol and dried in vacuo at 65 °C overnight.

8.3.4 Synthesis of Photodeactivatable Poly(2ethylhexyl acrylate-co-2-acryloylethyl methacrylate) PSA

Poly(EHA-*co*-HEMA) (6.0 g) was dissolved into approximately 60 mL THF in a 100 mL round-bottomed flask, followed by cooling to 0 °C. Triethylamine (3.5 g, 0.034 mol) was syringed into the reactor, followed by the slow-addition of 36 mL acryloyl chloride in THF (1.0 M). The reaction was allowed to proceed for 24 h, followed by precipitation into a 9:1 mixture of methanol and water. The product polymer was dried under vacuum overnight at 65 °C. The photosensitive PSA was prepared by adding 0.5 weight percent camphorquinone and the accelerator dimethylaminoethyl methacrylate (0.5 or 2 wt. %) to the purified PSA at least two days prior to use, followed by dark storage at -20 °C.

8.3.5 Adhesive Characterization

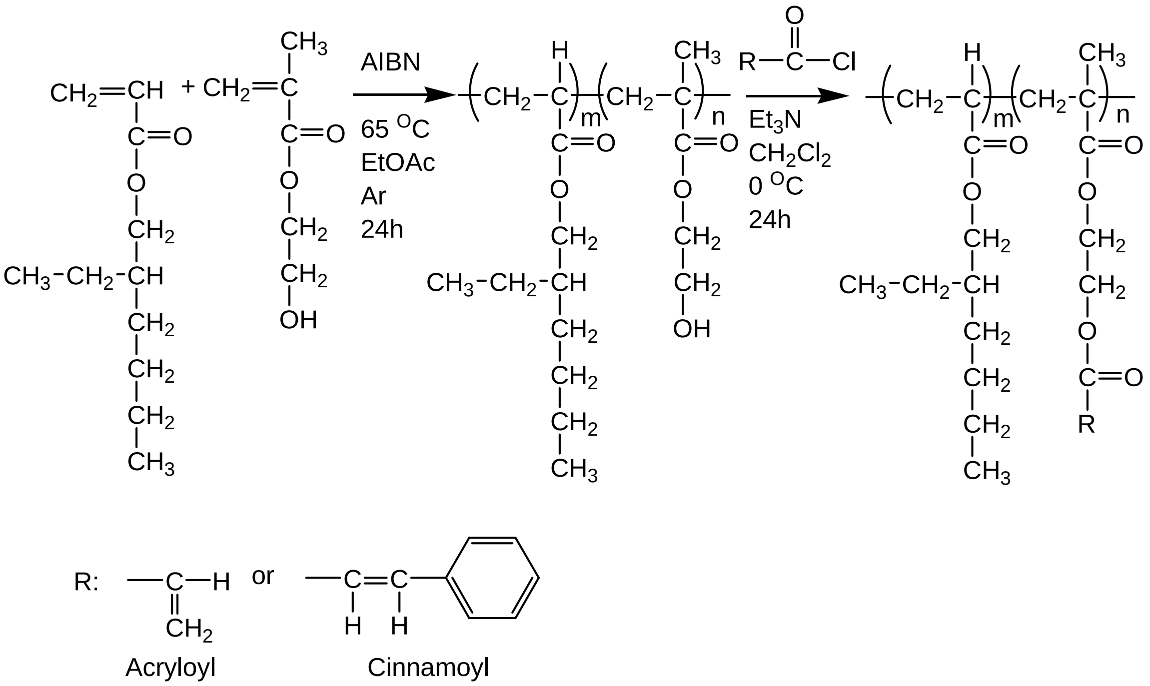
^{1}H NMR spectra were obtained using a Varian Unity 400 spectrometer at 400 MHz. The polymers were dissolved in deuterated chloroform. Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 ^{O}C / min under nitrogen, and reported as the midpoint of the change in heat capacity during the second heat. A Waters 717plus Autosampler coupled to a Waters 2410 refractive index detector and a Wyatt Technology miniDAWN® static triple-angle laser light scattering detector (absolute molecular weights) were used to determine the polymer molecular weights. SEC measurements were performed at 40 °C in chloroform at a flow rate of 1.0 mL/min. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement. The 180° peel test (ASTM #D903) was performed using an Instron Universal Testing Rig (Model 4411). Peel test samples were prepared by placing a 1” X 8” PET film (Mylar®, 0.002 in. thick) strip onto the PSA film (0.2 mm PSA film on glass slide) and debonding the PET film at a rate of 5 in. / min. The peel strength was determined as the average peak force versus displacement.

8.3.6 Photodeactivation of pressure-sensitive adhesives

The photodeactivatable PSAs were spread onto clean glass slides (1” X 2”) to a thickness of 0.2 mm using a BYK “Gardner” film-casting knife with a Mitutoyo Corporation adjustable elevation device. The PSA films were irradiated for varying lengths of time from 1 to 120 minutes using an Oriel Photoreactor with a light intensity of 38 mW / cm^2. A UV-cutoff filter (Oriel Filter # 51942) was used during the deactivation of the acrylate-pendent PSAs and a 325 nm λ_{max} filter (Oriel Filter # 59800) was used for the cinnamate containing PSAs.

8.3.7 Gel fraction determination

The photodeactivated PSA films on the glass slides were weighed prior to immersion in 55 mL of THF. Following immersion for 2 days, the films were dried under vacuum at 65 ^{O}C overnight and weighed. The percent gel fraction was determined by comparing the masses of the films before and after solvent immersion.



Scheme 8.1: Free-radical copolymerization of poly(EHA) and HEMA was followed by acid-chloride coupling with pendent acrylate and cinnamate functional groups.

8.4 Results and Discussion

8.4.1 Photodeactivatable PSA Synthesis

Photodeactivatable PSAs were synthesized via the post-polymerization modification of the poly(2-ethylhexyl acrylate-*co*-hydroxyethyl methacrylate) [Poly(EHA-*co*-HEMA)]. The poly(EHA-*co*-HEMA) PSA was obtained from the conventional free-radical copolymerization of EHA and HEMA (Scheme 8.1), and exhibited moderately high molecular weights ($\langle M_n \rangle$ = 30,000 to 60,000) and typical molecular weight distributions ($\langle M_w \rangle / \langle M_n \rangle$ = 2.0 to 2.5). The photocrosslinkable cinnamate and acryloyl functionalities were subsequently introduced to the polymer, since the pendent double bonds in the cinnamate and acryloyl functionalities led to premature crosslinking during polymerization. The corresponding monomer 2-cinnamoylethyl methacrylate was synthesized during the course of this study; however, extensive crosslinking occurred during copolymerization, and the resulting network polymers exhibited negligible adhesive properties. Direct comparisons between the cinnamate and acrylate-pendent PSAs were possible, as both PSAs were synthesized from the same starting poly(EHA-*co*-HEMA).

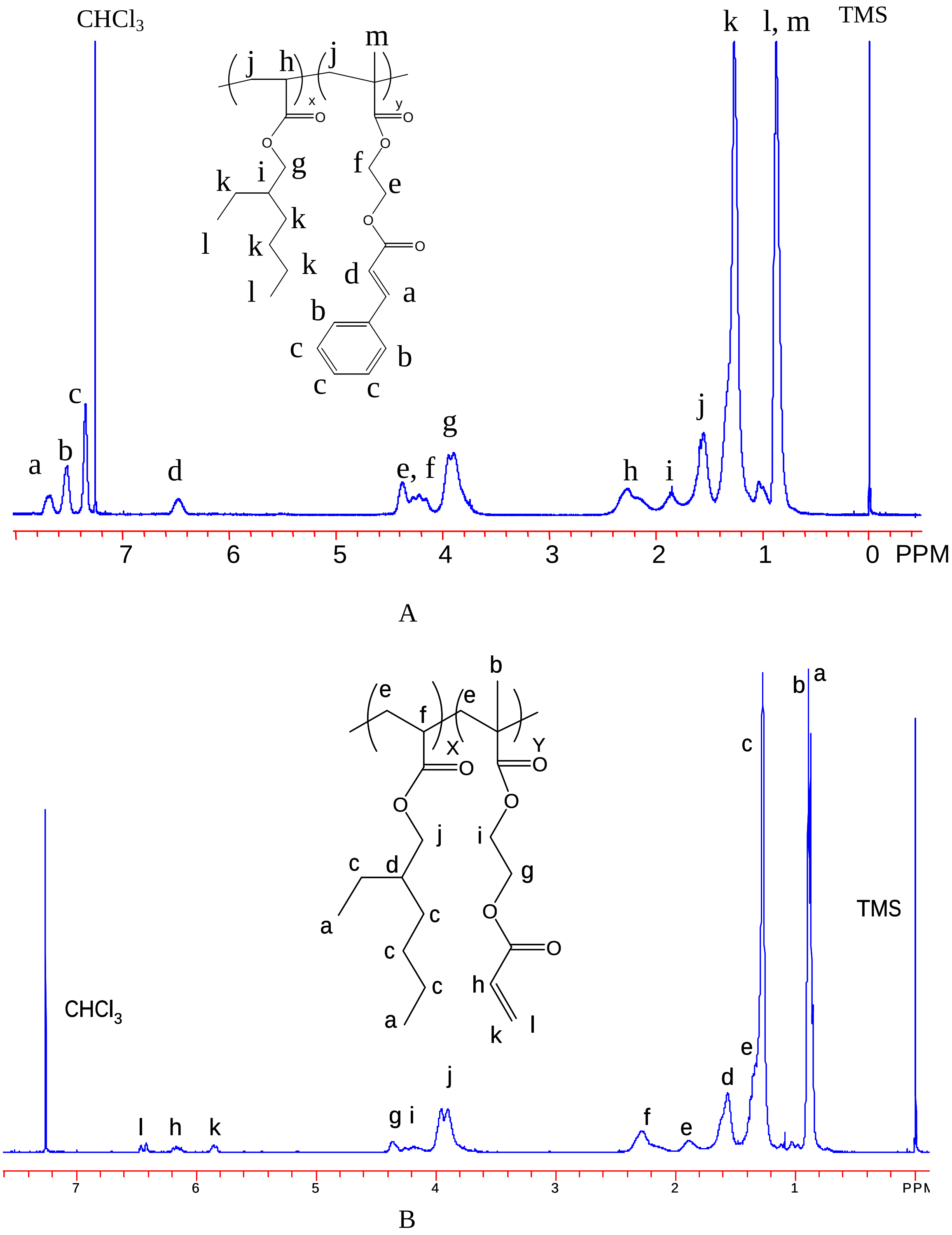


Figure 8.1: The ^{1}H NMR spectra of the photocrosslinkable PSAs show the incorporation of the cinnamate (8.1A) and acrylate (8.1B) functional groups.

Table 8.1: Molecular weights and adhesive characteristics of lightly branched and highly branched poly(EHA-*co*-CEMA) PSAs.

Mol. % CEMA & EGDMA	$<M_n>$	$<M_w>/<M_n>$	Peel Strength (N/m)	Peel Str. After irradiation	Gel %. after 30 min.
2 0	64900	2.0	13	29	35%
8 0	64900	2.0	11	58	61%
14 0	71600	2.3	20	41	73%
20 0	5000	3.1	3	24	81%
25 0	32800	3.2	136	8	77%
20 0.125	63000	4.5	232	4	73%
20 0.25	21200	10.1	128	17	70%
20 0.5	27900	18.5	129	17	70%

Table 8.2: Molecular weights of acrylate-pendent photodeactivatable PSAs.

Mol. % Acrylate & % EGDMA	$<M_n>$	$<M_w>/<M_n>$	Peel Strength (N/m)	Peel Str. After Irradiation
10 0	64900	2.0	364	54.6
20 0	63000	4.5	387	61.9
4 0.25	21200	10.1	412	57.7

Cinnamoyl chloride and acryloyl chloride reacted with the hydroxy-containing poly(EHA-*co*-HEMA) PSAs to produce photocrosslinkable PSAs (Scheme 8.1). The modification of the poly(EHA-*co*-HEMA) required a large excess of acid chloride to proceed to completion. Incorporation of the cinnamate functional group into the precursor polymer was evidenced by the ^{1}H NMR spectrum of the reaction product (Figure 8.1a). The incorporation of the cinnamate group resulted in the appearance of two resonances at 7.3 and 7.5 ppm corresponding to the phenyl ring in the cinnamate functional group. The cinnamate olefin resonances at 6.5 and 7.7 ppm were also quantified. The incorporation of the acrylate functionalities resulted in the appearance of ^{1}H NMR olefin resonances at 5.9, 6.2, and 6.4 ppm (Figure 7.1b). Several compositions of lightly branched poly(EHA-*co*-CEMA) PSAs were synthesized (Table 8.1), covering a range of molecular weights and cinnamate concentrations (2 to 25% CEMA). The acrylate moiety was incorporated at levels of 10 and 20 mole percent into a poly(EHA-

co-HEMA) copolymer with an $<M_n>$ of 65000 g/mol (Table 8.2). The glass transition temperatures of the lightly branched PSA polymers increased an average of 5 °C as a result of the modification with either the cinnamate or acrylate functionalities from –65 °C to –60 °C.

Poly(EHA-*co*-HEMA) copolymers and terpolymers containing EGDMA were synthesized to study the effect of PSA topology on peel strength and subsequent photodeactivation. Copolymers containing high amounts of 2-ethylhexyl acrylate are inherently lightly branched due to the high frequency of chain transfer to polymer that occurs during solution free-radical polymerization.[442] The poly(EHA-*co*-HEMA) PSAs in this study exhibited molecular weight distributions indicative of light branching ($M_w/M_n < 4.0$), and relatively low 180° peel strengths (5 to 9 N/m). The branching monomer ethylene glycol dimethacrylate (EGDMA) was used to synthesize highly branched poly(EHA-*co*-HEMA) PSAs (Table 1), which led to greater PSA weight-average molecular weights ($<M_w>$ = 220,000 to 560,000) and higher molecular weight distributions ($<M_w>/ <M_n>$ = 4.5 to 18), suggesting much higher degrees of branching. EGDMA could only be incorporated in low amounts, up to 0.5 weight percent, before gelation occurred during polymerization. Modification of the highly branched PSA polymers with cinnamate or acrylate functional groups led to adhesives exhibiting relatively high peel strengths. The average peel strengths of the highly branched poly(EHA-*co*-HEMA) PSAs (63 to 109 N/m) were significantly greater than those of the lightly branched poly(EHA-*co*-HEMA) PSAs (5 to 9 N/m). Due to the broad molecular

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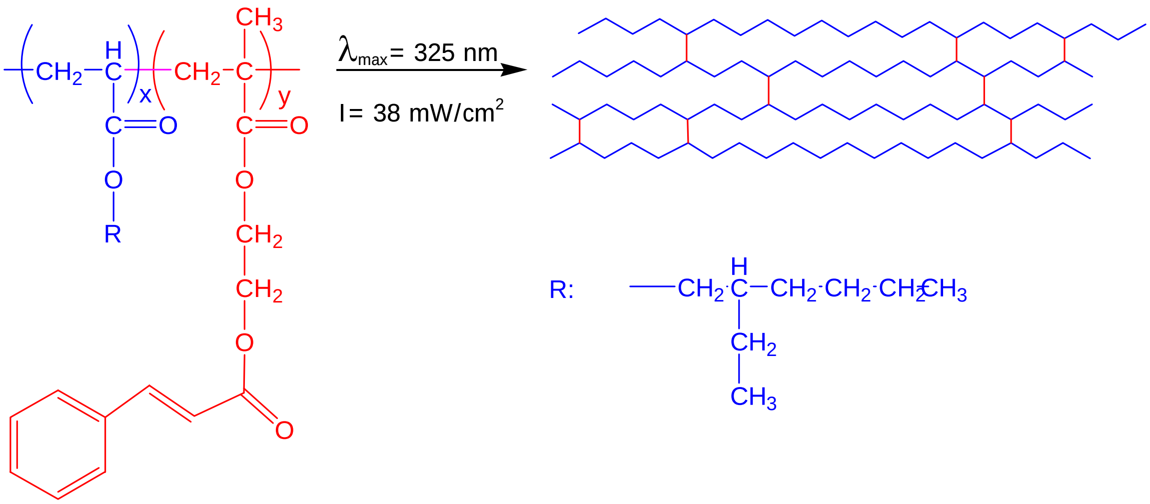
[442] F. Heatley, P. A. Lovell, and Y. Tsuyoshi, "Chain Transfer to Polymer in Free-Radical Solution Polymerization of 2-Ethylhexyl Acrylate Studied by Nmr," *Macromolecules*, **2001**, *34*(22), 7636-7641.

weight distributions of these polymers, a change in T_g resulting from the introduction of the photocrosslinkable groups could not be detected.



Scheme 8.2: Cinnamate-containing PSAs crosslinked under long-wavelength UV light to deactivate the adhesive.

8.4.2 PSA Photodeactivation

The lightly and heavily branched poly(EHA-*co*-HEMA) PSAs crosslinked upon exposure to UV light (Scheme 8.2), resulting in dramatic changes in peel strength. The PSA photodeactivation was verified visually (Figure 8.2), and the failure mode changed from cohesive to adhesive following irradiation. The behavior of the PSA upon irradiation showed a very strong dependence on the molar amount of CEMA in the polymer. High amounts of CEMA in both the lightly and the heavily branched polymers led to the deactivation of the adhesive (Figure 8.3A), while low amounts of CEMA in lightly branched polymers resulted in only partial crosslinking, leading to an overall increase in the 180° peel strengths (Figure 8.3B). The highly branched PSAs containing the highest amounts of CEMA (20 and 25%) underwent a significant degree of deactivation within the first 15 minutes of irradiation. Photodeactivation was typically complete after 30 minutes irradiation time. The amount of CEMA in the lightly branched PSAs had a more significant impact on deactivation behavior than the PSA number-average molecular weights. The peel strength of the adhesive samples containing 2 to 14 mole percent CEMA rose rapidly when the sample was irradiated. This was attributed to an increase in the PSA molecular weights as a result of branching and light crosslinking, which led to more chain entanglements and greater peel strengths. As the PSAs continued to crosslink, the peel strengths dropped slightly, but overall, these PSAs exhibited greater peel strengths following irradiation.

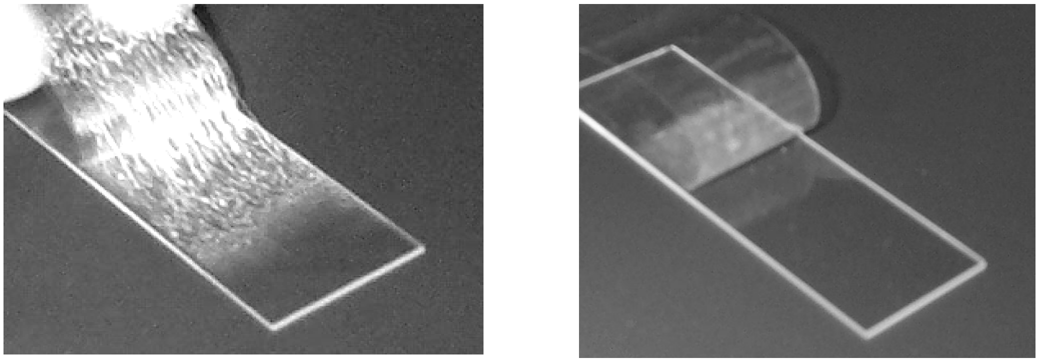


Figure 8.2: Photographs of the mol. 22% cinnamate sample illustrate the cinnamate containing PSA before (A) and after (B) photocrosslinking.

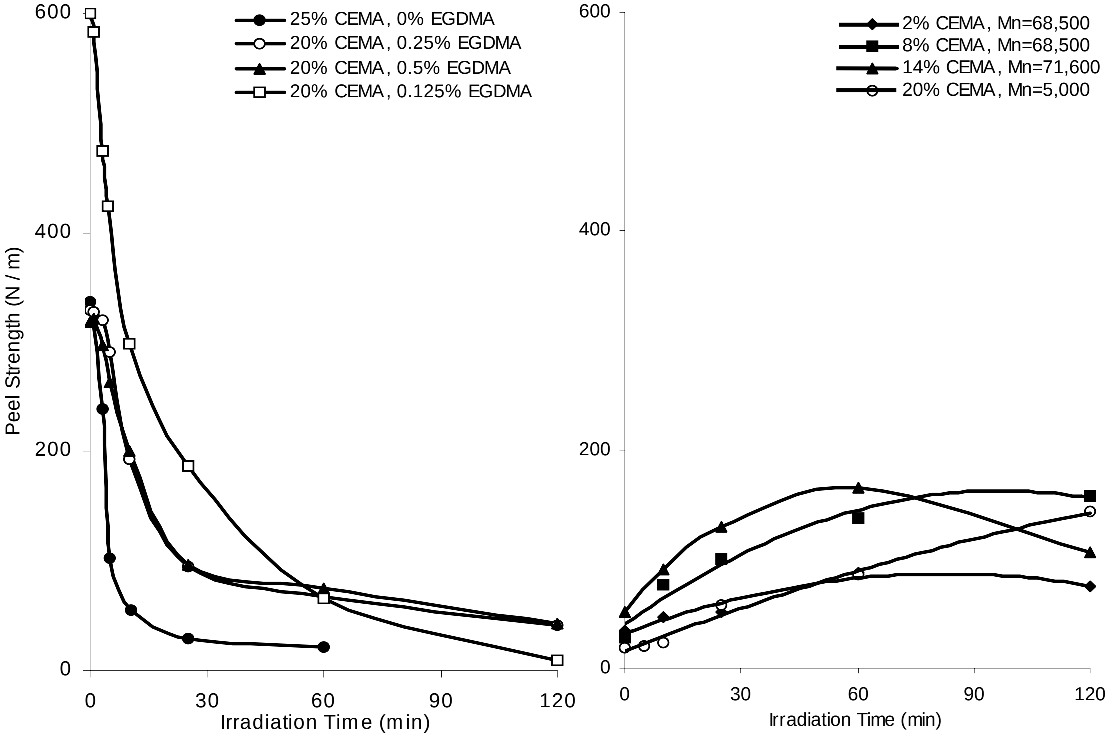


Figure 8.3: Adhesives containing >20% CEMA deactivated upon irradiation (A) while the peel strengths of adhesives with lower concentrations increased after exposure (B).

The highly branched photodeactivatable cinnamate PSAs containing EGDMA exhibited much greater weight-average molecular weights (M_w = 284,000 to 520,000) than the lightly branched PSAs (M_w = 16,000 to 170,000). These highly branched polymers photocrosslinked more rapidly than the lower molecular weight lightly branched PSAs lacking EGDMA. As a result, significant deactivation of the EGDMA-containing PSAs took place; peel strength losses of up to 98% were observed in the highly branched PSAs. High amounts of CEMA were necessary to induce similar extents of deactivation in the lightly branched PSAs (25% CEMA, 96% deactivation). Weight-average molecular weights of the photocrosslinkable PSAs played a significant role in the extent of deactivation following irradiation. The gel fractions following exposure to UV light in the highly branched PSAs were similar to the lightly branched polymers containing high amounts of cinnamate.

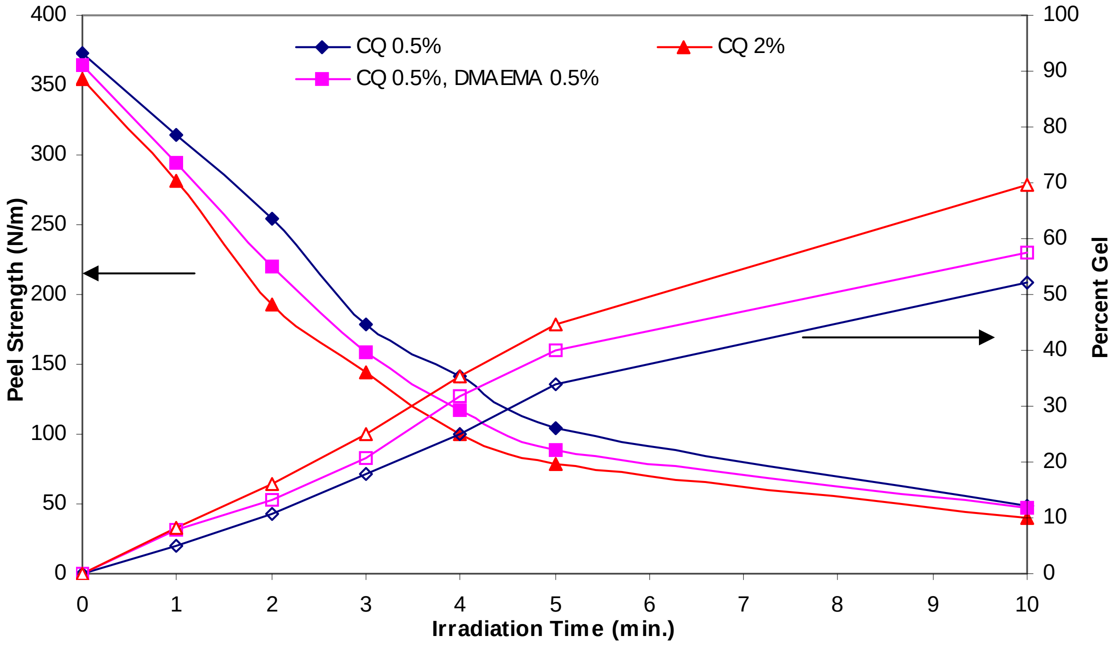


Figure 8.4: Increasing the amounts of the photoinitiator and the DMAEMA co-catalyst accelerated the rate of peel strength decrease and increased the network formation rate of the acrylate-pendent PSAs.

The free-radical crosslinking reaction of the PSAs with pendent acrylate groups was performed by mixing the PSA with the photoinitiator camphorquinone and the photoinitiation accelerating co-reagent dimethylaminoethyl methacrylate (DMAEMA).[443] Photocrosslinking of PSAs with pendent acrylate groups was achieved via the irradiation of the samples with visible light from the photoreactor. The rate of PSA peel strength deactivation was influenced significantly by the concentration of the photoinitiator and DMAEMA (Figure 8.4). Higher concentrations of initiator or DMAEMA increased the deactivation rate. The heavily branched acrylate containing PSA exhibited the similar deactivation behavior as the lightly branched adhesives. This similarity was attributed to the fact that the weight-average molecular weights of these polymers were comparable. The acrylate containing PSAs lost, on average, 85% of their peel strengths upon photocrosslinking. The gel fraction measurements of the adhesive during deactivation indicated that the gel fraction increased as the peel strength decreased (Figure 8.5).

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[443] J. Nie, J. F. Rabek, and L.-A. Linden, "Photopolymerization of Poly(Melamine-Co-Formaldehyde) Acrylate for Dental Restorative Resins," *Polym. Int.*, **1999**, *48*(2), 129-136.

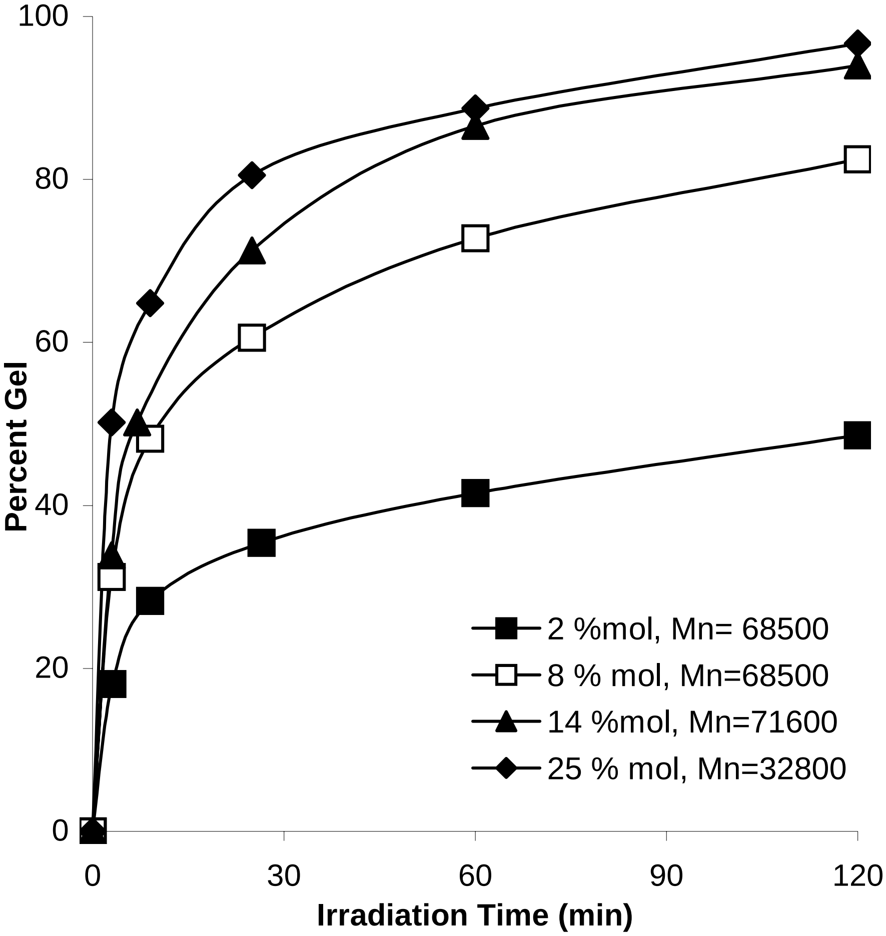

Figure 8.5: The rate of photocrosslinking of the CEMA adhesives was strongly dependent on the CEMA concentration.

The gel fraction was an important indicator for the extent of photocrosslinking. Greater amounts of CEMA in the PSAs accelerated the rate and extent of PSA crosslinking (Figure 8.5) due to the presence of more crosslinking groups. The adhesive containing 25% CEMA exhibited a gel fraction after 25 minutes that was three times greater than the 2% CEMA adhesive. The highest gel fraction of the 25% CEMA sample was measured to be 95%, and samples containing lower amounts of CEMA exhibited much lower gel fractions after irradiation for long periods of time.

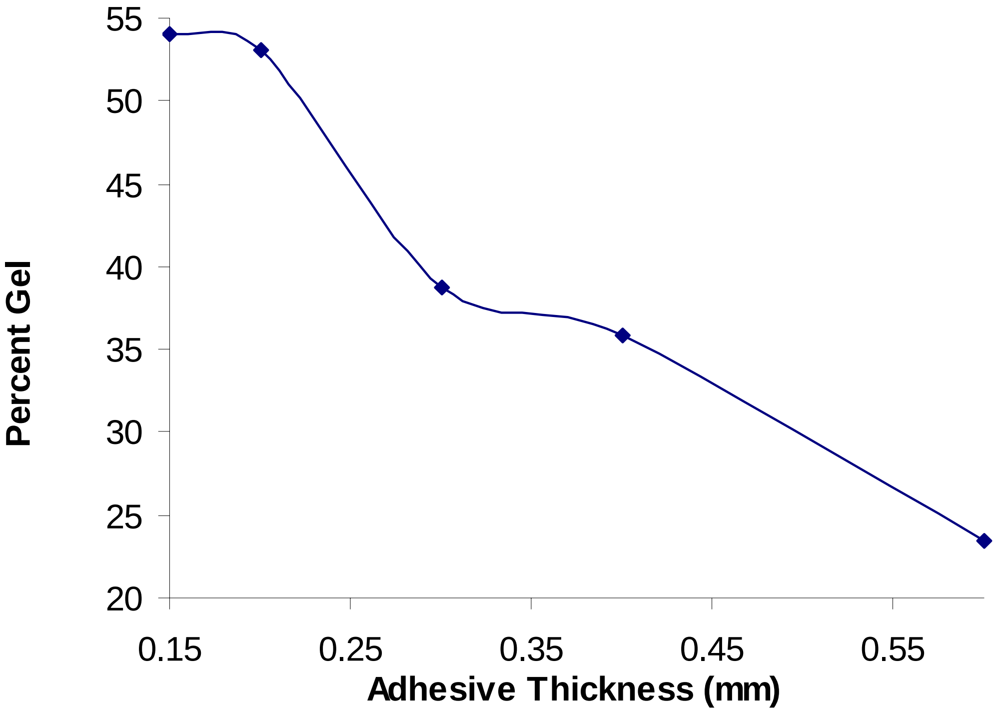

Figure 8.6: The gel fraction of the 14% CEMA PSA film decreased with increasing film thickness due to the UV light absorption of CEMA.

Since the CEMA functional group absorbs UV light, the thickness of the PSA sample impacted the extent of photodeactivation dramatically. Increasing sample thicknesses led to lower gel fractions due to the UV-light absorption of the cinnamate groups. For samples containing 14% CEMA, the gel fraction of a 0.2 mm film was one-third greater than a film with 0.4 mm thickness, after irradiating for 25 minutes. The 14% CEMA adhesive showed a 55% gel fraction when the sample was 0.2 mm thick. On average, a decrease of seven percent in the gel fraction was observed for each additional 0.1 mm of sample thickness from 0.1 to 0.6 mm (Figure 8.6). The use of UV-absorbing poly(ethylene terephthalate) [PET] films as the flexible PSA substrate also slowed the rate of network formation. This effect was examined using the lightly branched poly(EHA-*co*-CEMA) adhesives. On average, the adhesives covered with PET films exhibited a gel fraction that was only approximately 70% of the gel fraction from identical uncovered samples. This effect was much more pronounced in samples containing lower amounts of CEMA.

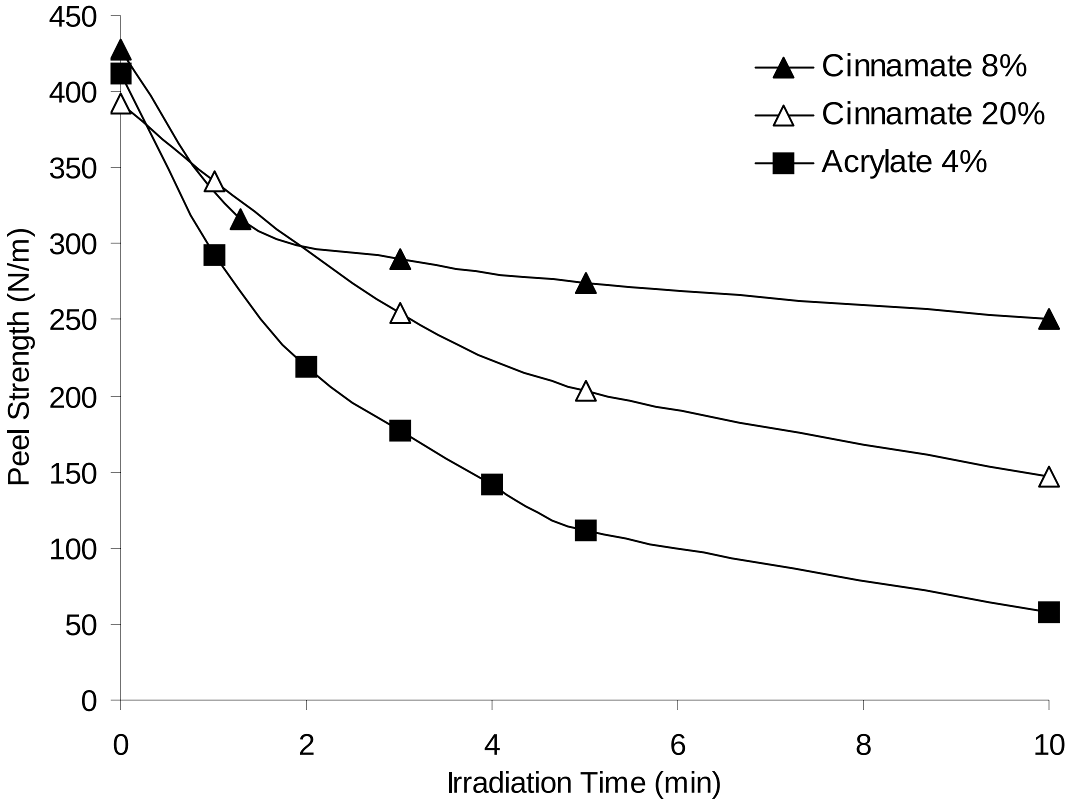

Figure 8.7: The acrylate-pendent PSAs deactivated much more rapidly than the cinnamate-pendent PSAs despite lower crosslinking group concentrations.

A comparison between the deactivation of the lightly branched CEMA and acrylate-pendent PSAs indicated that the acrylate PSAs underwent deactivation at a much faster rate than the cinnamate PSAs (Figure 8.7). The final extent of crosslinking was also greater for the acrylate-pendent PSAs. The acrylate PSA contained a much lower concentration of crosslinking moieties than the cinnamate PSAs. The rate of deactivation was much greater for PSAs containing a greater percentage of acrylate groups (> 10%). It was concluded that the crosslinking of the acrylate groups was more efficient, since the lightly branched 4 mole % acrylate adhesive crosslinked and deactivated while lightly branched cinnamate adhesives containing up to 20 mole % underwent varying degrees of activation. The highly branched PSAs containing the cinnamate functional groups exhibited greater weight average molecular weights and much higher degrees of deactivation than their lightly branched counterparts. The most significant deactivation was observed in the highly branched CEMA PSA containing 0.125 mole percent EGDMA.

8.5 Conclusions

Lightly branched pressure-sensitive adhesives (PSAs) containing photocrosslinkable cinnamate and acrylate moieties were synthesized from poly(hydroxyethyl methacrylate-*co*-2-ethylhexyl acrylate) [poly(EHA-*co*-HEMA)], while highly branched and photodeactivatable PSA polymers were synthesized from a terpolymer containing EHA, HEMA, and ethylene glycol dimethacrylate (EGDMA). The highly branched polymers exhibited much greater weight-average molecular weights, molecular weight distributions, and 180° peel strengths than the lightly branched counterparts. The modification of the lightly branched adhesives with photoreactive cinnamate or acrylate groups raised the peel strengths substantially, relative to the unmodified polymers.

Cinnamate-containing adhesives were deactivated within minutes using UV light. The crosslinking behavior was very sensitive to the levels of long-chain branching, the concentration of the photocrosslinking moieties, and the polymer weight-average molecular weights. The presence of high levels of long-chain branching led to the most significant adhesive photodeactivation in the cinnamate PSAs. The extent of crosslinking in these PSAs was also very sensitive to sample thickness due to UV light absorption of the cinnamate groups and the PET substrate. Due to the free-radical crosslinking mechanism and reactivity of the camphorquinone photoinitiator, the lightly branched acrylate containing PSAs deactivated at a much greater rate than the cinnamate PSAs. This trend was confirmed using both peel strength measurements and gel fraction determination.

8.6 Acknowledgements

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Chapter 9 : Synthesis and Characterization of PMMA Containing Terminal Aliphatic Diol Functionality

Taken From:
Polymer **2004**, in progress.

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9.1 Abstract

The novel anionic polymerization co-initiator 1,1-bis-4,4'-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene (BTOPE) was synthesized from 4,4'-dihydroxybenzophenone (DHB) utilizing a three-step synthetic methodology. Conversion of the aromatic diol functional group in DHB to an aliphatic diol was achieved by reacting DHB with ethylene carbonate in the presence of potassium carbonate. *Tert*-butyl dimethylchlorosilane was used to protect the diol functional group, and the ketone functional group was subsequently converted to the alkene in BTOPE using a Wittig reaction. The Wittig reaction proceeded in high yield and was shown to be complete after 90 min. at 0 °C using in-situ FTIR spectroscopy. The overall recovered yield of BTOPE was between 75 and 85 percent.

Following purification, BTOPE was reacted with *sec*-butyl lithium and used to initiate the anionic polymerization of methyl methacrylate. Well-defined poly(methyl methacrylate) [PMMA] with a molecular weight range from $\langle M_n \rangle = 10{,}000$ to $\langle M_n \rangle = 67{,}000$ was synthesized quantitatively. Narrow molecular weight distributions were observed, indicating good control over the polymerization. The BTOPE containing

PMMA was readily de-protected under slightly acidic conditions at elevated temperatures to yield α,α-dihydroxy PMMA. This aliphatic diol-capped polymer could be used in a variety of polymers from polyester graft macromonomer to lactide ring-opening polymerization initiator.

Keywords: anionic polymerization, methacrylate, protecting group, diphenylethylene, macromonomer

9.2 Introduction

One of the most useful aspects of living anionic polymerization is that functional groups can be placed of at the termini of the polymer chains during either the initiation or termination step in the polymerization. Propagating carbanions were previously terminated with a variety of electrophilic reagents to introduce terminal functional groups in almost quantitative yields.[444] For example, ethylene oxide was frequently used to introduce the alcohol functional group to living styrenic and diene polymers[445,446]. Termination with 4-vinylbenzoyl chloride, led to the introduction of the styrene functional group to yield a poly(methyl methacrylate) graft polymerization macromonomer. [447]

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[445] K. Hayashi and C. S. Marvel, "α,ω-Glycols and Dicarboxylic Acids from Butadiene, Isoprene, and Styrene and Some Derived Block Polymers, Esters, and Urethans." *J. Poly. Sci. A- Gen. Pap.*, **1964**, *2*(6), 2571-2594.

[446] R. P. Quirk, F. You, C. Wesdemiotis, and M. A. Arnould, "Anionic Synthesis and Characterization of ω-Hydroxyl-Functionalized Poly(1,3-Cyclohexadiene)." *Macromolecules*, **2004**, *37*(4), 1234-1242.

[447] S. D. Smith, "Synthesis of Poly(Methyl Methacrylate) Macromonomers Via Anionic Polymerizations." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1988**, *29*(2), 48-49.

Numerous bromine containing end-capping reagents were also utilized in the introduction of functional groups on living polymers. Living polyisoprene was functionalized in almost quantitative yields via termination with monobromodienes; similar functionalization of living poly(methyl methacrylate) occurred at only 70-80%.[448] Multiple bromine groups were also introduced via end-capping[449,450] to living styrenic and methacrylic polymers. These polymers were further functionalized via the nucleophilic substitution of the polymer-bound bromine atoms. Polymers containing multiple perfluoroalkyl groups at one terminus were used to study the surface-segregation behavior of the fluoroalkyl groups.[451] *Tert*-butylsilyl containing diphenylethylenes were used to terminate the anionic polymerization of styrene. The polymer was converted to the polymer into an atom transfer free-radical polymerization macroinitiator after the functional group was transformed into the *tert*-butylbromo group.[452] This approach was used in the synthesis of poly(alkyl methacrylate-*block*-alkyl acrylate) diblock copolymers.[453] Silylchloride reagents were also used to end-cap living polymers with

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[448] T. Mizawa, K. Takenaka, and T. Shiomi, "Synthesis of Polymers Containing Conjugated Dienyl End-Groups by Means of Anionic Living Polymerization." *J. Polym. Sci. A Polym. Chem.*, **1999**, *37*(17), 3464-3472.

[449] M. Hayashi, K. Kojima, and A. Hirao, "Synthesis of Star-Branched Polymers by Means of Anionic Living Polymerization Coupled with Functional Group Transformation." *Macromolecules*, **1999**, *32*(8), 2425-2433.

[450] A. Hirao and A. Matsuo, "Synthesis of Chain-End-Functionalized Poly(Methyl Methacrylate)s with a Definite Number of Benzyl Bromide Moieties and Their Application to Star-Branched Polymers." *Macromolecules*, **2003**, *26*(36), 9742-9751.

[451] A. Hirao, S. Sakai, and K. Sugiyama, "Synthesis of Well-Defined Chain-End-Functionalized Polystyrenes with Four, Eight, and Sixteen Perfluorooctyl Groups and Their Surface Characterization." *Polym. Adv. Tech.*, **2004**, *15*(1-2), 15-25.

[452] B. Masar, M. Janata, P. Vlcek, P. Policka, and L. Toman, "Tailoring of Polymers by Combination of Ionic and Radical Controlled Polymerizations." *Macromol. Symp.*, **2002**, *183(IUPAC International Symposium on Ionic Polymerization, 2001)*, 139-144.

[453] J.-D. Tong, C. Zhou, S. Ni, and M. A. Winnik, "Synthesis of Meth(Acrylate) Diblock Copolymers Bearing a Fluorescent Dye at the Junction Using a Hydroxyl-Protected Initiator and the Combination of Anionic Polymerization and Controlled Radical Polymerization." *Macromolecules*, **2001**, *34*(4), 696-705.

functional groups. Star-shaped polymers were synthesized when chlorosilane reagents with functional group f > 2 were employed as end-cappers.[454] The degree of functionalization is often limited by the purity of the terminating reagent, and in some cases, the reactivity of the propagating species.

The second method for introducing functional groups to anionically synthesized polymers is via the use of initiators bearing protected functional groups[455] An anionic polymerization initiator utilized to introduce the alcohol functional group is 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium.[456] This initiator was previously used to polymerize a variety of siloxane,[457] styrenic,[458] diene, and methacrylic monomers.[459] Polymerization was followed by acid-catalyzed hydrolytic deprotection of the alcohol group. Anionic polymerization initiators bearing protected functional groups are advantageous relative to end-capping in cases where end-capping is not quantitative. However, functional initiation is less versatile, relative to end-capping, due to the extremely high reactivity of alkyllithium initiators. Protected functional initiators

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[455] R. P. Quirk and S. H. Jang, "Recent Advances in Anionic Synthesis of Functionalized Elastomers Using Functionalized Alkyllithium Initiators." *Rubber Chem. Technol.*, **1996**, *69*(3), 444-461.

[456] J. A. Schwindeman, R. J. Letchford, E. J. Granger, and R. P. Quirk, "Functionalized Initiators for Anionic Polymerization, Protected Functionalized Polymers, Deprotected Analogues Thereof, and Methods of Making the Same." *US* 6,720,391, **1994**.

[457] C. L. Elkins and T. E. Long, "Living Anionic Polymerization of Hexamethylcyclotrisiloxane (D_3) Using Functionalized Initiation." *Macromolecules*, **2004**, *37*(17), 6657-6659.

[458] D. N. Schulz, A. F. Halasa, and A. E. Oberster, "Anionic Polymerization Initiators Containing Protected Functional Groups and Functionally Terminated Diene of Polymers." *J. Polym. Sci., Polym. Chem. Ed.*, **1974**, *12*(1), 153-166.

[459] R. P. Quirk, J.-J. Ma, G. Lizarraga, Q. Ge, H. Hasegawa, Y. J. Kim, S. H. Jang, and Y. Lee, "Anionic Synthesis of Hydroxy-Functionalized Polymers Using Functionalized Initiators and Electrophilic Termination." *Macromol. Symp.*, **2000**, *61(Controlled Synthesis of Functionalized Polymers)*, 37-44.

typically react slowly with their protected functional groups, drastically limiting the initiator shelf-life relative to conventional alkyllithium initiators. Protected functional initiation was used in conjunction with electrophilic termination to produce well-defined polymers bearing telechelic functional groups such as alcohols and amines.[460]

Methacrylic monomers could not be used in anionic polymerization until 1,1-diphenylethylene (DPE) was used to reduce the initiating reactivity of the alkyllithium.[461] Due to its inability to propagate as a homopolymer, DPE was frequently used as either an end-capping reagent or a co-initiator in anionic polymerization, depending on the reactivity of the propagating polymer.[462,463,464,465] Miktoarm star-shaped polymers were synthesized following deprotection of the functional groups that were incorporated into diphenylethylene.[466,467] Multiple variants of 1,1-diphenylethylene were synthesized and

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[460] R. P. Quirk, J. Yin, S. H. Guo, X. W. Hu, G. Summers, J. Kim, L. F. Zhu, and L. E. Schock, "Anionic Synthesis of Chain-End Functionalized Polymers." *Makromol. Chem., Macromol. Symp.*, **1990**, *32(Invited Lect. Int. Symp. Cationic Polym. Relat. Ionic Processes, 9th, 1989),* 47-59.

[461] D. M. Wiles and S. Bywater, "Polymerization of Methyl Methacrylate Initiated by 1,1-Diphenylhexyl Lithium." *Trans. Faraday Soc.*, **1965**, *61*(1), 150-158.

[462] R. P. Quirk, J. Yin, S. H. Guo, X. W. Hu, G. J. Summers, J. Kim, L. F. Zhu, J. J. Ma, T. Takizawa, and T. Lynch, "Recent advances in anionic synthesis of functionalized polymers." *Rubber Chem. Technol.*, **1991**, *64*(4), 648-660.

[463] A. Hirao and S. Nakahama "Recent developments in anionic living polymerization." *Trend. Polym. Sci.*, **1994**, *2*(8), 267-271.

[464] A. Hirao, M. Hayashi, and N. Haraguchi, "Synthesis of Well-Defined Functionalized Polymers and Star Branched Polymers by Means of Living Anionic Polymerization Using Specially Designed 1,1-Diphenylethylene Derivatives." *Macromol. Rapid Comm.*, **2000**, *21*(17), 1171-1184.

[465] R. P. Quirk, T. Yoo, Y. Lee, J. Kim, and B. Lee, "Applications of 1,1-Diphenylethylene Chemistry in Anionic Synthesis of Polymers with Controlled Structures." *Adv. Polym. Sci.*, **2000**, *153(Biopolymers, PVA Hydrogels Anionic Polymerisation Nanocomposites)*, 67-102.

[466] P. Dumas, C. Delaite, and G. Hurtrez, "Synthesis of Well-Defined Star Block Copolymers Using 1,1-Diphenylethylene Chemistry." *Macromol. Symp.*, **2002**, *183(IUPAC International Symposium on Ionic Polymerization, 2001)*, 29-33.

employed in the synthesis of poly(alkyl methacrylate)s when used as a co-initiator with *sec*-butyllithium. For example, 1-[4-(4-methylene-5-hexenyl)-phenyl]-1-phenylethylene, which contains a 1,3-butandienyl group was used to either initiate the polymerization of MMA or terminate the polymerization of styrene.[468] The diene functional groups were then readily converted into either anhydride or epoxy functional groups. DPE was also functionalized with glucose, followed by the initiation of anionic polymerization of various alkyl methacrylates.[469] The ability of a bismethoxy containing DPE to initiate anionic polymerization of alkyl methacrylates depended significantly on the placement of the methoxy groups on the phenyl rings.[470] This impact was due to the destabilization of the carbanion by the methoxy functional group.

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[467] M. Nasser-Eddine, S. Reutenauer, C. Delaite, G. Hurtrez, and P. Dumas, "Synthesis of Polystyrene-Poly(*Tert*-Butyl Methacrylate)-Poly(Ethylene Oxide) Triarm Star Block Copolymers." *J. Polym. Sci. A Polym. Chem.*, **2004**, *42*(7), 1745-1751.

[468] N. Haraguchi, Y. Sakaguchi, K. Sugiyama, and A. Hirao, "Synthesis of Functionalized Polymers by Means of Living Anionic Polymerization, 2A: Synthesis of Well-Defined Chain-End and in-Chain Functionalized Polymers with 1,3-Butadienyl Groups." *Macromol. Chem. Phys.*, **2001**, *202*(11), 2221-2230.

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[470] A. Hirao, Y. Negishi, M. Hayashi, K. Sako, S. W. Ryu, S. Loykulnant, A. Matsuo, and K. Sugiyama, "Living Anionic Polymerization of Monomers with Functional Groups. 15. Anionic Polymerization and Reaction of Styrene and 1,1-Diphenylethylene Derivatives Substituted with Alkoxymethyl Groups." *Macromol. Chem. Phys.*, **2001**, *202*(18), 3590-3605.

The DPE variant 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene was used to synthesize polymers containing a terminal bisphenol functional group.[471] This compound was used to initiate the polymerization of MMA, resulting in a well-defended macromonomer that was copolymerized with isophthaloyl chloride and azelaoyl chloride to yield graft polycarbonates that exhibited tunable glass transition temperatures, based on the backbone composition.[472] 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene-endcapped polystyrene was also functionalized with multiple perfluorooctyl functional groups.[473,474] These functional groups underwent microphase-separation from the polystyrene domain, aggregating of the surface and drastically raising water contact angles.

In this study, the novel protected aliphatic diol-containing 1,1-bis-4,4'-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene was synthesized utilizing a high-yield multi-step methodology. The advantage of BTOPE over the protected bisphenol DPE is that it the aliphatic diol makes it suitable as a co-monomer in the polycondensation reaction of polyesters. Although PMMA containing a single aliphatic alcohol was

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[471] R. P. Quirk and Y. Wang, "Anionic Difunctionalization with 1,1-Bis(4-Tert-Butyldimethyl-siloxyphenyl)ethylene. Synthesis of ω,ω-Bis(Phenol)-Functionalized Polystyrene Condensation Macromonomers." *Polym. Int.*, **1993**, *31*(1), 51-59.

[472] T. E. Long, R. D. Allen, L. J. Sorriero, B. A. Schell, and D. M. Teegarden, "Synthesis of Polyester Graft Copolymers Via the Macromonomer Technique: Application of near-IR Spectroscopy as a Process Monitor." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.),* **1996**, *37*(2), 678-679.

[473] A. Hirao, G. Koide, and K. Sugiyama, "Synthesis of Novel Well-Defined Chain-End- and in-Chain-Functionalized Polystyrenes with One, Two, Three, and Four Perfluorooctyl Groups and Their Surface Characterization." *Macromolecules*, **2002**, *35*(20), 7642-7651.

[474] A. Hirao, S. Sakai, and K. Sugiyama, "Synthesis of Well-Defined Chain-End-Functionalized Polystyrenes with Four, Eight, and Sixteen Perfluorooctyl Groups and Their Surface Characterization." *Polym. Adv. Tech.,* **2004**, *15*(1-2), 15-25.

reported in the literature,[475] BTOPE was not synthesized previously. The improved nucleophilicity of the aliphatic diol was expected to make BTOPE containing polymers suitable for the initiation of lactide ring-opening polymerizations and the solution polymerization of polyesters.

9.3 Experimental

9.3.1 Materials

4,4'-dihydroxybenzophenone (TCI America, 98%), ethylene carbonate (Aldrich, 97%), potassium carbonate (EM Science, 99%), *tert*-butylsilyl chloride (Aldrich, 98%), potassium *tert*-butoxide (TCI America, 98%), methyltriphenylphosphonium bromide (TCI America, 99%), N_2 (Air Products, 99.999%), and *sec*-butyllithium (FMC Lithium Division, 1.78 M) were used without further purification. Methyl methacrylate (MMA, Aldrich, 99%), was dried over CaH_2 (Aldrich, 95%) and vacuum distilled (0.08 mm Hg). MMA was then treated with triethylaluminum (Aldrich, 1.6 M) and distilled under vacuum (0.08 mm Hg).[476,477] THF (Burdick & Jackson, HPLC) was stirred over sodium (Aldrich, lump) and benzophenone (Aldrich, 99%), and distilled under nitrogen. Pyridine (Aldrich, 99%) was distilled under N_2.

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[475] M. Ohata and Y. Isono, "Preparation of ω-Hydroxy-ω-Carboxy-Poly(Methyl Methacrylate) by Anionic Polymerization. 1. Utilization of Initiator Derived from 1-[4-(2-*Tert*-Butyldimethylsiloxy)Ethyl]Phenyl-1-Phenylethylene." *Polymer*, **1993**, *34*(7), 1546-1548.

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9.3.2 Instrumentation

^{1}H and ^{13}C NMR spectra were obtained using a Varian Unity spectrometer operating at 400 and 100 MHz, respectively. Deuterated dichloromethane (Cambridge Isotope Laboratories) was used as the solvent, and spectra were obtained at 23 °C. A Waters 717plus Autosampler coupled to a Waters 2410 refractive index detector was used to determine polymer molecular weights. SEC measurements were performed in THF at 40 °C at a flow rate of 1.0 mL/min. Absolute molecular weights were determined using a Wyatt Technology miniDAWN® static three-angle laser light scattering detector (MALLS). Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C / min under nitrogen. Glass transition temperatures are reported as the midpoints of the changes in heat capacity during the second heat. In-situ reaction FTIR analysis was performed using an ASI Applied Systems ReactIR 1000 attenuated total reflectance reaction apparatus equipped with a light conduit and DiComp (diamond composite) insertion probe.

9.3.3 Synthesis of 4,4'-bis(2-hydroxyethoxy)benzophenone

4,4'-Dihydroxybenzophenone (30.0g, 141 mmol), ethylene carbonate (37.3 g, 424 mmol) and 420 mL DMSO (Aldrich, 99.8%) were added to a 500 mL 2-necked flask fitted with a reflux condenser and an N_2 purge. After magnetic stirring for 1 h, potassium carbonate (46.9 g, 339 mmol) was added, and the mixture was heated to 120 °C. The reaction proceeded for 8 hours followed by quenching in 500 mL 3M NaOH solution. The precipitate was filtered and washed with 750 mL 10% HCl solution. After filtration, the product was dried in vacuo at ~85 °C overnight.

9.3.4 Synthesis of 4,4'-bis-(2-(*tert*-butyldimethylsilyloxy)ethoxy)benzophenone

4,4'-bis(2-hydroxyethoxy)benzophenone (13.03 g, 43.39 mmol) was dissolved in 155 mL pyridine and cooled to 0 °C under N_2. *tert*-Butyldimethylsilyl chloride (15.04 g, 99.8 mmol) was dissolved in pyridine (80 mL) and introduced to the reactor via an addition funnel over 10 minutes. The reaction was allowed to proceed to 3 h while slowly warming to room temperature. The crude reaction mixture was precipitated in a mixture of 500 mL 0.5 M HCl and ice. Following precipitation, the product was extracted twice with dichloromethane. The organic layers were combined and condensed to approx. 50 mL. This solution was purified via silica chromatography, utilizing dichloromethane as the mobile phase, to produce pure product in 95% yield.

9.3.5 Synthesis of 1,1'-bis-4-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene and in-situ monitoring of reaction

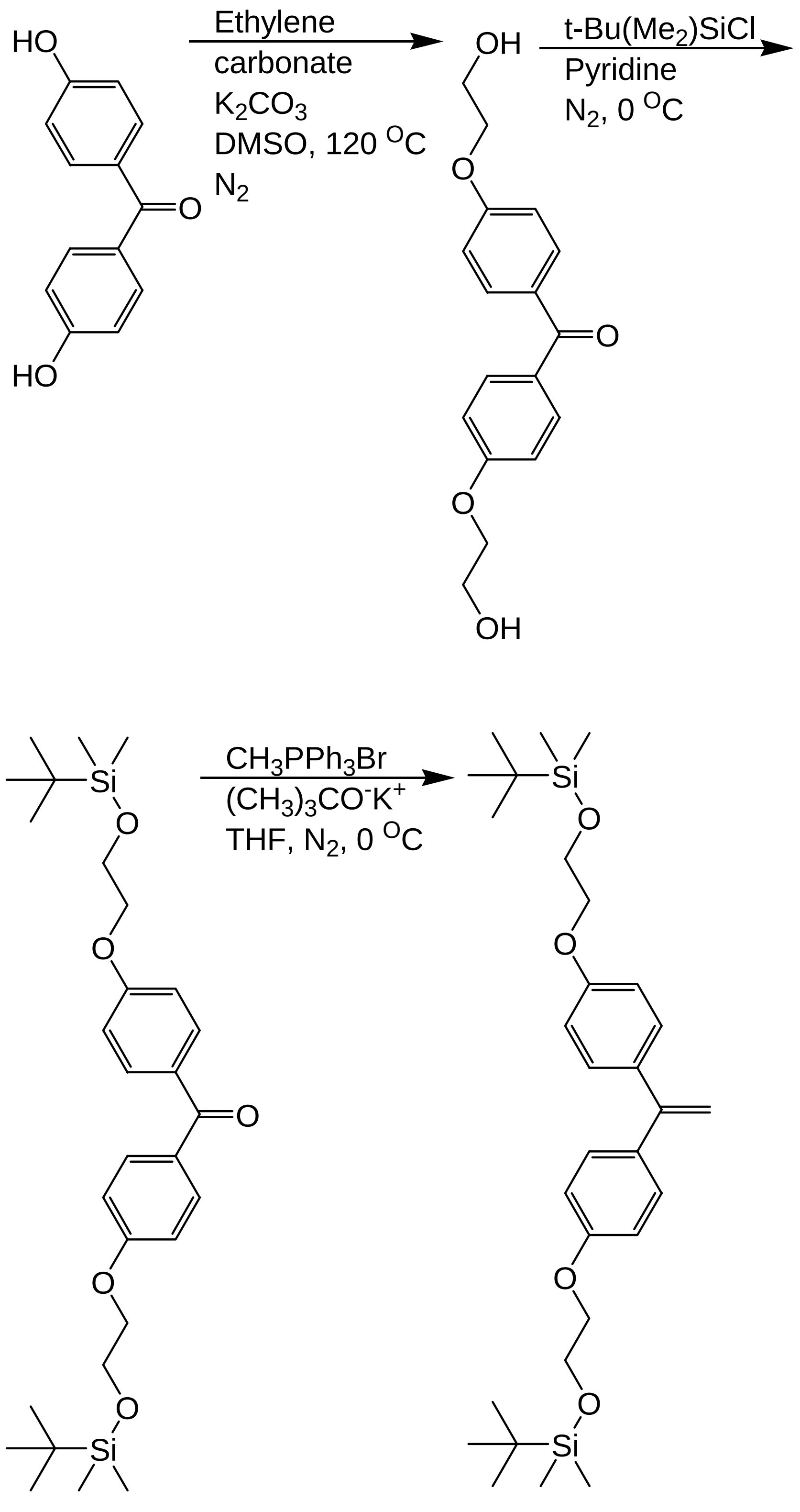
The reducing ylide was generated via the combination of potassium *tert*-butoxide (4.02 g, 35.8 mmol) and methyltriphenylphosphonium bromide (10.1 g, 28.3 mmol) into 20 mL THF cooled to 0 °C in a 50 mL round-bottomed flask. A three-necked 100 mL round-bottomed flask was fitted with a DiComp probe. 4,4'-bis-(2-(*tert*-butyldimethylsilyloxy)ethoxy) benzophenone (10 g, 18.8 mmol) was dissolved in 200 mL THF and cooled to 0 °C. The ylide was injected and an IR spectrum was collected every 2 min. The reaction was allowed to proceed for 3 hours and was terminated by precipitation into ice-cold 0.5 M HCl. BTOPE was then purified via 2X silica column chromatography using dichloromethane as the mobile phase.

9.3.6 Polymerization of MMA initiated via sBuLi and BTOPE

A 100 mL round-bottomed flask was flame-dried under N_2 purge, followed by the cannulation of ultrapure THF (60 mL) into the reactor and cooling to -78 °C. BTOPE was syringed into the reactor, followed by slow titration using *sec*-butyl lithium until the persistence of a deep-red color. The pre-determined amount of *sec*-butyl lithium (1.26 mL, 2.5 mmol) was subsequently injected. MMA (10 mL, 93.89 mmol) was syringed slowly into the reactor and polymerization was allowed to proceed for 30 min. Termination was achieved via the addition of 1 mL degassed methanol. The polymer was precipitated into a 9:1 methanol: water solution and vacuum-dried at 85 °C overnight. The polymer samples were subjected to Soxhlet extraction using methanol for three days in order to remove BTOPE that was terminated during titration. The purified polymer was vacuum-dried overnight at 85 °C.

9.3.7 Hydrolytic Deprotection of BTOPE PMMA.

Hydrolysis was conducted in a 50 mL round-bottomed flask containing 40 mL THF. 10 mL 1 M aq. HCl acid was added, followed by the dissolution of 5.0 g BTOPE poly(methyl methacrylate). The round-bottomed flask was fitted with a reflux condenser, and the reaction was carried out under a nitrogen atmosphere. The flask was then heated to reflux (65 °C) for 12 hours. The hydrolyzed polymer was precipitated into a 9:1 mixture of methanol and water.



Scheme 9.1: BTOPE was synthesized from 4,4'dihydroxybenzophenone following three high-yield steps.

9.4 Results and Discussion

9.4.1 BTOPE Synthesis

BTOPE was synthesized starting from 4,4’-dihydroxybenzophenone in three high-yield reactions (Scheme 9.1). The starting bisphenol was converted to the bisphenoxide using potassium carbonate and reacted with ethylene carbonate to synthesize 4,4’-bis(2-hydroxyethoxy)benzophenone [DHB] in high yields. Product structure was verified using ^{1}H NMR (Figure 9.1). The product resonances corresponded to their expected assignments. The phenyl resonances shifted from 6.9 and 7.6 ppm to 7.0 and 7.7 ppm in the product, following conversion of the phenol to the phenyl ether. Additionally, new resonances appeared at 3.9 and 4.0 ppm, corresponding to the α-ether and α-alcohol methylene protons, respectively. The phenol resonance at 10.2 ppm disappeared and was replaced by an aliphatic alcohol resonance at 4.0 ppm.

Following purification, DHB was dissolved in pyridine, which was the only solvent found that was suitable for the dissolution of large quantities. Protection of the alphatic diol functional group was achieved via coupling of DHB with *tert*-butyldimethylsilyl chloride. The relatively high hydrolytic stability of this protecting group enabled the precipitation of the product into cold dilute HCl. High product yields following extraction and silica column chromatography. The ^{1}H NMR spectrum of this product exhibited new resonances at 0.0 and 0.8 ppm, corresponding to the dimethylsilyl and *tert*-butylsilyl groups, respectively (Figure 9.2).

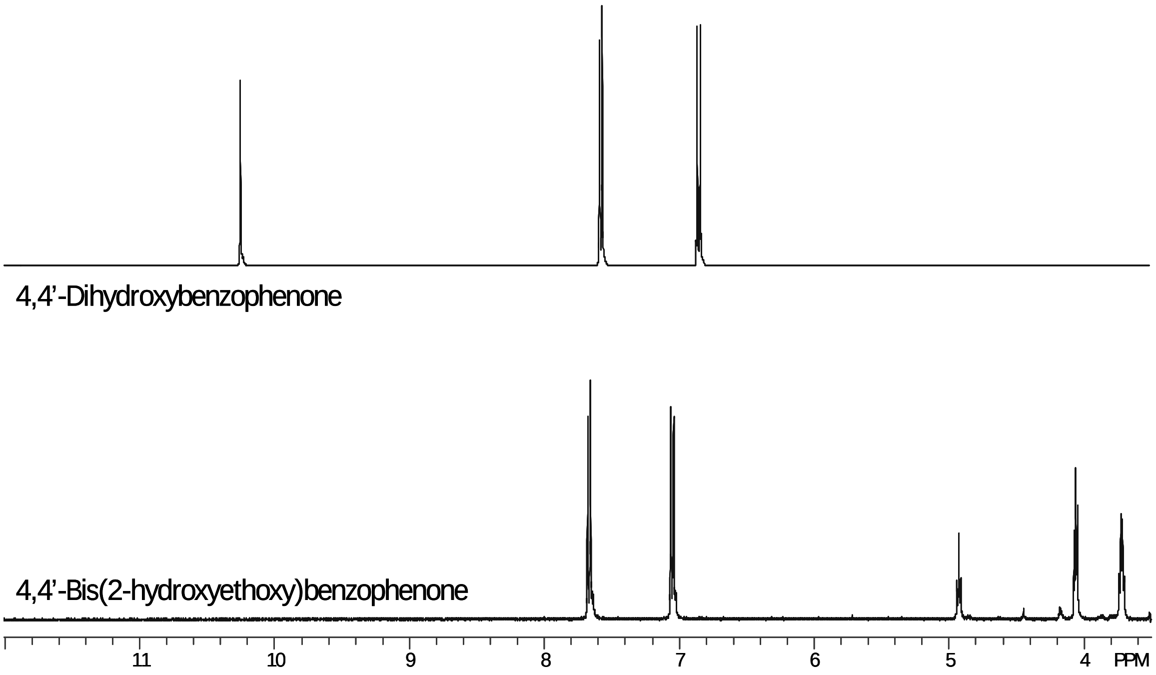


Figure 9.1: The ^{1}H NMR spectra of 4,4'-dihydroxybenzophenone and 4,4'-bis(2-hydroxyethoxy)benzophenone indicate the change from the phenol to the 2-hydroxyethoxy functional group.

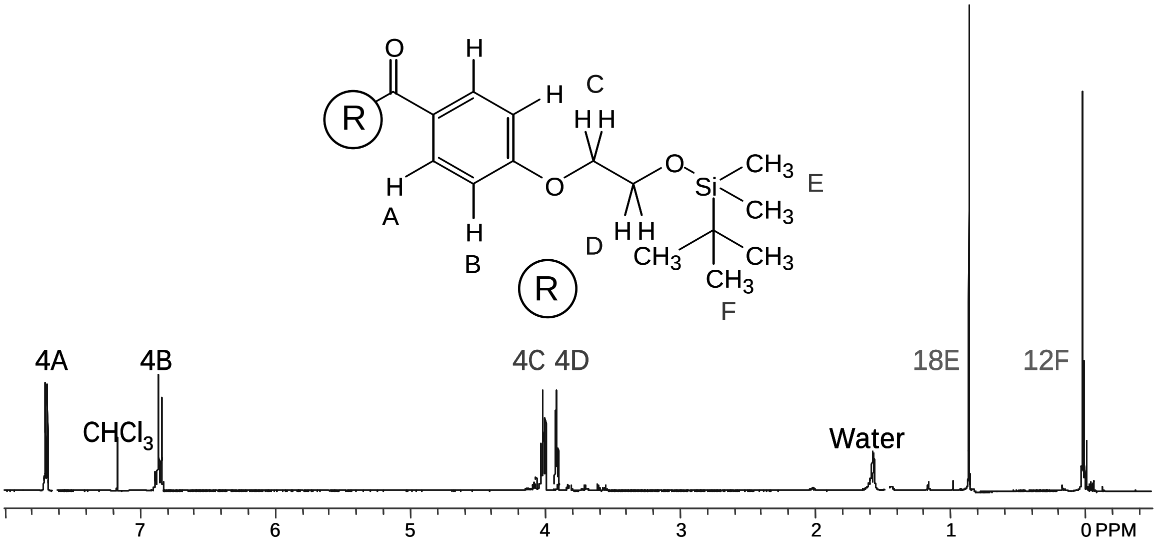


Figure 9.2: The *tert*-butyldimethylsilyl protecting group was present in the ^{1}H NMR spectrum of the product from the reaction of DHB with *tert*-butyldimethylsilyl chloride.

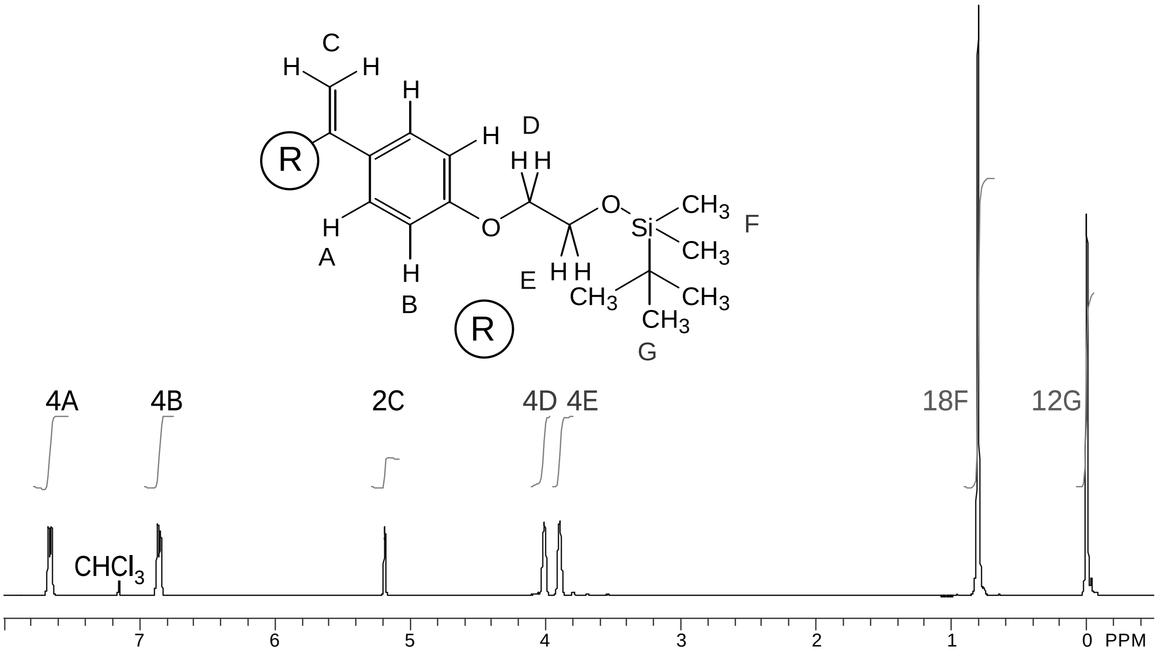


Figure 9.3: The ^{1}H NMR spectrum of BTOPE indicated good agreement with the expected assignments.

The Wittig reaction was performed on the protected benzophenone using the ylide that was generated in situ from methyl triphenylphosphonium bromide and potassium *tert*-butoxide. The conversion of the benzophenone functional group to the diphenylethylene was evidenced by the appearance of the benzylic olefin resonance at 5.2 ppm in the product ^{1}H NMR spectrum (Figure 9.3). This reaction was probed using in-situ infrared spectroscopy to ascertain whether the relatively high reaction times reported in the literature were necessary to achieve complete conversion.[478] During the reaction, an infrared spectrum was measured every two minutes, and the progression of the reaction was followed via both the disappearance of the C=O stretch at 1650 cm^{-1} as well as the appearance of the benzophenone olefin C-H wag at 721 cm^{-1} (Figure 9.4). It was concluded that the reaction required only 90 minutes at 0 °C, based on the fact that the normalized absorptions of both functional groups reached their limiting values at that point (Figure 9.5). The reaction kinetics did not conform to the expected 2nd order model due to the presence of a large excess of ylide was used to drive the reaction to completion. Mass spectroscopy of BTOPE was not possible due to the thermal instability of the *tert*-butylsilyl protecting groups.

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[478] C. B. McArdle, J. Burke, J. G. Woods, and E. K. Welch, Jr., "A Method of Forming High-Temperature Resistant Polymers." *EP* 490588, **1992**.

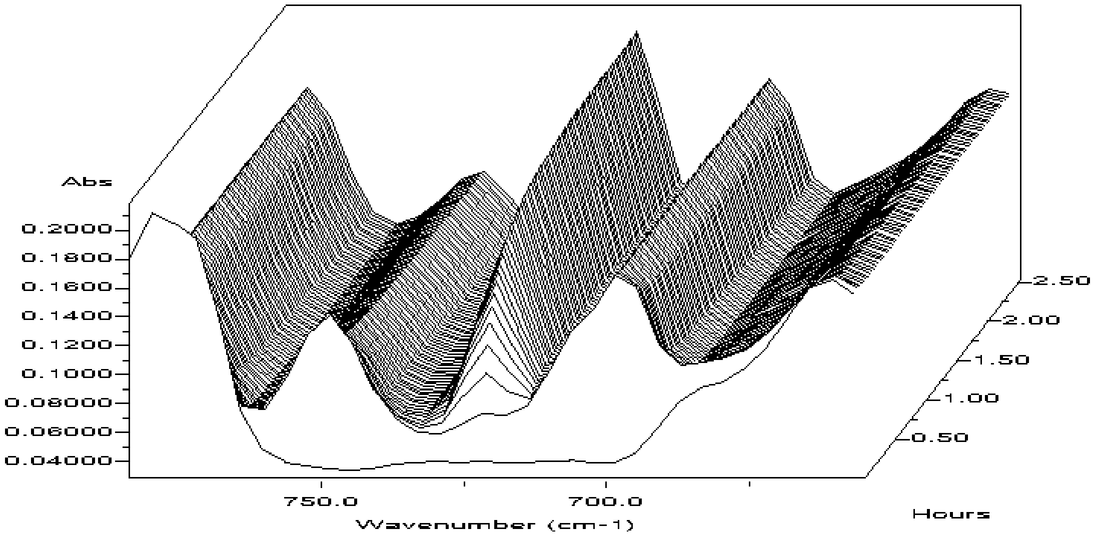


Figure 9.4: A waterfall IR plot shows the appearance of an IR absorbance at 751 cm^{-1} (olefin C-H wag) as the Wittig reaction proceeded.

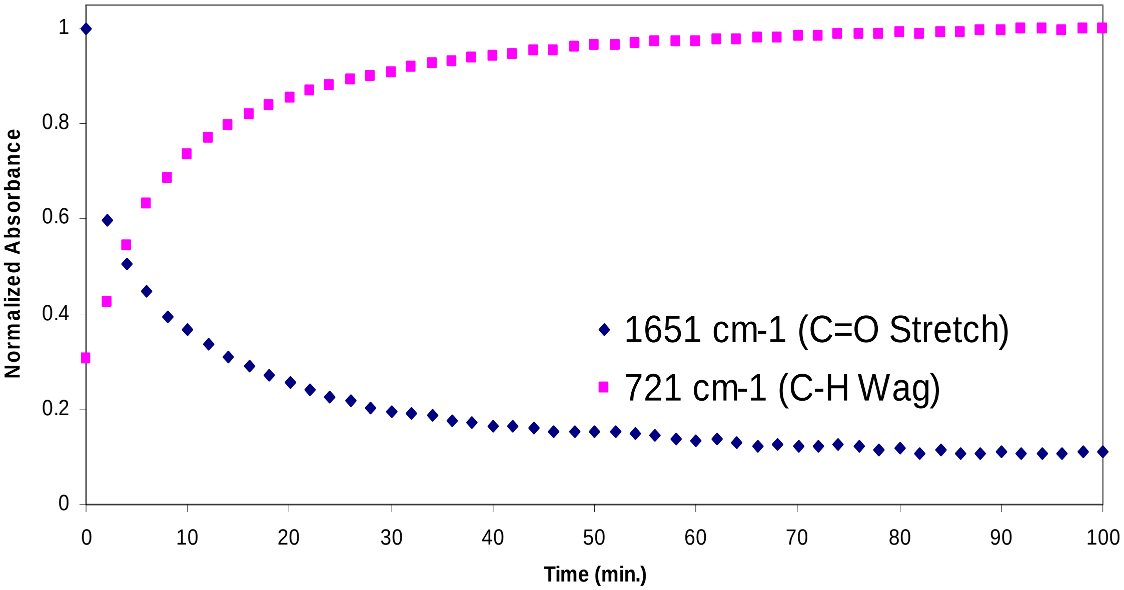
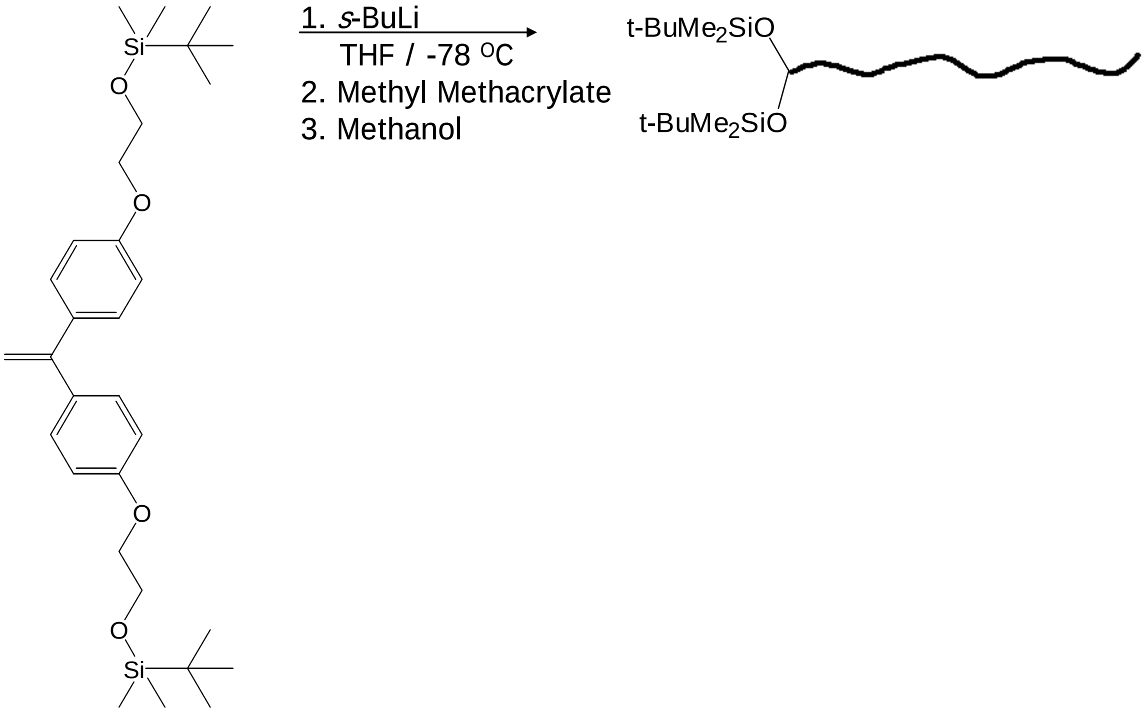


Figure 9.5: Examination of the Wittig reaction kinetics revealed complete conversion after 90 minutes based on both the appearance of the C-H wag (751 cm^{-1}) and the disappearance of the ketone stretch (1651 cm^{-1}).



Scheme 9.2: After coupling with *sec*-butyllithium, BTPOPE initiated the living anionic polymerization of methyl methacrylate.

9.4.2 Protected Functional Initiation with BTOPE

The addition of *sec*-butyllithium to BTOPE resulted in an initiator that exhibited a much deeper red color than the color observed with diphenylhexyllithium. Rapid initiation of MMA occurred in THF at -78 °C (Scheme 9.2). The anionic polymerizations of MMA resulted in quantitative yields and moderate molecular weight control. Due to the high molecular weight of BTOPE, a peak was observed in the SEC trace corresponding to the BTOPE that was consumed during titration of the reactor. The presence of this lower molecular weight fraction in the polymer samples necessitated Soxhlet extraction of the polymer using methanol for three days. The extraction completely removed the unreacted BTOPE from the polymer sample (Figure 9.6). For the molecular weight range synthesized, very narrow to moderately narrow molecular weight distributions were observed in all cases (Table 9.1). The BTOPE-PMMA exhibited a T_g that was similar to the T_g of PMMA initiated using DPE (105 °C)

Table 9.1: Molecular weight data for the broad molecular weight range of BTOPE PMMA synthesized.

NMR M_n	GPC M_n	GPC M_w	M_w / M_n
9,380	9,150	10,000	1.09
13,800	14,000	15,800	1.12
18,700	18,500	19,100	1.03
N/D	25,000	26,800	1.07
N/D	44,500	54,100	1.22
N/D	63,600	71,000	1.12

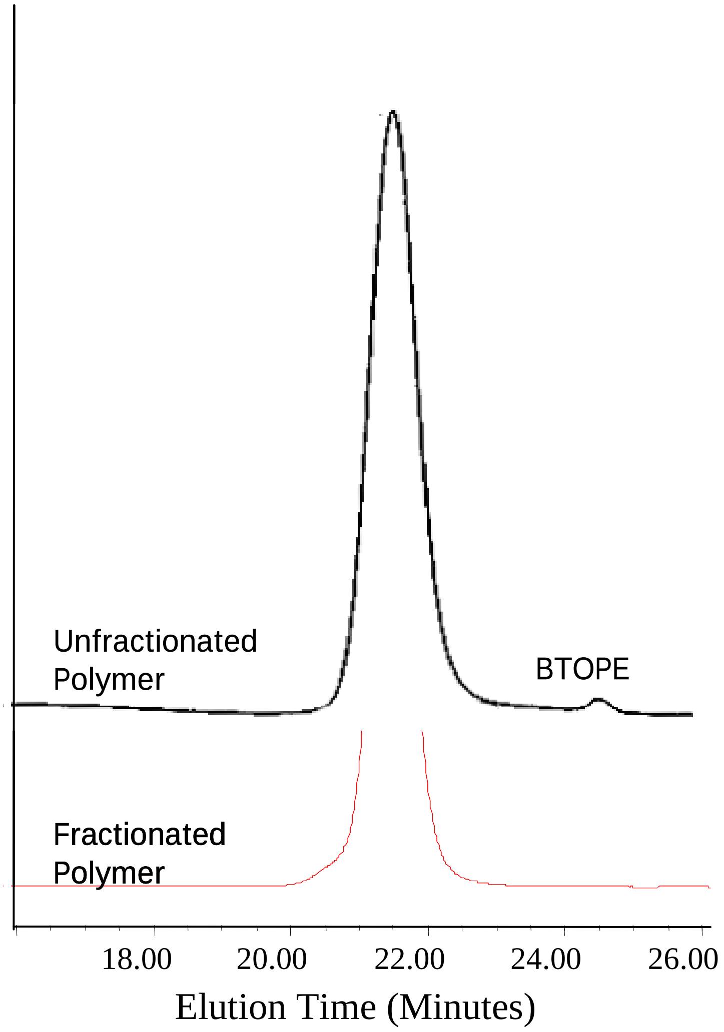
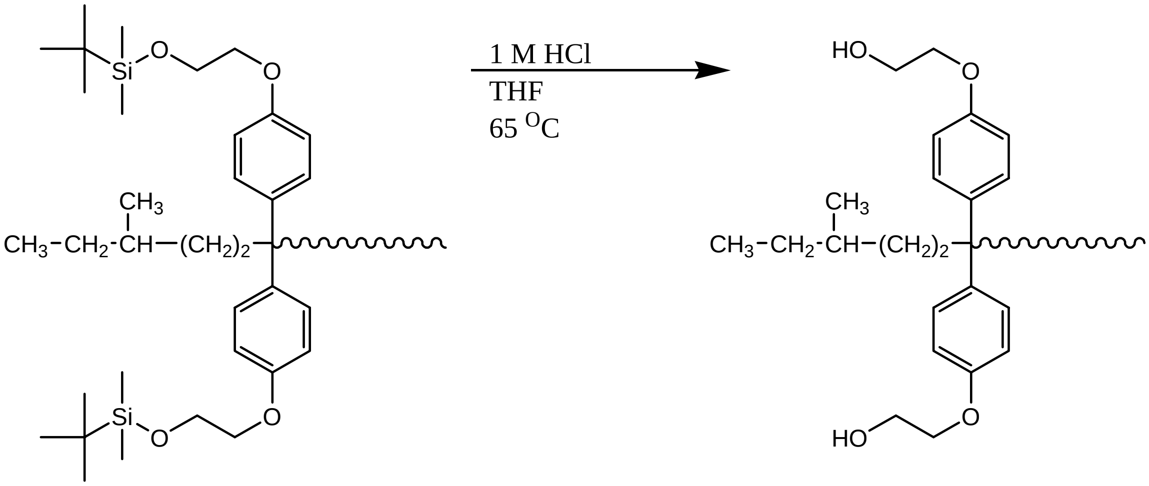


Figure 9.6: SEC traces of the BTOPE PMMA polymer sample before and after Soxhlet extraction with methanol indicated complete removal of terminated BTOPE.



Scheme 9.3: The aliphatic diol functional group in BTOPE PMMA was deprotected via acid-catalyzed hydrolysis.

Deprotection to the alcohol groups in BTOPE-PMMA was achieved using dilute acid in THF at 65 °C (Scheme 9.3). The reaction went to completion, as evidenced by ^{1}H NMR spectroscopy. Complete removal of the protecting groups resulted in the loss of the resonances of 0.0 and 0.8 ppm, corresponding to the removal of the *tert*-butyldimethylsilyl protecting group (Figure 9.7). This verification was not possible for the BTOPE PMMA with an $<M_n>$ = 65,000 due to the fact that the protecting group ^{1}H NMR resonances was not observed in the starting material. The T_g and polymer molecular weights did not change as a result of the removal of the *tert*-butyldimethyl silyl groups. The acid-catalyzed deprotection of BTOPE PMMA did not influence polymer molecular weights, as evidenced by SEC. For example, the polymer of $<M_n>$ = 18,500 Exhibited a molecular weight of 17,200 after hydrolysis, which fell within the 10% error expected for SEC. Hydrolytic removal of the *tert*-butyldimethylsilyl protecting groups did not impact the T_g for the molecular weight range synthesized.

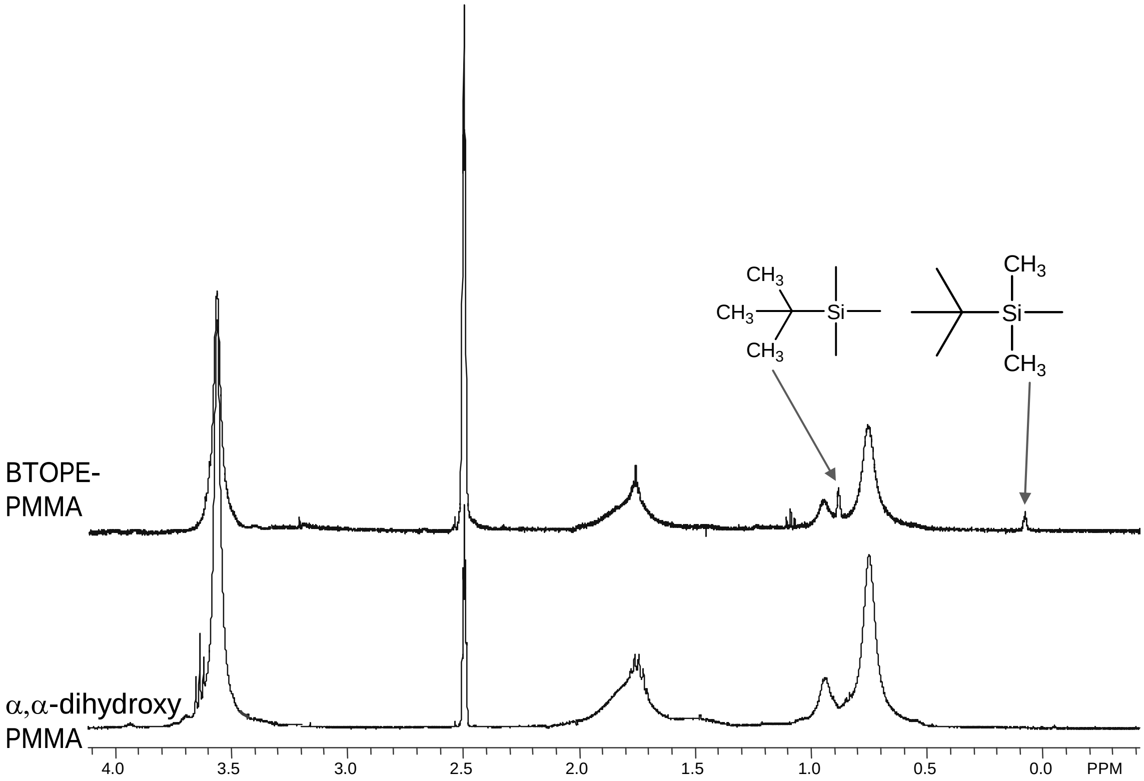


Figure 9.7: The removal of the *tert*-butyldimethylsilyl protecting groups from the PMMA terminus was evidenced by ^{1}H NMR.

Multiple attempts were made to copolymerize α,α-dihydroxy PMMA with isophthaloyl chloride and ethylene glycol under a variety of conditions. The polymerizations were carried out in either dichloromethane or neat, with or without triethylamine, and either at 0 °C or 100 °C. The poor incorporation of the macromonomer was attributed to the molecular weight of the macromonomer, which was much higher than those typically employed in macromonomers. High molecular weight macromonomers result in very low molar concentrations, hindering incorporation into graft copolymers.

9.5 Conclusions

BTOPE was synthesized from 4,4'-dihydroxybenzophenone in three high-yield synthetic steps. The structures of the synthetic intermediates were verified using ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. The Wittig reaction utilized in the conversion of the benzophenone to the olefin was complete after 90 minutes based on in-situ IR spectroscopy, which was three times faster than the reaction times that were typically employed. After coupling with *sec*-butyllithium, BTOPE initiated the anionic polymerization of MMA as well as diphenylhexyllithium, based on the molecular weight distributions of the product polymers. A molecular weight range of $\langle M_n \rangle$ = 10,000 to $\langle M_n \rangle$ = 70,000 was synthesized in THF at -78 °C without a loss in polymerization control at higher molecular weights. Titrated BTOPE was successfully removed from the product polymer via Soxhlet extraction using methanol. The diol protecting groups were quantitatively removed via acid-catalyzed hydrolysis at elevated temperatures. Despite the difficulty of incorporating α,α-dihydroxy PMMA into polyester graft copolymers, this problem was not attributed to any limitations of the macromonomer.

9.6 Acknowledgements

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Chapter 10 : Effect of Controlled Ionic Domain Placement on Styrenesulfonate-Containing Graft Copolymers

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10.1 Abstract

Poly(methyl methacrylate) graft copolymers containing poly(styrene-*block*-*tert*-butyl styrene) graft chains were synthesized and the styrene blocks were selectively sulfonated using acetyl sulfate. Anionic polymerization was used to synthesize poly(styrene-*block*-*tert*-butyl styrene) diblock copolymers, followed by end-functionalization with ethylene oxide. Poly(*tert*-butyl styrene-*block*-styrene) alcohol diblock copolymers were synthesized exhibiting similar molecular weight and molecular weight distributions. Extremely narrow molecular weight distributions were observed in the diblock copolymers regardless of block order. Graft macromonomers were synthesized in quantitative yield when the diblock alcohol was reacted with an excess of methacryloyl chloride. Solution free-radical copolymerization led to graft copolymers containing high-molecular weight graft chains. Two types of graft copolymers were synthesized. Depending of the graft macromonomer, styrenic blocks were placed either near the main chain or at the ends of the graft chains. The styrene blocks were selectively sulfonated using acetyl sulfate, leading to the formation of directed sulfonated domains on the graft copolymers.

Keywords: *tert*-butyl styrene, sulfonation, anionic polymerization, functionalization, graft copolymer.

10.2 Introduction

Ionic functional groups bonded to polymers aggregate strongly, leading to significantly stronger mechanical properties compared the same polymer lacking the ionic groups. However, if the ionic content becomes too high, the material becomes intractable, making processing impossible. Styrenesulfonate containing butadiene[479,480] and methacrylic[481,482,483] copolymers were previously synthesized using the monomer sodium styrenesulfonate. These ionic containing polymers exhibited significantly greater storage moduli and stress-strain behaviors relative to the nonionic counterparts. Sulfonate functional groups could also be introduced following polymerization. Selective sulfonation was performed previously on well-defined star macromolecules. Styrene blocks contained in polybutadiene star polymers were sulfonated quantitatively using acetyl sulfate.[484] *Tert*-butyl styrene cannot undergo sulfonation due to the steric bulk of the *tert*-butyl group. Styrene repeat units were selectively sulfonated in the

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[479] R. A. Weiss, R. D. Lundberg, and A. Werner, "The Synthesis of Sulfonated Polymers by Free Radical Copolymerization. Poly(Butadiene-*co*-Sodium Styrene Sulfonate)." *J. Polym. Sci. A Polym. Chem.*, **1980**, *18*(12), 3427-3439.

[480] R. A. Weiss, L. A. Pottick, and C. L. Willis, "Block Copolymer Ionomers: 2. Viscoelastic and Mechanical Properties of Sulfonated Poly(Styrene-Ethylene/Butylene-Styrene)." *Polymer*, **1991**, *32*(15), 2785-2792.

[481] R. D. Lundberg and J. E. McGrath, "Sulfonated Copolymers or Terpolymers." *EP* 82-305269, **1983**.

[482] I. Yilgor, K. A. Packard, J. Eberle, E. Yilgor, R. D. Lundberg, and J. E. McGrath, "Ion-Containing Polymers. I. Alkyl Acrylate-Sulfonated Styrene Copolymers by Emulsion Copolymerization." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.),* **1983**, *24*(2), 37-38.

[483] R. D. Allen, I. Yilgor, and J. E. McGrath, "Studies on the Synthesis of Novel Block Ionomers." *ACS Symp. Ser.*, **1986**, *302(Coulombic Interact. Macromol. Syst.),* 79-92.

[484] R. F. Storey, S.E. George, and M. E. Nelson, "Star-Branched Block Copolymer Ionomers: Synthesis, Characterization, and Properties." *Macromolecules*, **1991**, *24*(10), 2920-2930.

presence of unreactive repeat units including *tert*-butyl styrene and hydrogenated dienes. Amphiphilic poly(*tert*-butyl styrene)-*block*-poly(styrene) diblock copolymers were prepared previously via living anionic polymerization followed by sulfonation.[485,486,487]

The use of living polymerization enables the functionalization of the polymer chain by end-capping.[488] End-capping was used extensively to either introduce a terminal functional group to a living polymer[489,490] or to synthesize branched polymer topologies.[491] The end capping of PMMA by a cyclic anhydride[492] was an improvement over a prior synthetic route to the functionalized polymer, which was hampered by thermal degradation of the polymer. It was also possible to synthesize graft polymers through this modification.[493] By capping the growing poly (*t*-butyl acrylate) chain with acryloyl chloride, a macromonomer resulted which was copolymerized with methyl

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[485] J. Bock, R. M. Kowalik, and P. L. Jr. Valint, "Water-Soluble Block Polymers." *EP* 114525, **1984**.

[486] P. L. Valint, Jr. and J. Bock, "Synthesis and Characterization of Hydrophobically Associating Block Polymers." *Macromolecules,* **1988**, *21*(1), 175-179.

[487] J. Yang and J. W. Mays, "Synthesis and Characterization of Controlled Architecture Ionic/Neutral Block Copolymers." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.),* **2000**, *41*(2), 1523-1524.

[488] M. A. Peters, A. M. Belu, R. W. Linton, L. Dupray, T. J. Meyer, and J. M. DeSimone, "Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers." *J. Am. Chem. Soc.*, **1995**, *117*(12), 3380-3388.

[489] K. Hayashi and C. S. Marvel, "α,ω-Glycols and Dicarboxylic Acids from Butadiene, Isoprene, and Styrene and Some Derived Block Polymers, Esters, and Urethans." *J. Poly. Sci. A- Gen. Pap.*, **1964**, *2*(6), 2571-2594.

[490] R. P. Quirk, J. Yin, S. H. Guo, X. W. Hu, G. Summers, J. Kim, L. F. Zhu, and L. E. Schock, "Anionic Synthesis of Chain-End Functionalized Polymers." *Makromol. Chem., Macromol. Symp.*, **1990**, *32(Invited Lect. Int. Symp. Cationic Polym. Relat. Ionic Processes, 9th, 1989),* 47-59.

[491] A. Hirao and M. Hayashi, "Recent Advance in Syntheses and Applications of Well-Defined End-Functionalized Polymers by Means of Anionic Living Polymerization." *Acta Polymerica*, **1999**, *50*(7), 219-231.

[492] I. Fallais, N. Pantoustier, J. Devaux, C. Zune, and R. Jerome, "Anionic Synthesis of Cyclic Anhydride End-Capped Poly(Methyl Methacrylate)." *Polymer*, **2000**, *41*(14), 5535-5539.

[493] O. W. Webster, "Living Polymerization Methods." *Science*, **1991**, *251*(4996), 887-892.

acrylate to form a graft copolymer.[494] Poly(Alkyl methacrylate) macromonomers were also synthesized via termination of the propagating methacrylate enolate anion using 4-vinylbenzoyl chloride[495] or allyl bromide.[496]

Living anionic polymerization was utilized in the synthesis of poly(*tert*-butyl styrene)-*block*-poly(styrene) methacrylate macromonomers, which were subsequently copolymerized with methyl methacrylate to form novel graft copolymers. The methacrylate functional group was placed at either the styrene or *tert*-butyl styrene block by changing the order of monomer addition during anionic polymerization. The methacrylate functional group was placed on either block by switching the order of monomer addition. The styrene blocks were selectively sulfonated using acetyl sulfate, leading to sulfonated domains that were controllably placed either at the terminus or the interior of the graft polymer.

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[494] K. Antolin, J.-P. Lamps, P. Rempp, and Y. Gnanou, "Synthesis of Poly (*T*-Butyl Acrylate) Macromonomers." *Polymer*, **1990**, *31*(5), 967-970.

[495] S. D. Smith, "Synthesis of Poly(Methyl Methacrylate) Macromonomers Via Anionic Polymerizations." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **1988**, *29*(2), 48-49.

[496] B. C. Anderson, G. D. Andrews, P. Arthur, Jr., H. W. Jacobson, L. R. Melby, A. J. Playtis, and W. H. Sharkey, "Anionic Polymerization of Methacrylates. Novel Functional Polymers and Copolymers." *Macromolecules*, **1981**, *14*(5), 1599-1601.

10.3 Experimental

10.3.1 Materials.

Styrene (Aldrich, 99%) and *tert*-butyl styrene (Scientific Polymer Products, 95% para), were dried over CaH_2 (Aldrich, 95%) and vacuum distilled (0.08 mm Hg). The monomers were then treated with dibutyl magnesium (Aldrich, 1.0 M) and distilled under vacuum (0.08 mm Hg). THF (Burdick & Jackson, HPLC) was stirred over sodium (Aldrich, lump) and benzophenone (Aldrich, 99%), and distilled under nitrogen. Cyclohexane (Burdick & Jackson, HPLC) was passed through an activated molecular sieve column (Aldrich, 60 Å mesh) and activated alumina column immediately prior to use. Dichloromethane (Burdick & Jackson, HPLC), dichloroethane (Aldrich, 99%), triethylamine (Aldrich, 99%), and acetic anhydride (Aldrich, 98%) were stirred over CaH_2 and distilled under nitrogen. N_2 (Air Products, 99.999%) was used as received. Methacryloyl chloride (Aldrich, 96%) was distilled under N_2 prior to use. Acetyl sulfate was generated via the sequential addition of acetic anhydride (3.8 mL, 41 mmol) and sulfuric acid (1.4 mL, 25 mmol) to a sealed bottle containing dichloroethane (20 mL) at 0 °C.[497,498] Acetyl sulfate was stored under N_2 at -20 °C.

10.3.2 Instrumentation.

^{1}H NMR spectra were obtained using a Varian Unity spectrometer operating at 400 MHz. Deuterated dichloromethane (Cambridge Isotope Laboratories) was used as the solvent, and spectra were obtained at 23 °C. A Waters 717plus Autosampler coupled to a

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[497] J. G. Balas, W. P. Gergen, C. L. Willis, L. A. Pottick, R. Gelles, and R. A. Weiss, "Sulfonated Block Copolymers" *US* 5,239,010, **1993**.

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Waters 2410 refractive index detector was used to determine polymer molecular weights. SEC measurements were performed in THF at 40 °C. Absolute molecular weights were determined using a Wyatt Technology miniDAWN® static three-angle laser light scattering detector (MALLS). Glass transition temperatures were determined using a Perkin-Elmer Pyris 1 DSC at a heating rate of 10 °C/ min under nitrogen. Glass transition temperatures are reported as the midpoints of the changes in heat capacity during the second heat.

10.3.3 Synthesis of γ-hydroxy-poly(*tert*-butyl styrene-*block*-styrene): Method A.

The polymerizations were performed in flame-dried 100 mL round-bottomed reactors. The reactors were cooled to -78 °C, following the addition of 60 mL THF. *Tert*-butyl styrene (10 mL, 8.84 g) was syringed into the reactor followed by titration using *sec*-butyl lithium. *Sec*-butyl lithium (0.70 mL, 0.98 mmol) initiated the polymerization, which was allowed to proceed for 30 minutes. The second block monomer, styrene (1.0 mL, 0.94 g), was added, and polymerization proceeded for another 30 minutes. Ethylene oxide (Aldrich, 99.99%) was purged through the reactor for 2 min., followed by termination using de-gassed 1.0 M HCl in methanol. The polymer was precipitated in methanol and filtered. After recovery, the product was dried in vacuo at ~85 °C overnight. The diblock polymer γ-hydroxy-poly(styrene-*block*-*tert*-butyl styrene) was synthesized in the same manner, with the order of monomer addition being the reverse.

10.3.4 Synthesis of γ-hydroxy-poly(*tert*-butyl styrene-*block*-styrene): Method B.

A 500 mL-capacity anionic polymerization reactor was filled with ultrapure cyclohexane (350 mL) and heated to 50 °C. *Tert*-butyl styrene (60.0 mL, 53.0 g) was syringed into the reactor, and the system was titrated via *sec*-butyl lithium. Upon the persistence of a red color, the measured amount of *sec*-butyllithium (5.9 mL, 7.36 mmol) was added rapidly. After a polymerization time of 1 hour, the second block monomer, styrene (6.3 mL, 5.9 g), was added. After another hour of polymerization time, ethylene oxide was bubbled through the reaction solvent for 2 minutes. After termination using acidic (1 M HCl) methanol, the reaction solvent was purged out of the reactor. Precipitation was performed in methanol, and the recovered polymer was dried at 85 °C in vacuo.

10.3.5 Conversion of γ-hydroxy diblock copolymer to methacrylate macromonomer.

In a 500 mL round bottomed flask, the hydroxyl terminated diblock copolymer (35 g) was dissolved in a 1:4 THF/CH_2Cl_2 solution (500 mL), and triethylamine (17 mL, 120 mmol) was syringed into the reaction vessel. After cooling to 0 °C, methacryloyl chloride (10.2 mL, 104 mmol), dissolved in 20 mL THF, was slowly added over the course of 5 minutes. The reaction was allowed to proceed for 8 hours while slowly warming to room temperature. The macromonomer was precipitated into a 9:1 methanol: water mixture and dried at 75 °C for 24 hours.

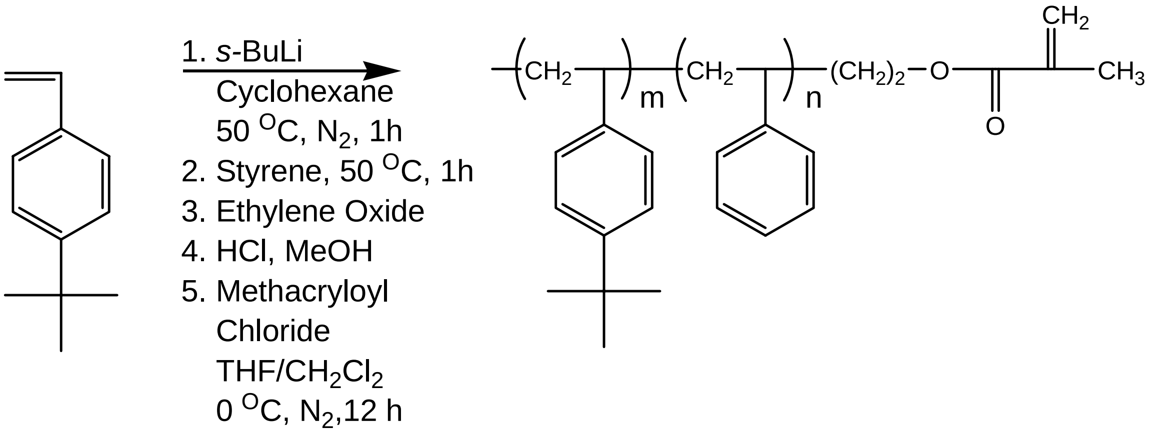
10.3.6 Graft Polymerization of Diblock Macromonomer and MMA.

The poly(methyl methacrylate-*graft*-poly*(tert*-butyl styrene-*block*-styrene)) graft copolymers were synthesized via solution free radical polymerization. Diblock macromonomer (11.6 g) and methyl methacrylate (12.3 mL, 11.6 g) were dissolved in a 3:1 ethyl acetate: hexane mixture (65 mL) and de-gassed for 20 minutes using a nitrogen purge. The sealed reactor was immersed in a temperature-controlled mineral oil bath for 15 min and 0.2 weight percent AIBN (46.3 mg) dissolved in de-gassed hexane (1 mL) was syringed into the reactor. The reaction proceeded for 48 h at 65 °C. The polymers were precipitated in a cold 9:1 mixture of methanol and water and dried under vacuum at 85 °C upon recovery. The graft polymers were fractionated via cyclohexane Soxhlet extraction and dried overnight at 85 °C under vacuum following precipitation.

10.3.7 Selective Sulfonation and Neutralization of Graft Copolymer.

The PMMA-*graft*-poly(styrene-*block*-*tert*-butyl styrene) (3 g) was dissolved in dichloroethane (20 mL) in a dry, N_2-purged 50 mL round- bottomed flask. The reactor was submerged in a mineral oil bath held at 50 °C and the acetyl sulfate solution (6 mL, 1.0 M in dichloroethane) was slowly syringed into the reaction. The reaction proceeded in the presence of a light pink color for five hours until methanol was added to terminate the reaction. The styrenesulfonic acid-containing polymer was precipitated in methanol and dried under vacuum at 50 °C. The dried polymer was re-dissolved in THF, and the acid groups were neutralized via the addition of 1 M NaOH in THF. The product polymer was isolated via rotary evaporation at 40 °C.

10.4 Results and Discussion



Scheme 10.1: Synthesis of the diblock macromonomer via anionic polymerization, followed by end-capping with ethylene oxide and conversion to the methacrylate functional group.

10.4.1 Diblock Alcohol Synthesis and Functionalization to Macromonomer

Diblock copolymers containing short styrene blocks and longer *tert*-butyl styrene blocks were synthesized via living anionic polymerization and functionalized with ethylene oxide to introduce the alcohol functional group. The relative block molecular weights were designed to be 1:9 styrene : *tert*-butyl styrene in order to ascertain the impact of the controlled ionic block placement in the graft copolymers. The initial polymerizations performed at low temperatures in tetrahydrofuran resulted in diblock copolymers exhibiting good molecular weights and extremely narrow molecular weight distributions. Diblock molecular weight distributions as low as 1.02 were reproducibly observed. The molar crossover efficiencies between blocks were quantitative when crossing over either from styrene to *tert*-butyl styrene or *tert*-butyl styrene to styrene.

The determination of block molecular weights in the poly(styrene-*block*-*tert*-butyl styrene) was complicated by the fact that overlap occurred between the resonances of styrene and *tert*-butyl styrene. This overlap prevented a direct calculation of block molecular weight based on the initiating end group. In order to directly compare block molecular weights, poly(*tert*-butyl styrene) was sampled from the polymerization reactor prior to crossover to styrene. A comparison between the molecular weights of the two blocks (Figure 10.1) indicated that the block molecular weights in poly(*tert*-butyl styrene-*block*-styrene) were and 9,700 and 1,400 g/mol, respectively.

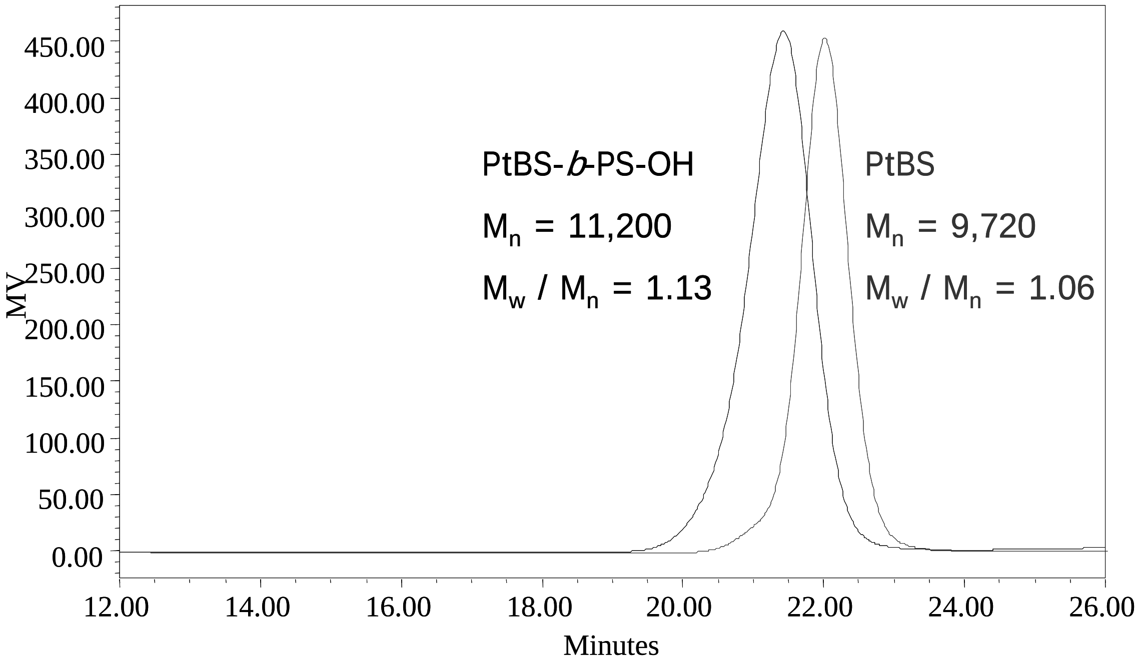


Figure 10.1: Relative block molecular weights were verified via sampling of the poly(*tert*-butyl styrene) block prior to crossover to styrene.

Despite the good polymerization control demonstrated at cryogenic temperatures, the low temperature anionic polymerization technique was limited to the synthesis of small quantities of identical diblock copolymers, less than 20 g. Large quantities of diblock copolymers were synthesized using a custom-built anionic polymerization reactor that was controlled to 50 °C. The cyclohexane was purified using molecular sieves and silica columns that were plumbed directly into the reactor. Poly(styrene-*block*-*tert*-butyl styrene) diblock copolymers were synthesized in quantities as high as 60 g, exhibiting good molecular weight distributions and molecular weight control. Although the molecular weight distributions of the polymers produced by the high temperature polymerizations were broader, the use of the diblocks as macromonomers in graft copolymers eliminated any practical disadvantage in regards to the use of these diblock copolymers.

Table 10.1: Molecular weight data for the poly(*tert*-butyl styrene-*block*-styrene) alcohols indicated excellent polymerization control.

Diblock Structure	GPC M_n	M_w / M_n	Initiator NMR M_n	-CH_2OH NMR M_n	Percent Funct.
9:1 tBuSt-St-OH	11,200	1.13	12,500	11,600	93%
1:9 St-tBuSt-OH	12,200	1.12	13,700	12,700	93%
1:9 St-tBuSt-OH	12,200	1.03	11,900	11,600	97%
9:1 tBuSt-St-OH	9,380	1.02	9,260	9,170	99%
9:1 tBuSt-St-OH	9,560	1.02	9,480	9,100	96%
1:9 St-tBuSt-OH	9,890	1.02	10,100	9,770	97%
7.2:0.8 tBuSt-St-OH	9,720	1.07	10,100	9,870	98%
0.8:7.2 St-tBuSt-OH	10,300	1.04	10,400	10,700	102%
0.8:St-tBuSt-OH	9,550	1.03	9,210	9,050	98%

Following polymerization at either high or low temperatures, the diblock copolymers were functionalized via ethylene oxide and terminated to introduce the alcohol functional group. The integration of the alcohol methylene ^{1}H NMR resonance at 3.2 ppm was divided by the normalized resonance of the *sec*-butyllithium methyl ^{1}H NMR resonance at 0.8 pm, in order to determine the degree of diblock copolymer functionalization. Based on this calculation, 96 to 99 percent functionalization to the terminal alcohol occurred in these polymerizations (Table 10.1).

The alcohol functional groups were reacted with a large molar excess of methacryloyl chloride under standard acid chloride coupling conditions to produce the diblock macromonomers in high yields. Conversion rates to the methacrylate ranging from 98 to 100 percent relative to the starting material were observed via ^{1}H NMR (Figure 10.2). A shift in the ethylene oxide end-group ^{1}H NMR resonance was observed, changing from 3.2 to 3.8 ppm as the alcohol methylene protons were converted to ester methylene protons. Overall, 95 to 99 percent functionalization of the diblock copolymers with the methacrylate functional group occurred (Table 10.2).

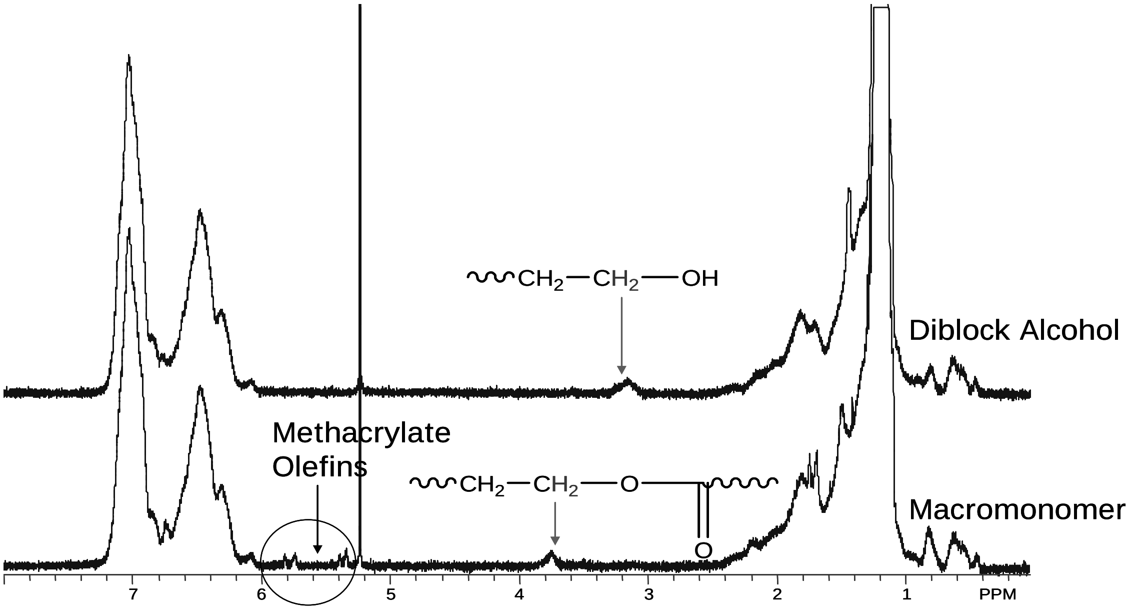
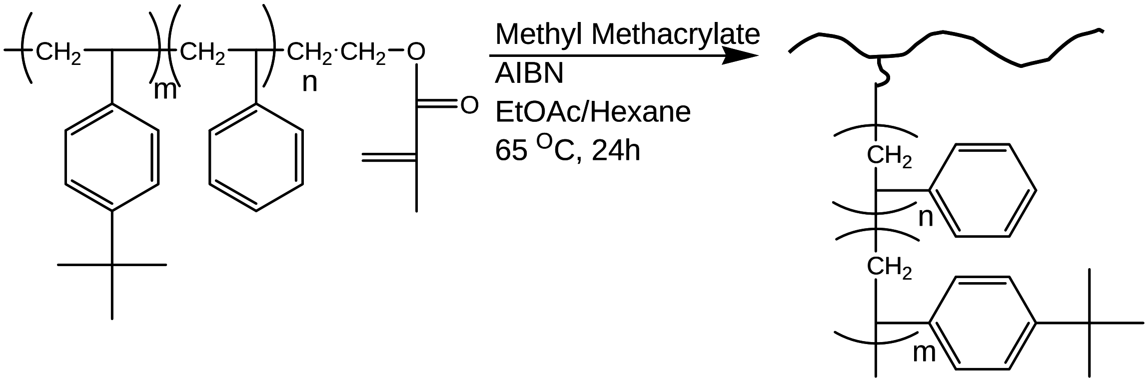


Figure 10.2: Conversion of the diblock alcohol to the diblock methacrylate was followed by ^{1}H NMR spectroscopy.

Table 10.2: Almost quantitative conversion of alcohol to methacrylate was observed based on ^{1}H NMR

Diblock	M_n (SEC)	M_n (NMR)	EsterCH$_2$: BuLi	Methacrylate Functional.
*t*BuSt-St-Meth	9,380	10,100	.97	97%
*t*BuSt-St-Meth	9,560	10,300	.97	96%
St-*t*BuSt-Meth	9,890	10,500	.98	97%

10.4.2 Graft Polymerization of Diblock Macromonomer and MMA



Scheme 10.2: Graft copolymers were synthesized from MMA and the poly(*tert*-butyl styrene-*block*-styrene) macromonomers via free-radical polymerization.

The ability of macromonomers to copolymerize in free-radical graft copolymerizations is governed by the reactivity of the polymerizing unsaturated group, and not the molecular weight of the macromonomer.[499] As a result, lower molecular weight macromonomers tend to be incorporated at higher levels than higher molecular weight polymers if the same weight concentrations are employed. Limited incorporation of the 10K diblock macromonomers was observed during graft copolymerization, even when a 1:1 weight ratio of macromonomer to MMA was employed. One of the reasons that MMA was chosen as the backbone monomer for these graft copolymers was the high polarity relative to styrene. Although MMA containing polymers exhibit no solubility in cyclohexane, the poly(styrene-*block*-*tert*-butyl styrene) diblock copolymers were very soluble in cyclohexane. Unreacted diblock macromonomer was completely removed from the graft copolymer samples as a result of this solubility difference. The changes in molecular weight from macromonomer to crude graft polymer to fractionated graft copolymer are shown in Figure 10.3. Graft copolymers featuring 2-ethylhexyl methacrylate backbones were also synthesized in this study. However, the graft copolymers could not be separated from the unreacted macromonomer, and these polymers were not examined further as a result. The fractionated graft copolymers exhibited only somewhat significant molecular weights (Table 10.3), relative to the unfractionated polymer. ^{1}H NMR spectroscopy (Figure 10.4) indicated that the graft copolymers contained only 1 to 3 mole percent of the graft chain repeat units (Table 10.4). Future graft copolymers will be synthesized via ATRP to improve graft macromonomer incorporation.

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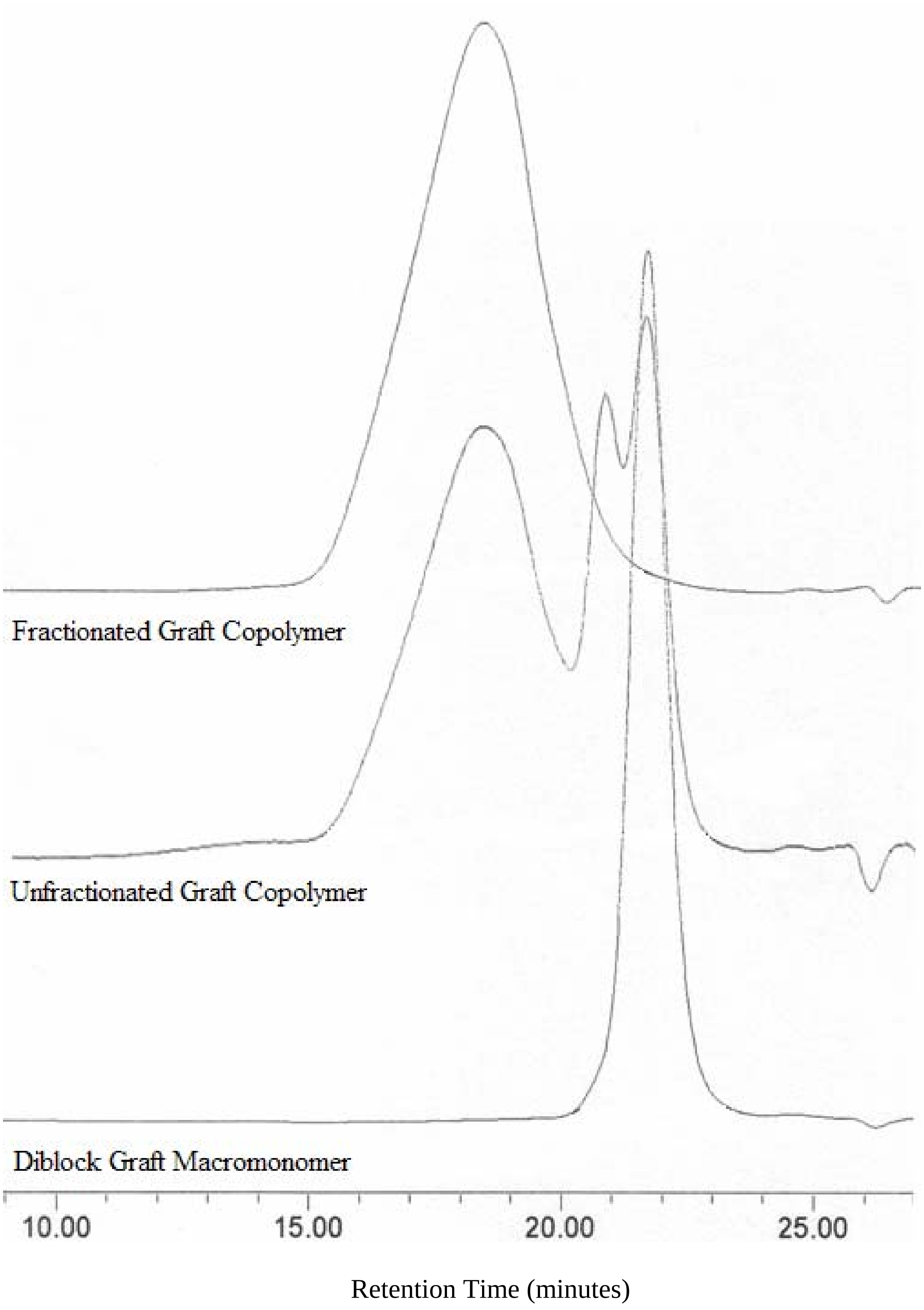
[499] Y. Gnanou and P. Lutz, "The Ability of Macromonomers to Copolymerize. A Critical Review with New Developments." *Makromol. Chem.*, **1989**, *190*(3), 577-588.

Table 10.3: Molecular weights data of the PMMA-*graft*-poly(*tert*-butyl styrene-*block*-styrene) graft copolymers.

Before Fractionation			After Fractionation		
M_n	M_w	M_w / M_n	M_n	M_w	M_w / M_n
27,200	71,800	2.64	58,400	125,000	2.14
24,100	42,900	1.78	48,400	113,000	2.33
29,700	58,200	1.96	52,900	91,500	1.73
31,700	77,000	2.43	53,100	116,000	2.18
26,700	43,500	1.63	43,400	71,200	1.64
37,200	189,000	5.08	124,000	336,000	2.71
50,500	209,000	4.13	36,600	65,500	1.76
42,000	204,000	4.86	82,500	233,000	2.84
21,500	57,700	2.86	54,000	114,000	2.11



Retention Time (minutes)

Figure 10.3: SEC overlays of the macromonomer, as well as the unfractionated and fractionated graft polymer, traces indicated complete removal of unreacted macromonomer.

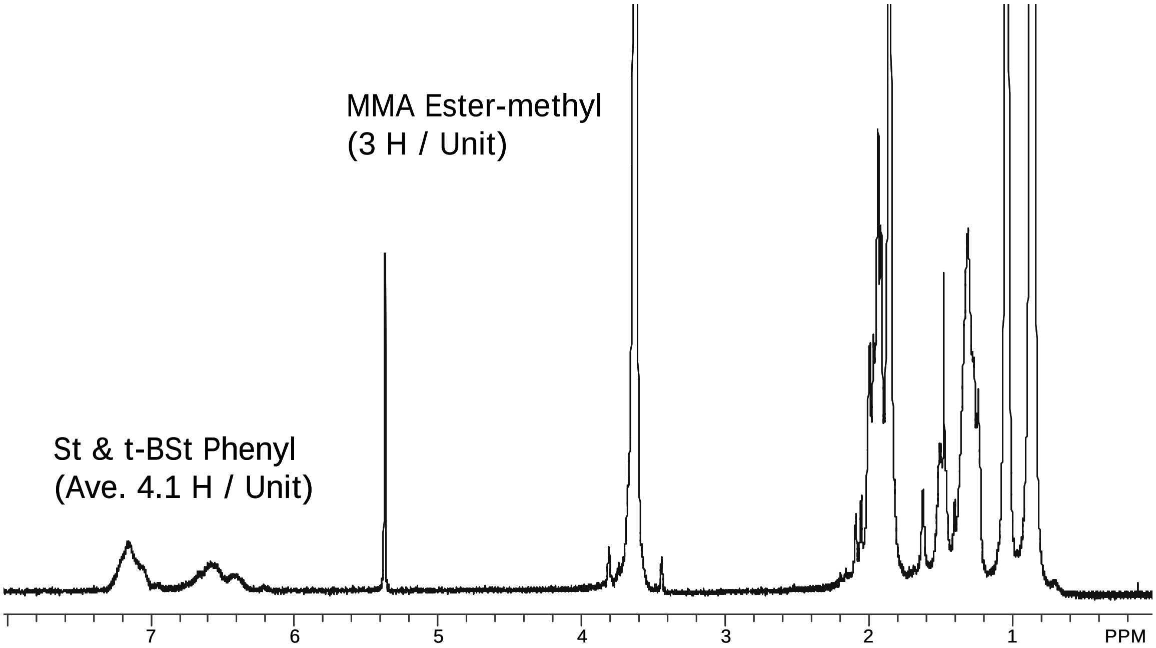


Figure 10.4: ^{1}H NMR Spectrum of Poly(Methyl Methacrylate)-*graft*-poly(styrene-*block*-*tert*-butyl styrene)

Table 10.4: Molar content of graft chains in graft copolymer based on ^{1}H NMR spectroscopy

Graft Chain	M_n	M_w / M_n	Mol. Graft Content
10K PtBS-PS-	48,400	2.33	8.6%
10K PS-PtBS-	124,000	2.71	8.1%
10K PS-PtBS-	43,400	1.64	7.2%

Graft copolymers were previously synthesized via the direct coupling of the propagating center with a functional group contained in the backbone polymer.[500,501,502] A similar anion coupling methodology was attempted in this study. Following the synthesis of high molecular weight PMMA via anionic polymerization, living polystyrene of <M_n> = 9,900 was cannulated into the reactor containing the dissolved backbone. Attack of the polystyryllithium on the MMA ester led to a significant increase in polymer molecular weight observed following cyclohexane extraction. The only difference between graft copolymers synthesized via this technique and the free-radical macromonomer technique is that the graft chains were bonded to the backbone via a ketone linkage, rather than the 2-methacryloyloxyethyl group introduced via the macromonomer. Although, the viability of his technique was hampered by the extremely poor incorporation of the living polystyrene chains, very high molecular weight graft copolymer was obtained following fractionation (Figure 10.5).

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[500] M. Morton and L. J. Fetters, "Homogeneous Anionic Polymerization of Unsaturated Monomers." *Macromol. Rev.*, **1967**, *2*, 71-113.

[501] P. Rempp and D.. Decker-Freyss, "Polystyrenes with Controlled Branching." *J. Polym. Sci. Polym. Symp.*, **1968**, *16*(Pt. 7), 4027-4034.

[502] R. A. Kee and M. Gauthier, "A Novel Synthetic Route to Highly Branched Graft Copolymers." *Poly. Mat. Sci. Eng.*, **1995**, *73*, 335.

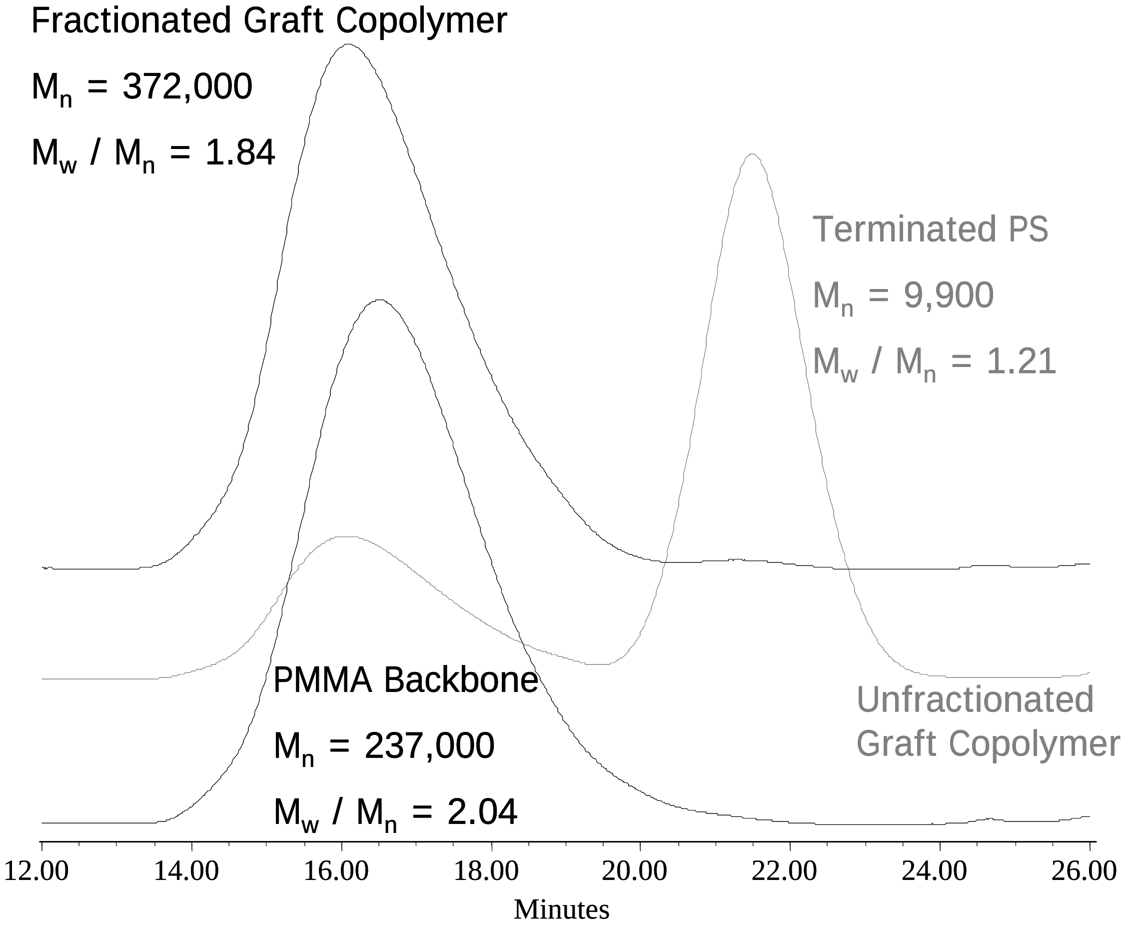
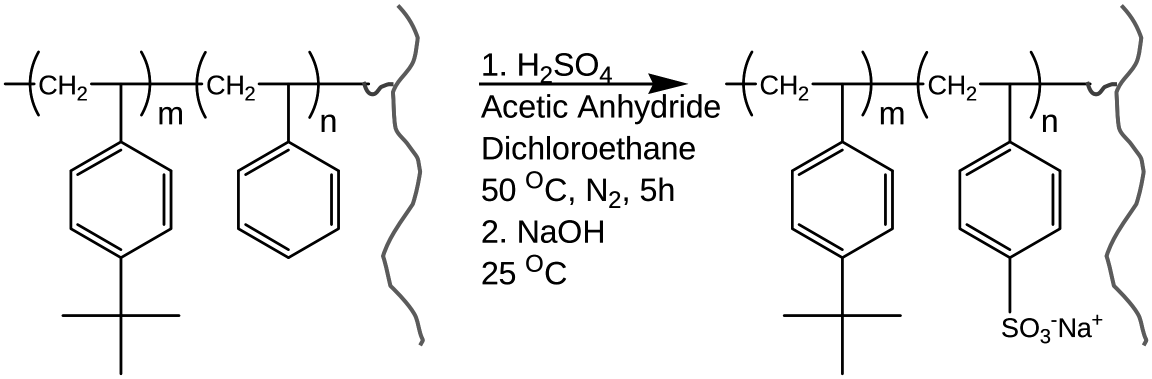


Figure 10.5: Synthesis of the graft copolymers via direct anion coupling and purification were followed via SEC.

10.4.3 Selective Styrene Sulfonation in Graft Copolymers



Scheme 10.3: Styrene was selectively sulfonated using acetyl sulfonate and neutralized with sodium hydroxide.

Acetyl sulfate was used to selectively sulfonate the styrene blocks in the graft copolymer without sulfonating the *tert*-butyl styrene blocks. The product styrenesulfonic acid containing graft copolymers were recovered via precipitation and subsequently neutralized using sodium hydroxide. The sodium styrenesulfonate containing graft copolymers exhibited solubility in an extremely wide range of solvents. The polymers could not be precipitated in water, methanol, ethanol, dichloromethane, toluene, or cyclohexane. The only feasible method of polymer isolation following neutralization was the removal of the solvent via rotary evaporation.

Table 10.5: Sulfonation of graft copolymers was verified via titration

Polymer	Acid Content		Expect. Acid Mol. Content
	meq/g	Mol.	
48K PMMA-*g*- α PSS	0.076	0.8%	0.9%
124K PMMA-*g*- γ PSS	0.071	0.7%	0.8%
43K PMMA-*g*- γ PSS	0.056	0.6%	0.7%

The styrenesulfonate content was determined via acid-base titration of the styrenesulfonic acid groups (Table 4). Molar acid contents between 0.056 to 0.076 meq / g were determined, corresponding to 0.6 to 0.8 mole percents. The titrated molar amounts of sulfonic acid corresponded well to the molar styrene content of the graft copolymers. This agreement indicated that complete sulfonation of the styrene repeat units was achieved. The ^{1}H NMR spectra of both the styrenesulfonic acid and the sodium styrenesulfonate containing graft copolymers did not exhibit any differences relative to the spectrum of the graft copolymers due to the low amounts of styrene that underwent sulfonation. Current efforts in our laboratories are focused on examining the physical, rheological, and morphological properties of these unique graft copolymers.

10.5 Conclusions

The living anions at the termini of the diblock copolymers poly(*tert*-butyl styrene-*block*-styrene) were end-capped in very high yields using ethylene oxide. The diblock copolymers were synthesized in very controlled fashion either at high or low temperatures, leading to good molecular weight control and molecular weight distributions, as well as complete crossover between blocks. The crossover between blocks did not depend on the order that the blocks were synthesized. The diblock alcohols were functionalized with the methacrylate end group, resulting in very well-defined macromonomers.

The diblock macromonomers were copolymerized with MMA via solution free-radical polymerization. Although the polymerizations were charged with up to 50 weight percent macromonomer, the incorporation of the diblock graft chains into PMMA was very limited due to the high molecular weight of these macromonomers. High molecular weights led to very low mole percents of macromonomer that were charged to the polymerizations, leading to only limited incorporation of the diblocks. The graft polymers were purified using cyclohexane and selectively sulfonated with acetyl sulfate, followed by neutralization to sodium styrenesulfonate. Selectively sulfonation, verified via titration, led to graft copolymers containing short sodium styrenesulfonate blocks either close to the main chain or at the termini of the graft chains.

10.6 Acknowledgements

This material is based upon work supported in part by the U.S. Army Research Laboratory and the U.S. Army Research Office under contract/grant number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors thank KRATON Polymers and the Carilion Biomedical Institute for financial assistance.

Chapter 11 : Overall Conclusions

Cleavable star-shaped polymers containing acid and thermally labile crosslinking monomers were synthesized via arm-first living anionic polymerization. Arm polymers comprised of methyl methacrylate, isobutyl methacrylate, *tert*-butyl methacrylate, or 2-ethylhexyl methacrylate were incorporated into the star polymer cores. The acid-cleavable dimethacrylate monomers utilized to form the star polymer cores were designed to exhibit varying degrees of reactivity to acid-catalyzed hydrolysis. Hydrolysis of the novel cleavable coupling monomer dicumyl dimethacrylate was twice as rapid as 2,5-dimethyl-2,5-hexanediol dimethacrylate. The sensitivity of the star-shaped polymers to thermal cleavage was tunable, based on the chemical structure of the crosslinking unit. The onset of thermal degradation in DHDMA star polymers was 50 °C greater than the DCDMA containing star polymers. Despite the improvement in the anionic polymerization of the star-shaped polymers, significant termination occurred during the star polymer coupling reaction.

2-ethylhexyl acrylate pressure-sensitive adhesive polymers were copolymerized with either 2,5-dimethyl-2,5-hexanediol dimethacrylate or dicumyl dimethacrylate in order to introduce cleavable long-chain branching sites. High amounts of these cleavable dimethacrylate monomers were incorporated during free-radical polymerization due to the ability of 2-ethylhexyl acrylate to undergo chain transfer to polymer. Complete incorporation of the DCDMA branching monomers was observed via ^{1}H NMR; however, all DHDMA NMR resonances overlapped with those of EHA. PSA molecular weights in excess of 2,000,000 g/mol were observed when high amounts of DHDMA or DCDMA were charged to the polymerizations. The 180° peel strengths increased drastically as weight-average molecular weights increased above 300,000 g/mol. Acid-catalyzed hydrolysis resulted in drastic reductions in the cohesive strength of the PSA. Reductions in 180 peel strengths as great as 95% were observed. Greater initial PSA molecular weights led to greater final adhesion, although the percent deactivation was comparable to lower molecular weight branched PSAs.

Pressure-sensitive adhesives bearing photocrosslinkable functional groups were synthesized that contained either light or heavy levels of long-chain branching. The photocrosslinkable cinnamate and acrylate groups were introduced by reacting HEMA functional groups with either cinnamoyl chloride or acryloyl chloride. Heavy levels of long-chain branching were observed in terpolymers of EHA, HEMA, and ethylene glycol dimethacrylate (EGDMA). Cinnamate functionalization up to 25 mole percent were performed, raising the peel strengths of the PSAs significantly compared to the unfunctionalized PSA. The cinnamate containing adhesives underwent photodeactivation in the presence of UV light. The rates and extents of deactivation were strongly dependent on the level of long-chain branching and concentrations of cinnamate groups. UV-light deactivation was reduced by thicker adhesive samples and the presence of the UV-absorbing PET Mylar substrate. PSAs functionalized with the acrylate functional group were mixed with the photoinitiator camphorquinone and deactivated under visible light. Acrylate containing PSAs with lower degrees of functionalization exhibited deactivation behavior that was similar to CEMA adhesives with high levels of functionalization.

A novel PMMA anionic polymerization co-initiator containing two aliphatic alcohols was developed. The initiator 1,1-bis-4,4’-(2-(*tert*-butyldimethylsilyloxy)ethoxy)phenylethylene (BTOPE) was synthesized from 4,4’-dihydroxybenzophenone in three high-yield synthetic steps. The formation of the synthetic intermediates was confirmed utilizing ^{1}H NMR, ^{13}C NMR, and IR spectroscopic methods. Following purification, BTOPE was reacted with *sec*-butyllithium. Subsequent initiation of MMA polymerization led to the formation of low molecular weight distribution polymers containing a single BTOPE functional group. Acid-catalyzed deprotection of the *tert*-butyldimethylsilyl functional groups resulted in the formation of α,α-dihydroxy PMMA. Incorporation of this polycondensation macromonomer in a variety of polyesters was difficult due to the relatively high molecular weights of the macromonomers.

Diblock poly(*tert*-butyl styrene-*block*-styrene) methacrylate and poly(styrene-*block*-*tert*-butyl styrene) alcohols were synthesized via living anionic polymerization, followed by ethylene oxide end-capping. Perfect crossover between blocks was observed in almost all cases regardless of monomer addition order. The diblock alcohols were converted to the macromonomers via methacryloyl chloride coupling in yields that were in excess of 95%. The macromonomers were copolymerized in relatively high amounts with 2-ethylhexyl methacrylate and methyl methacrylate. Limited incorporation of less than 5% was observed due to the relatively high molecular weights (9,000 to 11,000 g/mol) of the macromonomers that were synthesized. The PMMA graft polymers were separated from the unreacted graft macromonomer via Soxhlet extraction in cyclohexane. The graft copolymers containing short styrene blocks either in the interior of the molecule or at the ends of the graft chains were selectively sulfonated using acetyl sulfate, as evidenced by titration.

Chapter 12 : Suggested Future Research

12.1 Well-Defined Cleavable Acrylic Star Polymers via ATRP

- Improve crossover efficiencies and molecular weight over previous cleavable methacrylic star polymers synthesized by anionic polymerization.
    - Examine effect of crosslinker : arm molar ratio on star polymer molecular weight.
    - Compare relative rates of star core degradation based on crosslinker structure (DHDMA relative to DCDMA).
    - Tailor level of star polymer core responsiveness to hydrolysis by copolymerizing DCDMA and DHDMA in cores.
- Synthesize cleavable star polymers with low T_g arms (e.g. 2-ethylhexyl acrylate, n-butyl acrylate) to act as well-defined cleavable adhesives.
    - Investigate effect of initial star and arm molecular weights on deactivation.
    - Optimize extent of adhesive deactivation.
    - Conduct physical testing including 90° and 180° peel testing, tack testing, and melt rheology.

12.2 Hydrolysable Microgel Adhesives via Emulsion Polymerization

- Utilize emulsion polymerization in synthesis of network microgel adhesives
    - Vary crosslinker density to optimize adhesion

  - Examine effect of M_c on initial and final adhesive strengths
  - Alter typical emulsion polymerization conditions including agitation rate, dispersant to tune adhesion.
- Encapsulate drug/nutrient molecules in cleavable microgels
  - Tune release rates by altering *tert*-butyl ester linking group
  - Change particle size by changing polymerization conditions and examine effect on release rates.

12.3 Aliphatic Polyurethane Copolymers Containing PMMA Graft Chains

- Synthesize high molecular weight polyurethane-urea graft copolymer via diisocyanate functionalization prior to polymerization
  - Copolymerize using variety of low-T_g backbone monomers
  - Examine interaction between graft chains and hard segments
- Develop DPE variant containing protected diamine functional group for use in polyurethane macromonomer
  - Utilize in initiation of alkyl methacrylate
  - Terminate living polystyrene polymerization following purification
- Synthesize polyurethanes using diamino-PMMA
  - Compare properties of graft polyurethanes and graft polyurethane-ureas

Chapter 13 : Vita of Lars Kilian

Lars Kilian was born on the banks of the Weser River in Hameln, Germany on May 11, 1977. He grew up in the town of Springe, Germany until the age on 9, moving to North Carolina in January of 1987. Following graduation from Ravenscroft School in Raleigh, Lars spent the summer of 1995 working at the GlaxoWellcome Research Institute in Research Triangle Park. His experience programming robotics sparked a fascination with technology that continues today.

At the conclusion of his summer internship, Lars began pursuing his B.S. in Chemistry degree at the University of North Carolina at Chapel Hill. He quickly realized that polymer research was his calling, working as an undergraduate researcher for almost three years under the guidance of Profs. Edward Samulski and Joseph DeSimone. The two most important things Lars received from his college experience were his wife-to-be, Tara, and his love for polymer chemistry. He graduated from UNC in May of 1999.

Wanting to continue polymer research, Lars began his Ph.D. studies at Virginia Tech in August 1999 under the direction of Timothy Long and Alan Esker. The joint project enabled Lars to gain a deep appreciation for both synthetic, as well as physical, polymer chemistry. In the summer of 2000, he married Tara in her hometown of Seven Springs, NC. Following the completion of his second year, Lars decided to focus exclusively on polymer synthesis, working for Prof. Long until August 2004. During his graduate studies, he had the good fortune of working as a summer intern in 2002 at

National Starch and Chemical Co. under the guidance of Dr. Paul Foreman. Following a very successful proof-of-concept project, Lars returned to Virginia Tech and continued working towards his degree. Seven weeks before his defense, Lars became a father when Cole Matthias Kilian was born on June 3, 2004. Following the completion of his degree, Tara, Cole, and Lars will move to Columbus, OH where Lars will work as a Senior Development Chemist for the Ashland Specialty Chemicals Company in the PSA Development & Technical Service group.

Lars' parents, Herbert and Renate Kilian, reside in Chicago, while his brother Jarno Kilian calls North Charleston, SC home. Since his entire extended family still resides in Germany, Lars is grateful that Tara's family has welcomed him with open arms. In his occasional spare time, Lars enjoys reading, hiking, and tinkering with computer technology.