Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

for

Star and Miktoarm Star Block (Co)polymers via Self-Assembly of ATRP Generated Polymer Segments Featuring Hamilton Wedge and Cyanuric Acid Binding Motifs

Ozcan Altintas,[1] Umit Tunca,[2] and Christopher Barner-Kowollik[1]*

[1]Preparative Macromolecular Chemistry, Institut für Technische Chemie und Polymerchemie, Karlsruhe Institute of Technology (KIT), Engesserstr. 18, 76128 Karlsruhe, Germany, *christopher.barner-kowollik@kit.edu*, www.macroarc.de

[2]Department of Chemistry, Istanbul Technical University, Maslak, Istanbul 34469, Turkey

Materials

Styrene (St) (Sigma-Aldrich) and methyl methacrylate (MMA) (Sigma-Aldrich) were passed through a column of basic alumina (Acros) prior to use and subsequently stored at -19°C. 6-Bromohexanol (97%, ABCR GmbH and Co. KG), 11-bromoundecanol (97%, ABCR GmbH and Co. KG), ethylenediaminetetraacetic acid disodium salt (99%, Acros), 2,2-dimethoxypropane (99%, Acros), *p*-toluenesulfonic acid monohydrate (99%, Aldrich), 2,2-bis(hydroxymethyl)propionic acid (99%, Aldrich), cyanuric acid (CA) (99%, ABCR GmbH and Co. KG), 4-dimethylamino pyridine (DMAP) (99%, Acros), N,N-dicyclohexylcarbodiimide (DCC) (99%, Acros), N,N-dimethylformamide extra dry (DMF) (99.8%, Acros), tetrahydrofuran extra dry (THF) (99.8%, Acros), sodium azide (99.8%, Acros), α-bromo isobutyric acid (98%, Aldrich), 2-bromo-2-methylpropanoyl bromide (98%, Aldrich), 5-hydroxyisophthalic acid (97%, Aldrich), sulfuric acid (95%, Carl Roth GmbH and Co. KG), propargyl bromide, 80 wt.% solution in toluene (80%, Acros), 3,3-dimethylbutyryl chloride (99%, Aldrich), 2,6-diamino pyridine (98%, Aldrich), triethylamine (99.7%, ABCR GmbH and Co. KG), CuBr (99.9%, Acros) N,N,N',N'',N''-pentamethyldiethyltriamine (PMDETA) (99.9%, Merck), cupric sulfate pentahydrate (99.5%, Aldrich), (+)-sodium L-ascorbate (98%, Aldrich) were used as received. Methylene chloride (DCM) was distilled over phosphorus pentoxide and stored over molecular sieves. Toluene, diethyl ether, ethanol, methanol and chloroform were purchased as analytical grade (Aldrich) and used as received.

Characterization

Size Exclusion Chromatography (SEC)

SEC measurements were performed on a Polymer Laboratories PL-GPC 50 Plus Integrated System, comprising an autosampler, a PLgel 5 μm bead-size guard column (50 × 7.5 mm)

followed by three PLgel 5 μm Mixed-C and one PLgel 3 μm Mixed-E columns (300 × 7.5 mm) and a differential refractive index detector using THF as the eluent at 40 °C with a flow rate of 1 mL min^{-1}. The SEC system was calibrated using both linear poly(styrene) (PS) standards ranging from 160 to $6 \cdot 10^6$ g mol^{-1} and linear poly(methyl methacrylate) (PMMA) standards ranging from 700 to $6 \cdot 10^6$ g mol^{-1}. Calculation of the molecular weight proceeded via the Mark-Houwink parameters for these polymers, i.e. $K = 14.1 \cdot 10^{-5}$ dL·g^{-1}, $\alpha = 0.70$ (PS)[1] and i.e. $K = 12.8 \cdot 10^{-5}$ dL·g^{-1}, $\alpha = 0.69$ (PMMA).[2]

Electrospray Ionization-Mass Spectrometry (ESI-MS)

Mass spectra were recorded on an LXQ mass spectrometer (ThermoFisher Scientific, San Jose, CA, USA) equipped with an atmospheric pressure ionization source operating in the nebulizer assisted electrospray mode. The instrument was calibrated in the *m*/*z* range 195-1822 using a standard containing caffeine, Met-Arg-Phe-Ala acetate (MRFA) and a mixture of fluorinated phosphazenes (Ultramark 1621) (all from Aldrich). A constant spray voltage of 3.5 kV and a dimensionless sheath gas of 8 and a sweep gas flow rate of 2 were applied. The capillary voltage, the tube lens offset voltage, and the capillary temperature, were set to 60 V, 120 V and 275 °C, respectively.

Nuclear Magnetic Resonance (NMR) Spectroscopy

The structures of the synthesized compounds were confirmed via ^{1}H- and ^{13}C-NMR spectroscopy using a Bruker AM 400 MHz spectrometer for hydrogen nuclei and 100 MHz for carbon nuclei. Samples were dissolved in $CDCl_3$, DMSO-d_6 or CD_2Cl_2 (for the self-assembly study). The δ-scale was referenced with tetramethylsilane (δ = 0.00) as internal standard. Abbreviations used below in the description of the materials' syntheses include

singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), broad multiplet (bm), and unresolved multiplet (m).

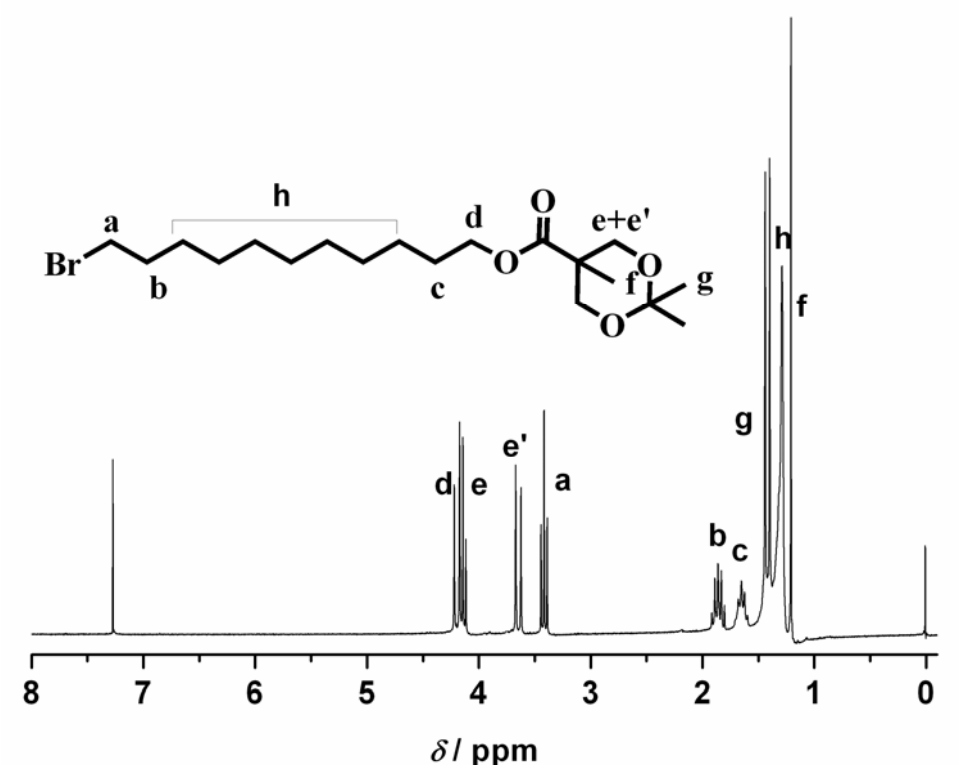

Figure S1. ^{1}H-NMR spectrum of 11-bromoundecyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (**2)** in $CDCl_3$.

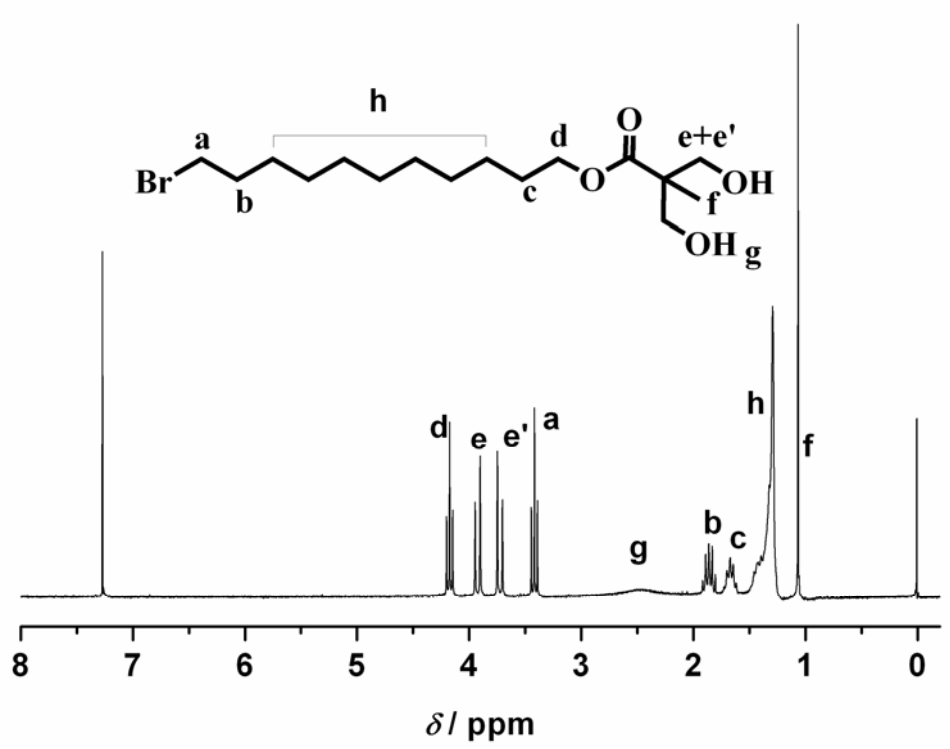

Figure S2. ^{1}H-NMR spectrum of 11-bromoundecyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (**3)** in $CDCl_3$.

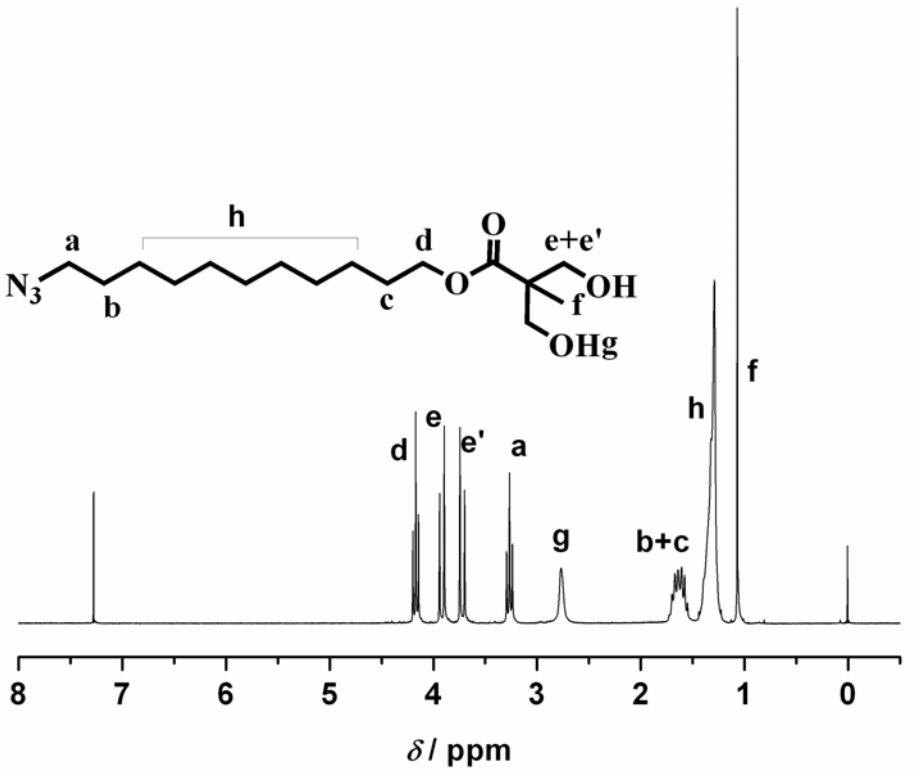

Figure S3. ^{1}H-NMR spectrum of 11-azidoundecyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (**4)** in $CDCl_3$.

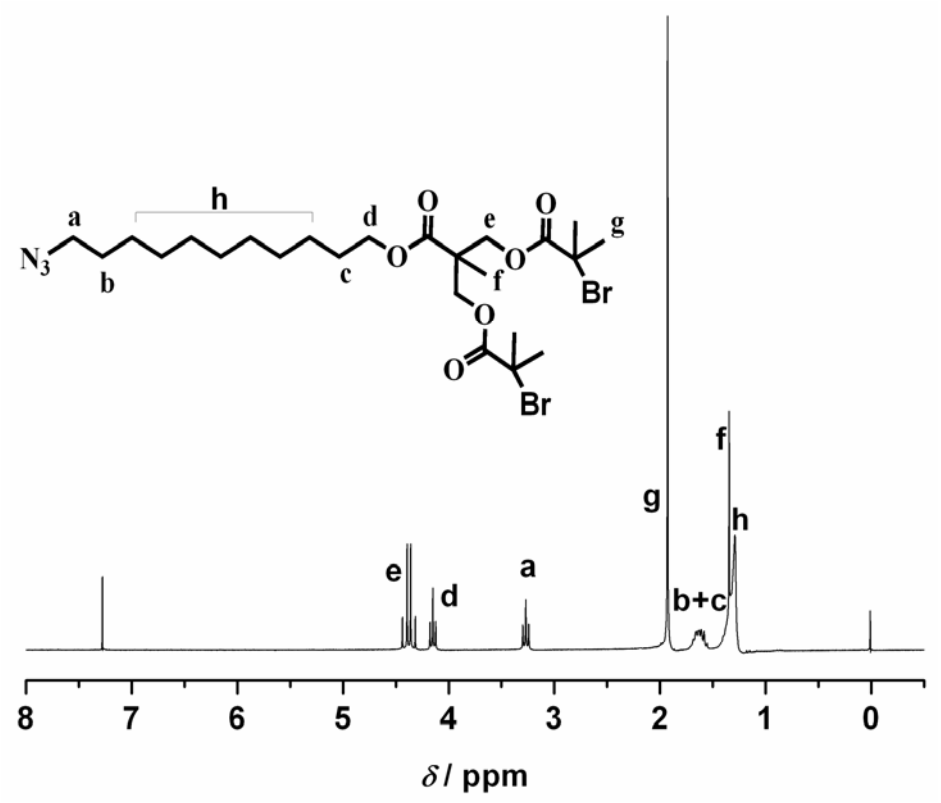

Figure S4. ^{1}H-NMR spectrum of azido-functionalized ATRP initiator **(5)** in $CDCl_3$.

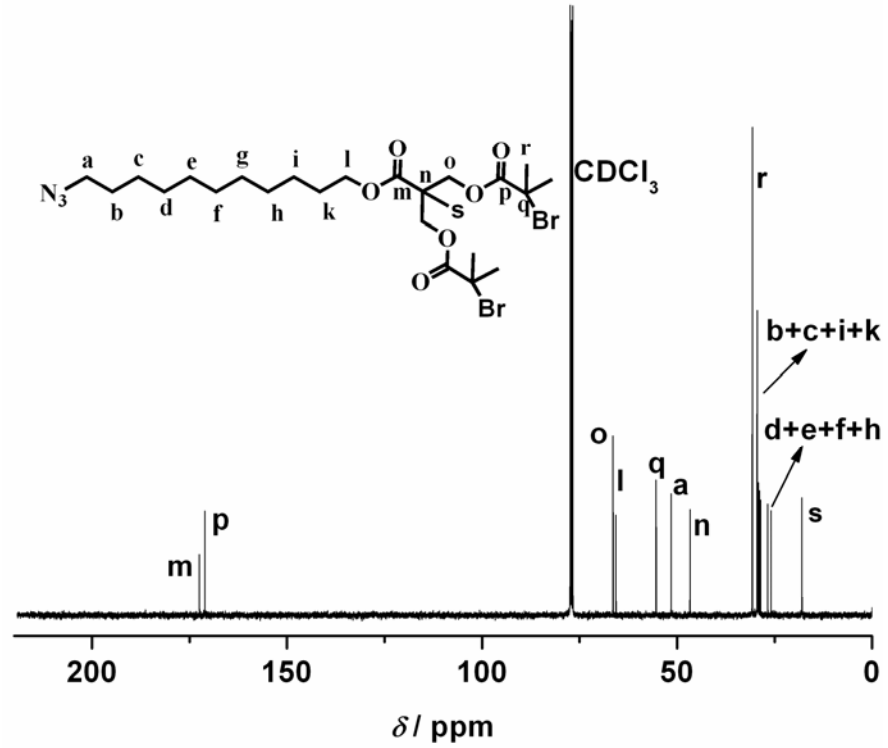

Figure S5. ^{13}C-NMR spectrum of azido-functionalized ATRP initiator **(5)** in $CDCl_3$.

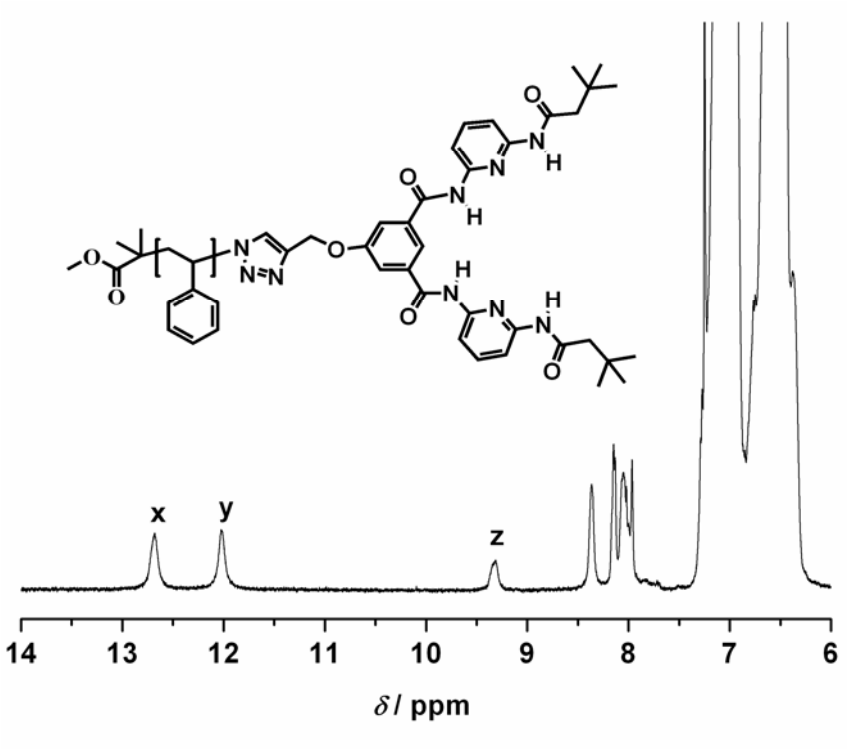

Figure S6. Expanded ^{1}H NMR spectrum of HW end-functionalized polystyrene (**PS-HW**) in $CDCl_3$ at ambient temperature.

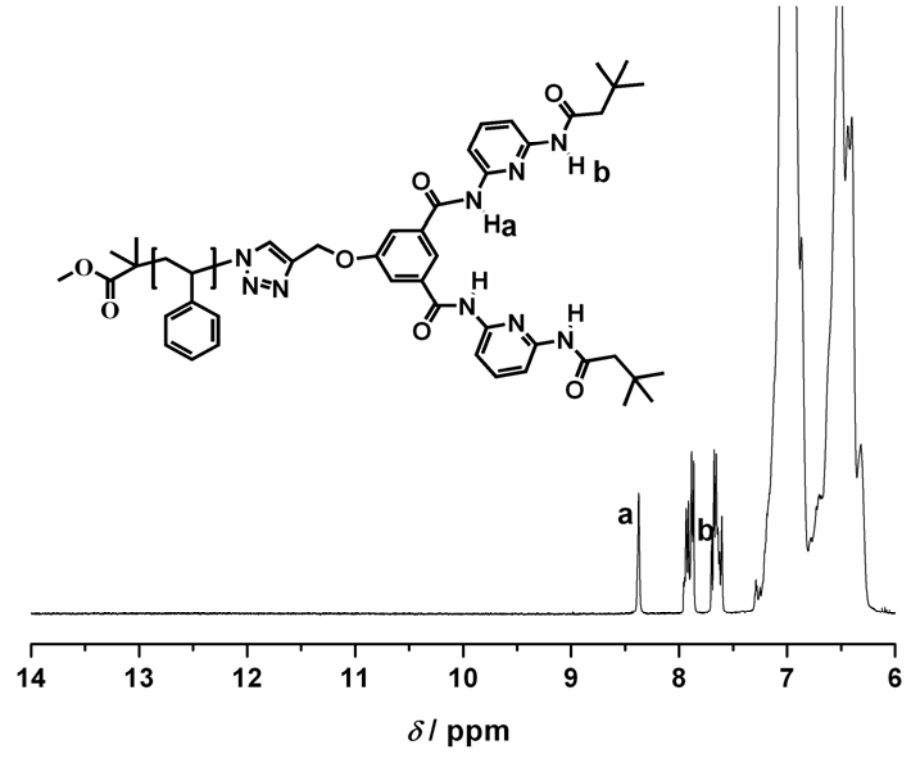

Figure S7. Expanded ^{1}H-NMR spectrum of HW end-functionalized polystyrene (**PS-HW**) in CD_2Cl_2 at ambient temperature.

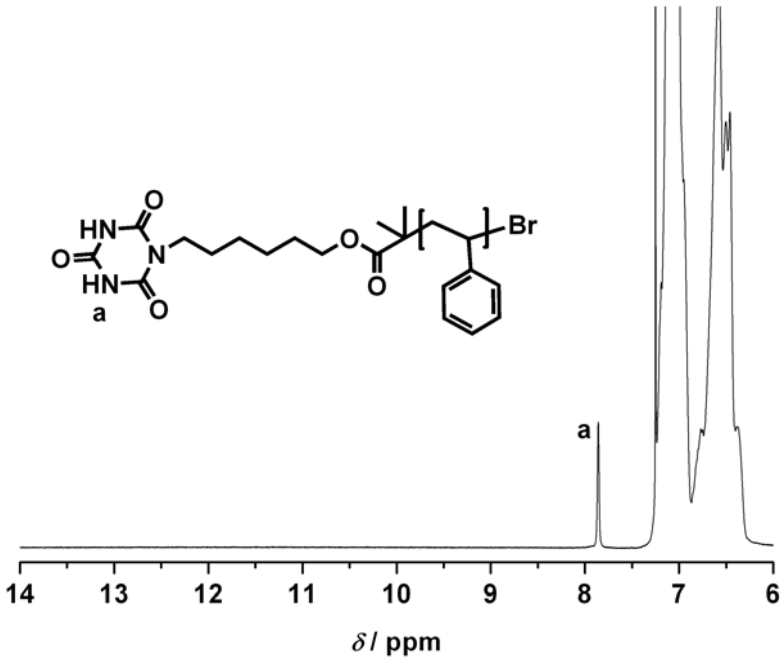

Figure S8. Expanded ^{1}H-NMR spectrum of CA end-functionalized polystyrene (**PS-CA**) in $CDCl_3$.

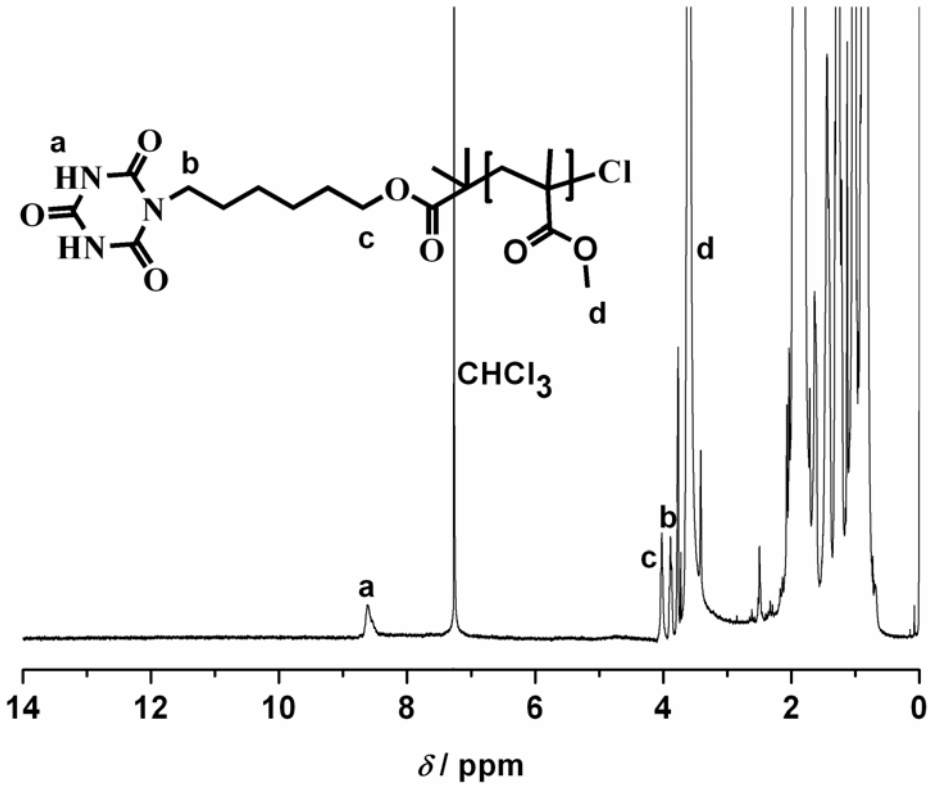

Figure S9. ^{1}H-NMR spectrum of CA end-functionalized poly(methyl methacrylate) (**PMMA-CA**) in $CDCl_3$.

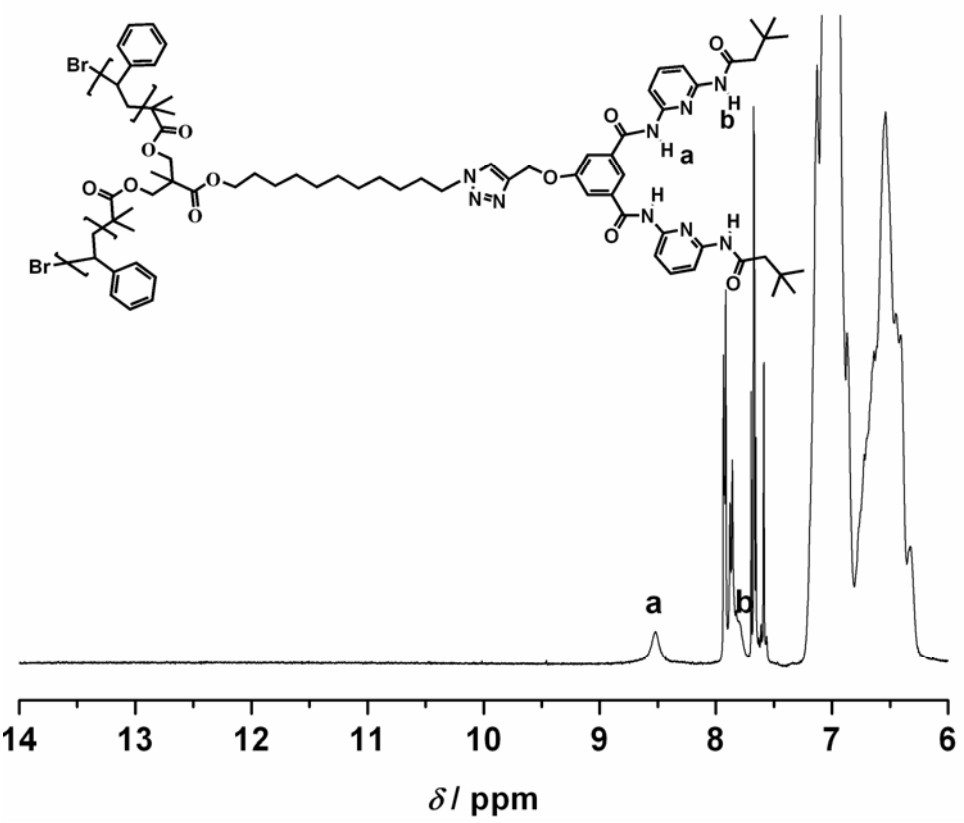

Figure S10. Expanded ^{1}H-NMR spectrum of HW mid-functionalized polystyrene (**PS-HW-PS**) in CD_2Cl_2.

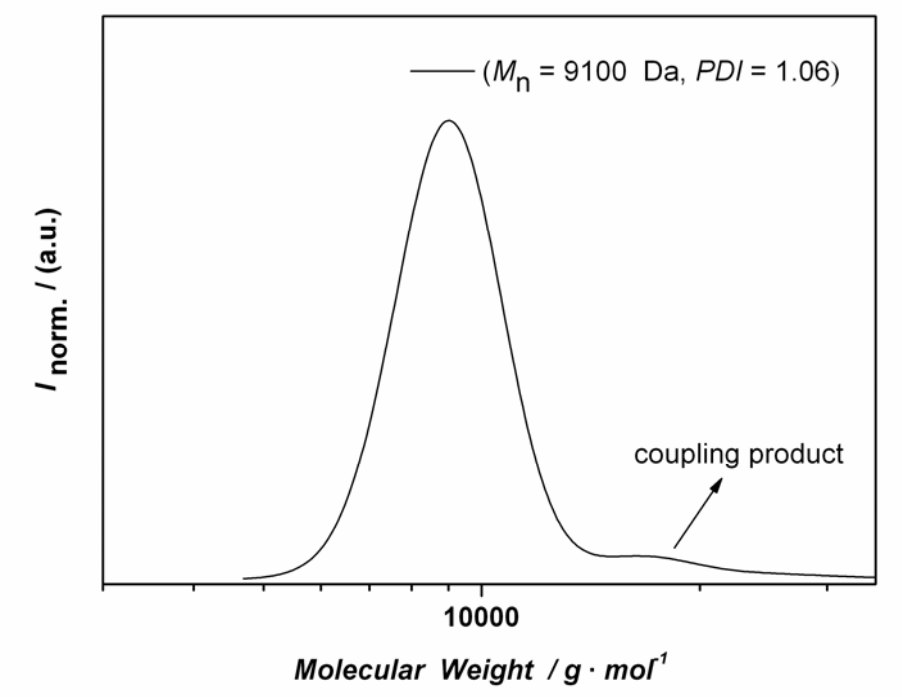

Figure S11. SEC trace of polymer prepared via ATRP using initiator **8.** The condtions were the same as those used to prepare polymer **9** (PS-CA) (see experimental section) with the exception that the reaction time was 2h.

References and Notes

1 C. Strazielle, H. O. Benoit, O. Vogl, O. *Eur. Polym. J.* 1978, **14**, 331-334.

2 I. Brandrup, E. Immergut, *Polymer Handbook*, Wiley & Sons 4th Edition, New York, **2003**.