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# Radical aqueous emulsion copolymerization of eugenol-derived monomers for adhesive applications

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ABSTRACT

Biobased monomers derived from eugenol were copolymerized by emulsion polymerization to produce latexes for adhesive applications. Stable latexes containing ethoxy dihydroeugenyl methacrylate and ethoxy eugenyl methacrylate with high total solids content of 50 wt% were obtained and characterized. Latexes synthesis was carried out using a semi-batch process and latexes with particle diameters in the range of 159 - 178 nm were successfully obtained. Glass transition temperature values of the resulting polymers ranged between $-32$ and $-28°C$. Furthermore, tack and peel measurements confirmed the possibility to use these latexes in adhesive applications.

INTRODUCTION

New biobased monomers are surging from renewable resources to produce sustainable materials, such as polymers.[1–5] Nevertheless, it is fundamental not only to aim for the replacement of their petroleum counterparts, but also to explore the possibility of harnessing their potential additional properties and to polymerize them by means of environmentally friendly processes.[6] Aqueous emulsion polymerization,[7–9] where the continuous phase is water, rises as a very suitable option for a myriad of applications. Furthermore, emulsion polymerization is a well-established polymerization technique for the production of adhesives and coatings at the industrial scale. Indeed, in 2019, the annual production of synthetic latex approached 20Mt.[10]

Different kinds of biobased monomers have been used in the production of biobased latexes including vegetable oils, lipids, terpenes, carbohydrates, lignin derivatives and proteins.[11] However, the hydrophilic character of the monomers plays a central role on the selection of the emulsion polymerization technique that can be used. Aqueous emulsion polymerization requires monomer diffusion through the continuous aqueous phase from monomer droplets to growing latex particles, which are the main loci of polymerization. Therefore, vegetable oils and lipids, which are very hydrophobic substances, are often difficult to polymerize via aqueous emulsion polymerization. Aqueous miniemulsion polymerization can be used for highly hydrophobic monomers as polymerization occurs in the monomer droplets.[12–14] Nevertheless, this technique has not been fully adapted for industrial scale.[15,16] Monomers which can be polymerized by aqueous emulsion polymerization are preferred. The introduction of the highest amount of biobased monomer in the latex formulation is often desired. Several examples of biobased monomers (mainly derived from vegetable oils) for coatings and adhesive formulations have been

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reported.[13,14,17–19] Vegetable oil- and lipid-derived monomers are of particular interest since they introduce soft segments in the adhesives formulation and thus yield low $T_g$ polymers.[19] Nevertheless, as previously mentioned, most of the vegetable oil-derived monomers need to be polymerized through miniemulsion due to their low hydrophilicity. This hinders their wider use in industry.[16] Moreover, monomers derived from olive, soybean and linseed oils possess allyl groups that can engage in secondary reactions (cross-propagation of the allylic double bond and/or allylic hydrogen abstraction) and crosslink, therefore increasing the $T_g$ and even producing small coagula[20] which are undesirable in soft polymers for adhesive applications. Additionally, oxidative curing can occur as a post-polymerization process modifying the properties of the final latex film.[21,22] Thus, it is necessary to use hydrophobic biobased monomers, capable of diffusing through the aqueous phase which can yield filmogenic polymers. Therefore, the adopted approach in this work is the gradual replacement of the monomers that increase $T_g$ values in the latex formulations with biobased monomers. This approach has been reported using biobased monomers such as isobornyl methacrylate (IBOMA, poly(IBOMA) $T_g$=155ºC[23] ), limonene (poly(limonene) $T_g$=78ºC) and sugar-based vinyl monomers.[23–25] Regarding lignin-derived monomers, Wang et al. produced a triblock copolymer from acrylates synthesized using molecules derived from lignin depolymerization.[26] These materials possessed adequate properties for adhesive applications. Nevertheless, the polymerization was executed in solution and not in emulsion. Recently, our team developed a monomer platform derived from eugenol, isoeugenol and dihydroeugenol.[27] These molecules are mainly obtained from clove oil, but can also be produced from lignin depolymerization.[28,29] Moreover, these biobased methacrylate monomers were proven to polymerize under radical aqueous emulsion polymerization with different radical initiating systems.[30]

To the best of our knowledge, eugenol-derived monomers have not been used in latex formulations for adhesive purposes yet. For this reason, a general adhesive formulation including butyl acrylate (BA), methyl methacrylate (MMA) and methacrylic acid (MAA),[31] has been modified by the gradual replacement of MMA with a eugenol-derived monomer. Ethoxy dihydroeugenyl methacrylate (EDMA) was selected as the main replacement monomer as it does not possess any pending double bonds that could engage in secondary reactions. Furthermore, the use of ethoxy eugenyl methacrylate (EEMA) was tested to study its effect on the formulation while bearing an allylic double bond. The simplicity of the semi-batch process used for the latex synthesis makes this study suitable for scale up.

**EXPERIMENTAL**

**Materials**

Ethoxy eugenol methacrylate (EEMA) and ethoxy dihydroeugenyl methacrylate (EDMA) monomers were synthesized as described in a previous article from our group.[27] Sodium persulfate (NaPS, ≥98.0 %, Aldrich), sodium bicarbonate (NaHCO$_3$, ≥99.0 %, Aldrich), sodium dodecylbenzenesulfonate (SDBS, Aldrich), 1,4-bis(trimethylsilyl)benzene (1,4-BTMSB, 96%, Aldrich), tert-dodecyl mercaptan (98.5%, Aldrich), tetrahydrofuran (THF, ≥99.0 %, VWR), 4-methoxyphenol (MEHQ, ≥99.0 %, Acros Organics), deuterated benzene (C$_6$D$_6$, 99.5%, Eurisotop) and Disponil® A 3065 (65 wt% active substance, BASF) were used as received. Butyl acrylate (BA, ≥99.0 %, Aldrich), methyl methacrylate (MMA, ≥99.0 %, Aldrich) and methacrylic acid (MAA, ≥99.0 %, Aldrich) were distilled under vacuum prior to use. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Fluka, 98%) was purified by recrystallization in methanol and dried under vacuum before use. Deionized water (DI water) (1 µS.cm$^{-1}$) was obtained using a D8 ion exchange demineralizer from A2E Affinage de L'Eau.

**Methods**

**Determination of the reactivity ratios (Table S1-S3 and Figure S1-S4).** The solution copolymerizations of EDMA and MMA were carried out at 70°C in benzene-$d_6$ (1 mol $L^{-1}$ with respect to monomers) to minimize any transfer reactions to solvent. The concentration of AIBN used was 2 wt% with respect to monomers and 1,4-BTMSB was used as internal standard (5.5 mol% with respect to monomers) to determine monomer conversions by $^1H$ NMR analysis. The feed molar fractions of EDMA ([EDMA]/([EDMA]+[MMA])) was varied from 0.1 to 0.9. The reactivity ratios were determined using three different methods: the Kelen-Tüdös method,[32] non-linear regression based on the method of the visualization of the sum of squared residual space proposed by van den Brink,[33] and non-linear curve fitting using the Levenberg-Marquardt algorithm.[34]

**Dynamic light scattering (DLS) (Table S4 and Figure S5-S16).** Particle size measurements were performed by dynamic light scattering on a Vasco 3 nanoparticle size analyzer supplied by Cordouan Technologies at 25°C using the cumulant model. Samples for DLS measurements were prepared by diluting one drop of latex with 5 mL of DI water. The laser power, time interval, and number of channels were adjusted for each sample to obtain a good autocorrelation function (ACF). The presented results are the average of 5 measurements.

**Total solids content measurement (TSC).** 250-500 mg of latex were placed on an aluminum pan loaded with 3-5 mg of MEHQ (inhibitor) and subsequently placed in an oven at 80°C for 24 h under vacuum at $5 \times 10^{-2}$ mbar. The final weight was measured and the TSC calculated according to Eq. (1).

$$TSC(\%) = \frac{W_{latex} \times 100}{W_{dry\ latex}} \qquad\qquad Eq.(1)$$

Where $W_{latex}$ is the weight of the latex (without inhibitor) and $W_{dry\ latex}$ is the final weight of the dried latex (without inhibitor).

**Gel content measurements.** The gel content of the polymers was measured by placing 500 mg of dried polymer in a 60 mL cellulose thimble and extracted over 24 h by Soxhlet using 180 mL of THF, at 35°C and 100 mbar. The thimble was then recovered and washed with 10 mL of THF, then dried under the fume hood overnight and in a ventilated oven at 40°C and atmospheric pressure for 2-4 hours (till the weight was constant). The gel content was calculated according to Eq. (2) below.

$$Gel\ content(\%) = \frac{W_{final\ solid} \times 100}{W_{initial\ solid}} \qquad\qquad Eq.\,(2)$$

Where $W_{initial\ solid}$ is the initial polymer weight and $W_{final\ solid}$ is the weight of the polymer remaining in the thimble.

**Thermogravimetric analysis (TGA) (Table S7-S8 and Figure S17-S18).** Thermogravimetric analysis was performed on 5-10 mg samples on a TGA Q50 apparatus from TA Instruments from 20°C to 580°C, in an aluminum pan, at a heating rate of 20°C min$^{-1}$, under nitrogen and air.

**Differential scanning calorimetry (DSC) (Figure S19-S22).** DSC measurements were performed on 10–15 mg samples, under nitrogen atmosphere, with a Netzsch DSC 200 F3 instrument using the following heating/cooling cycle: first cooling ramp from room temperature (ca. 20°C) to −100°C at 20°C min$^{-1}$, isotherm plateau at −100°C for 10 min, first heating ramp from −100°C to 100°C at 20°C min$^{-1}$, second cooling stage from 100°C to −100°C at 20°C min$^{-1}$, isotherm plateau at −100°C for 10 min, second heating ramp from −100°C to 100°C at 20°C min$^{-1}$, third cooling stage from 100°C to −100°C at 20°C min$^{-1}$, isotherm plateau at −100°C for 10 min, third heating ramp from −100 to 100°C and last cooling stage from 100°C to room temperature (ca. 20°C). $T_g$ values are given from the evaluation of the third heating ramp. Calibration of the instrument was performed with noble metals and checked with an indium sample.

**Contact angle measurements.** The hydrophobicity was determined using a contact angle system OCA20 coupled with a CCD-camera from Data Physics Instrument using the software SCA20 4.1. The measurements were made on 100 µm dried film of polymer prepared by casting a latex with a bar coater at 200 µm on glass plates previously cleaned with acetone. Films were dried at 25ºC for 24 h, under ambient atmosphere. Contact angle measurements were done at room temperature by the sessile drop technique with deionized water.

**Size exclusion chromatography (SEC) (Table S9 and Figure S23).** GPC from Agilent Technologies with its corresponding Agilent software, equipped with two PL1113-6300 ResiPore $300 \times 7.5$ mm columns (up to 500,000 g mol$^{-1}$) was used. The detector suite comprised of a 390-LC PL0390-0601 refractive index detector. The entire SEC-HPLC system was thermostated at 35°C. Calibration was performed with PMMA narrow standards. THF was used as the eluent at a flow rate of 1 mL min$^{-1}$. Typical sample concentration was 10 mg mL$^{-1}$.

**Tack and peel measurements (Figure S24-S33).** Tack and peel measurements were done using a texture analyser XT. Plus from Stable Micro System equipped with a load cell of 50 kg. Films of 100 µm were prepared using a bar coater on poly(ethyleneterephtalate) (PET) sheets. Samples were dried at 25ºC for 24 h. 19 mm wide strips were cut.

For the peel test, the PET-supported adhesive was applied on a glass surface and a 2 kg hand roller was rolled 3 times on the strip. The glass plates were clamped vertically and the PET-supported adhesive bended strip was clamped to the moving cell at 180º. The PET support was pulled at a constant speed of 5 mm min$^{-1}$ and the force necessary to pull out the paper was recorded.

For the tack measurements, the PET-supported adhesive was folded and clamped in the moving cell of the apparatus. The specimen was put in contact with a glass plate previously cleaned with

ethanol and acetone and then the loop was moved upwards at 5 mm min$^{-1}$. The force required to peel off the loop was measured.

**General procedure for emulsion polymerization.** The emulsion polymerization design and conditions were inspired by literature.[31,35] It was carried out in a 200 mL double-walled jacketed glass reactor with a U-shaped glass stirring rod. A solution (S1) containing NaPS (0.31g), NaHCO$_3$ (0.34g) and DI water (4.72g) was prepared. Butyl acrylate (BA), methyl methacrylate (MMA), methacrylic acid (MAA), ethoxy dihydroeugenyl methacrylate (EDMA) and tert-butyl mercaptan (as indicated in the formulations, **Table 1**) were weighed and mixed together. In all formulations, 15% of the total monomer mixture weight was separated and purged with argon for 30 min (S2). A monomer emulsion (S3) containing SDBS (0.24g), DI water (13.43g) and the rest of the monomers was prepared under vigorous agitation (500 rpm). When ethoxy eugenyl methacrylate (EEMA) was present in the formulation, it was only added to the S3 mixture. The rest of the surfactants (SDBS and Disponil® A 3065) was introduced as initial load in the reactor. The water was adjusted to target a TSC of 50%. After purging the reactor with argon for 30 min, S2 was introduced in the reactor under stirring at 200 rpm followed by 12% of S1 (at 80ºC under stirring at 200 rpm) and counted as time 0 min. After 10 min of reaction, the continuous feeding of S3 and 76% of S1 started and fed separately over 3 hours (under 200 rpm stirring, 80ºC and argon flow). The remaining S1 (12%) was introduced as a shot at the end of the polymerisation. The reaction was left under stirring at 200 rpm for 50 min at 80ºC as a post-polymerization step.

**Table 1.** General radical aqueous emulsion polymerization recipe.

| Ingredient | Mass (g) | % wbm[a] |
|---|---|---|
| Butyl acrylate | 45.00 | 87.00 |
| MMA | 0-6.21 | 0-12 |
| EDMA | 0-6.21 | 0-12 |
| EEMA | 0-0.52 | 0-1 |
| Methacrylic acid | 0.52 | 1.00 |
| Tert-dodecyl mercaptan | 0.03 | 0.06 |
| Sodium persulfate | 0.31 | 0.60 |
| Sodium bicarbonate | 0.34 | 0.66 |
| Disponil® A 3065 (65% active substance) | 1.12 | 2.17 |
| SDBS | 0.28 | 0.55 |
| Water | Adjusted for TSC of 50% | Adjusted for TSC of 50% |

[a] % wbm: weight fraction based on monomers.

## RESULTS AND DISCUSSION

Homopolymerization of eugenol-derived methacrylates by aqueous emulsion polymerization using different radical initiators was previously reported by our group.[30] It was demonstrated that EDMA (ethoxy dihydroeugenyl methacrylate) and EEMA (ethoxy eugenyl methacrylate) were readily polymerizable under aqueous emulsion polymerization conditions using different initiation systems without using special or high quantities of surfactants. In the present work, the copolymerization of EDMA, the eugenol-derived monomer without pendant double bonds, with BA, MMA and MAA was studied. Moreover, EEMA, which contains an allyl group, was later introduced in the formulation in a small quantity to observe the effect of a biobased functional

structural unit on the properties of the resulting acrylic latex. The synthesis of both EDMA and

EEMA monomers is achieved through a simple two-step pathway as reported previously.[27] Briefly,

the phenol group is ethoxylated using ethylene carbonate in a solvent-free reaction, followed by

the methacrylation using methacrylic anhydride (**Figure 1**). Both EDMA and EEMA are liquid at

25°C (EDMA m.p.:<0°C, EEMA m.p.:11°C)[27] and are miscible in the monomer mixture with up

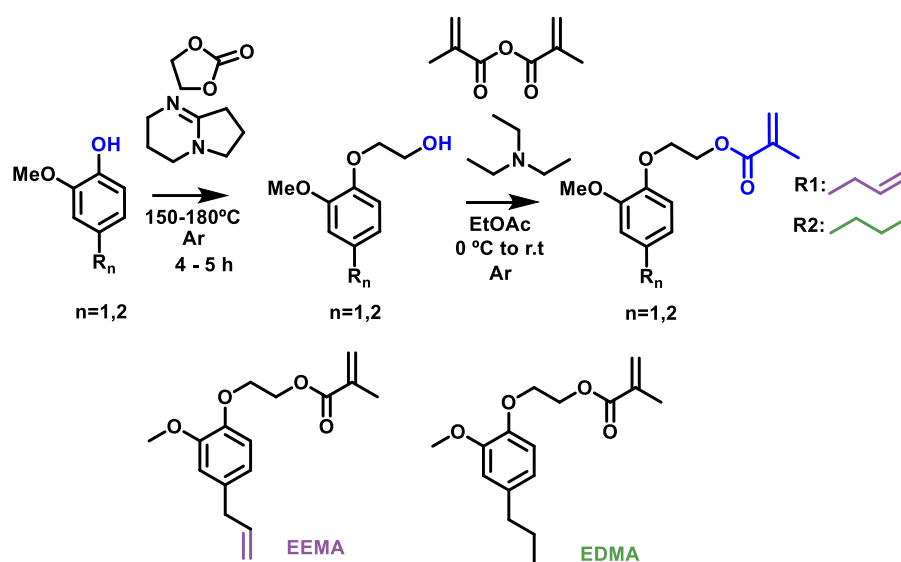to 87% wbm of butyl acrylate. No incompatibility was observed between MMA, BA, MAA and

EDMA or EEMA.



**Figure 1.** Synthesis of eugenol-derived methacrylates.

As part of this study, the reactivity ratios $r_{EDMA}$ and $r_{MMA}$ for the copolymerization of EDMA with

MMA were determined in benzene-$d_6$ at 70°C. These reactivity ratios are very close to unity

(**Table 2**), indicating that an almost ideal statistical copolymerization took place without

significant drift of monomer composition. Thus, EDMA behaves like MMA in radical

copolymerization.

**Table 2.** Reactivity ratios of EDMA and MMA (solution copolymerization in benzene-d$_6$ at 70°C).

| Reactivity ratios | Kelen-Tüdös | Non-Linear Least Squares[a] | Levenberg-Marquardt[b] |
|---|---|---|---|
| $r_{EDMA}$ | 1.08 | 0.95 | 1.06 |
| $r_{MMA}$ | 0.98 | 1.02 | 1.19 |

[a] Refer to Supporting Information for joint confidence intervals

[b] Refer to Supporting Information for standard errors

To begin the investigation on the emulsion polymerization, an initial formulation containing only petroleum-derived monomers (BA, MMA and MAA) was designed to obtain a theoretical $T_g$ value of −30°C, suitable for adhesive applications. Using the Fox equation[36] and the $T_g$ of the respective homopolymers (*i.e.* poly(BA) $T_g$ = −43°C,[37] poly(MMA) $T_g$ = 105°C,[37] poly(MAA) $T_g$ =228°C),[38] the target latex formulation shown in **Table 1** was designed (run F1 in **Table 3**). MMA was then replaced by EDMA and EEMA ($T_g$ of poly(EDMA) = 26°C, $T_g$ of poly(EEMA) = 48°C)[30] and the emulsion polymerization formulation was adapted so that the resulting copolymer had a $T_g$ close to the non-biobased one. All formulations are described in **Table 3**.

**Table 3.** Different latex formulations composition.

| Run | Monomer formulation (% wbm[a]) | Calculated $T_g$ |
|---|---|---|
| F1 | BA:MMA:MAA (87:12:1) | −30ºC |
| F2 | BA:MMA:EDMA:MAA (87:6:6:1) | −33ºC |
| F3 | BA:EDMA:MAA (87:12:1) | −35ºC |
| F4 | BA:EDMA:EEMA:MAA (87:11:1:1) | −35ºC |

[a] % wbm: weight fraction based on monomers.

All latexes were synthesized through a semi-batch process.[31] A period of pre-polymerization of 10 minutes was given between the first initiator shot (addition of 12% of the total persulfate solution to promote nucleation) and the continuous addition of the rest of the monomers and initiator (for particle growth).[39] At the end of the pre-emulsion mixture (S3) and initiator solution addition (3 h), a final shot of 12% of the total initiator and buffer was added to the latex to promote full conversion. Particle size, pH, gel content, solids content, number average molar mass and decomposition temperature under air and nitrogen are indicated in **Table 4**.

The first objective was to confirm that replacing a monomer that increases the $T_g$, such as MMA, with a eugenol-derived methacrylate in an emulsion polymerization formulation can be done while preserving acceptable properties for the resulting adhesives. As mentioned before, EDMA, the eugenol-derived monomer without a pendant double bond, was selected to avoid crosslinking and gel formation. EDMA has been proven to homopolymerize readily under aqueous emulsion polymerization conditions with different initiator systems and conditions such as potassium persulfate (KPS) at 70ºC, 4,4-azobis(4-cyanovaleric acid) (ACVA) at 70ºC and redox system

sodium metabisulfite/potassium persulfate (SMB/KPS) at 40ºC.[30] EDMA was introduced gradually into the formulation, starting with half of the total MMA weight fraction, reaching 6% wbm (run F2 in **Table 3**), then 100% of the MMA weight fraction, increasing to 12% wbm (run F3 in **Table 3**). In a second study, a small quantity of EEMA (possessing a pendant allyl group, **Figure 1**) was also included in the formulation (1% wbm of EDMA was replaced with EEMA). This experiment, which corresponds to run F4 in **Table 3**, casts some light on the effect of this functional monomer on the polymer properties.

The instantaneous monomer conversions and the cumulative monomer conversions are reported in **Figure 2** and **Figure 3** (Table S5-S6), respectively. All latexes exhibited instantaneous monomer conversions of above 83%, as expected for starved-feed conditions[40].
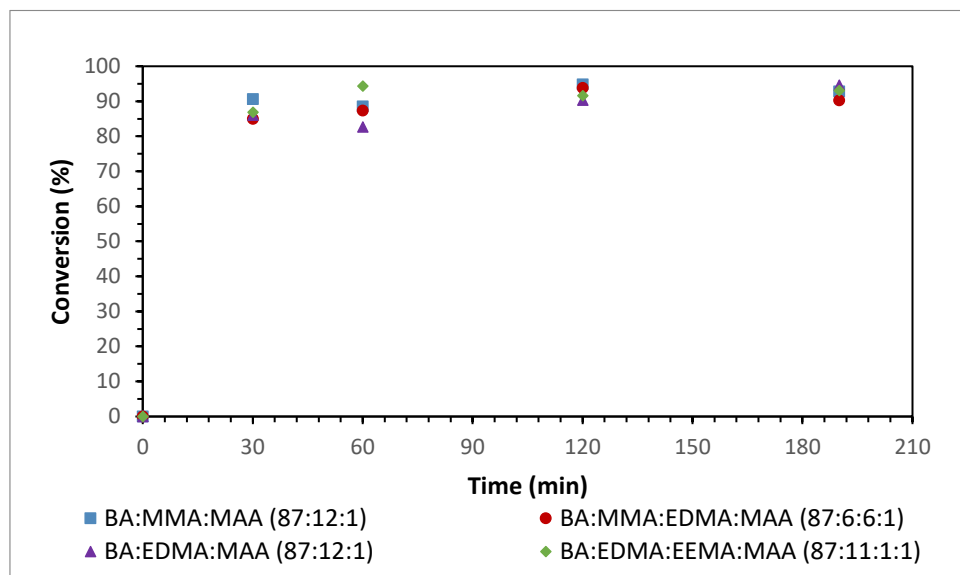


**Figure 2.** Instantaneous monomer conversions for semi-batch aqueous emulsion copolymerization initiated by NaPS at 80°C of the different latex formulations.
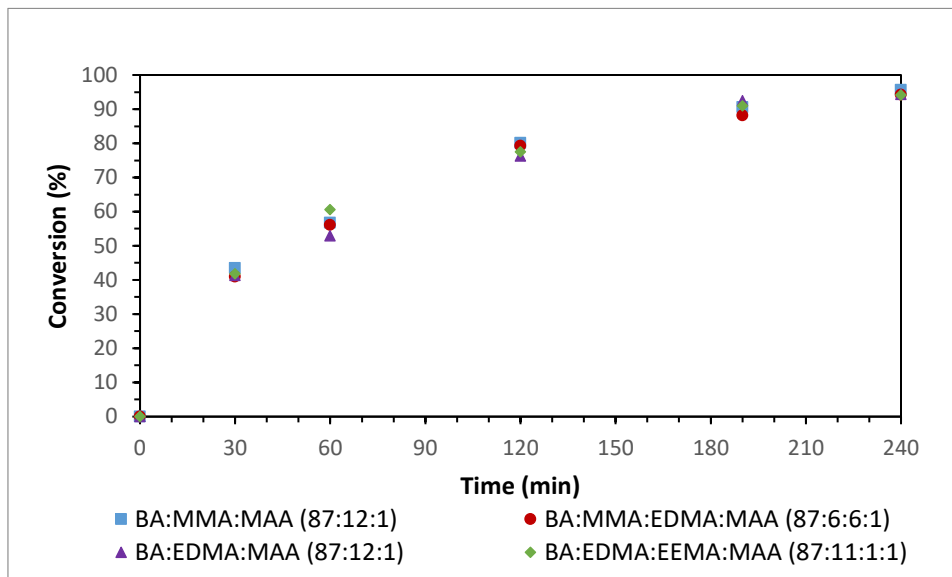
**Figure 3.** Cumulative monomer conversions for semi-batch aqueous emulsion copolymerization initiated by NaPS at 80°C of the different latex formulations.

**Table 4.** Latex characterizations.

| Formulation | F1 | F2 | F3 | F4 |
|---|---|---|---|---|
| Composition in % wbm[a] | BA:MMA:MAA (87:12:1) | BA:MMA:EDMA: MAA (87:6:6:1) | BA:EDMA: MAA (87:12:1) | BA:EDMA:EEMA MAA (87:11:1:1) |
| pH | 7.6 | 7.3 | 7.4 | 7.8 |
| $D_i$ (nm)[b] | 158 | 159 | 173 | 178 |
| TSC (%)[c] | 50.9 | 49.8 | 50.0 | 49.8 |
| Gel content (%) | 64 | 68 | 69 | 92 |
| $T_{d,5\%}$ Air (°C) | 320 | 324 | 321 | 313 |
| $T_{d,5\%}$ $N_2$ (°C) | 335 | 320 | 340 | 333 |
| $M_n$ (g.mol$^{-1}$) | 51,700 | 36,100 | 31,200 | 20,300 |
| Đ=$M_w$/$M_n$ | 5.58 | 3.27 | 2.78 | 2.55 |
| $T_g$ (°C) | −26 | −28 | −31 | −32 |
| Contact angle, DI Water (º) | 98.6±1.9 | 103.2±2.9 | 107.2±1.7 | 100.4±0.9 |

[a] % wbm: weight fraction based on monomer

[b] $D_i$: intensity-average particle diameter

[c] TSC (%): total solids content by gravimetry

The pH of the final latex did not change significantly with the addition of the biobased monomer (**Table 4**). This was expected as a buffer was used to avoid the acidification produced by NaPS decomposition,[41] which could lead to colloidal instability or coloration of the latexes.

Total solids contents superior to 49% were reached in all cases without using seeding techniques or high amounts of surfactants (**Table 4**). The latex particle size was only slightly increased (14 nm in F3 and 20 nm in F4) by the introduction of the biobased monomers in comparison to F1 (158 nm), but no loss of colloidal stability was observed.

Gel content was observed in all the formulations. The presence of butyl acrylate in the formulation enables intramolecular and intermolecular chain transfers to polymer. In both cases, tertiary radicals will be produced, which exhibit lower reactivity in comparison with secondary radicals. In the case of intramolecular chain transfer to polymer, usually known as backbiting, short chain branches would be obtained, whereas intermolecular chain transfer to polymer yields long chain branches. Subsequent termination by combination, after long chain branching, will produce a crosslinked network giving rise to gel formation.[42–44]Tert-dodecyl mercaptan was added as a chain transfer agent to decrease the degree of crosslinking in the resulting polymers. If some gel is desirable in adhesive formulations to increase shear strength, the content should not be so high that it affects the adhesive properties.[31] In the present experiments, gel content increased moderately with increasing EDMA biobased monomer fraction in the latex formulation (**Table 4**). However, a substantial increase in gel content was measured when EEMA was included in the formulation. The replacement of 1% wbm of EDMA in F3 by 1% wbm of EEMA to produce F4 resulted in an increase in gel content from 69% to 92%. The reactivity of a C-H bond towards hydrogen abstraction follows the order: allyl~benzyl>tertiary>secondary>primary>aryl~vinyl.[45,46] In the particular case of bis-allylic hydrogens, their dissociation energy is approximately 10 kcal mol$^{-1}$ lower than allylic hydrogen,[47] making them more labile. EEMA abstractable hydrogens can be considered as bis-allylic due to their position with respect to the aromatic ring and the allylic double bond. Thus, more hydrogen abstraction is expected in the case of EEMA than in the case

of EDMA. This has been observed in previous works, related to emulsion homopolymerization reaction, as the formation of crosslinked polymers and slower kinetics of polymerization (degradative chain transfer) were observed in the case of poly(EEMA) while poly(EDMA) remained soluble.[30] The F4 formulation, shows that even at very low concentrations, EEMA acts as an efficient crosslinking agent via side reactions involving its allyl group (cross-propagation with BA, and transfer to polymer by hydrogen abstraction, followed by termination by combination).[27,30] The molar mass and dispersity of the THF-soluble fraction of the polymer decreased with increasing biobased content. This could be due to the abstraction of the benzylic hydrogens present in EDMA, by butyl acrylate propagating radicals which are more prone to abstract hydrogens, leading to crosslinking and gelation. Thus, only the low molar mass fraction would stay soluble, artificially decreasing the molar masses.

The different contents of eugenol-derived monomers did not affect the thermal stability of the latexes as the 5% weight loss occurred between 320ºC and 340ºC under nitrogen, and 313ºC and 324ºC under air for all the polymers synthesized and did not follow any particular tendency (**Table 4**).

$T_g$ values for all formulations ranged between −26ºC and −32ºC (**Table 4**). The expected values according to the Fox equation for the formulations were −30ºC for F1, −33ºC for F2, and −35ºC for F3 and F4 (**Table 3**). All the formulations showed a slightly higher $T_g$ value, most probably due to some degree of crosslinking.[36]
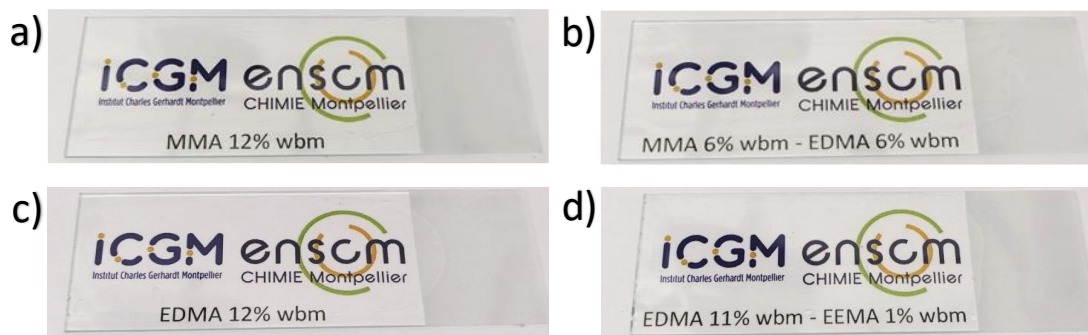
**Figure 4.** Polymer films prepared from latex formulations a) F1, b) F2, c) F3 and d) F4. ICGM and ENSCM are acknowledged for permission of using their logo.

Films were dried at 25ºC for 24 h and transparent films were obtained at the end of the drying period (**Figure 4**). Water contact angle measurements showed a decrease in hydrophilicity when MMA was replaced with eugenol-derived methacrylate, as the highest contact angle was reported for formulation F3 (107.2º) with 12% wbm of EDMA and the lowest for F1 (98.6º) with 12% wbm of MMA. The hydrophobic character of the eugenol-derived monomers is responsible for this effect. In the particular case of F4 with 11% wbm of EDMA and 1% wbm of EEMA, a reduction in the contact angle (100.4º) was observed in spite of the biobased monomer content. Possibly, the larger gel content in the case of F4 made the film formation less complete, leaving some hydrophilic channels and leading to a film with a less hydrophobic character (**Table 4**). Higher hydrophobicity is an advantageous characteristic as it reduces the wetting ability or hydration of the surface of the adhesive films.

Peel and tack tests were executed to assess the adhesive properties of the latexes (**Table 5**). A reduction in the peel force was observed when MMA was replaced with EDMA in the latex formulations. However, the value observed for the MMA-free latex (F3), 3.18 N.cm⁻¹, was higher than that of latex F2 (containing MMA and EDMA), 2.49 N.cm⁻¹. The addition of EEMA (latex F4) resulted in a drastic reduction of the peel force, in which the value dropped to 0.35 N.cm⁻¹

(**Figure 5**). This was expected due to the high gel content in F4 which decreases the adhesion performance of the polymer.[48] Commercial product Scotch Magic™ Tape was also assessed for comparison. Although peel force values of F2 and F3 were lower than the peel force value of F1, they were higher than that of commercial Magic™ Tape (2.00 N.cm⁻¹).[26] In the case of the loop tack tests, the reduction of force was also observed as the amount of biobased monomer increased (6.39 N for F2 compared to 9.35 N for F1), with again a significant drop for the formulation containing EEMA, F4 (2.75 N), due to the higher gel content. However, F2 and F3 had loop tack values of 6.39 N and 6.26 N respectively, which are higher than that measured for the commercial formulation Scotch Magic™ Tape (4.81 N) (**Figure 6**). Thus, the overall performance of the latexes is comparable to current commercial products, opening up the possibility for these two partially biobased formulations, F2 and F3, to be used as part of commercial adhesives.

**Table 5.** Adhesive properties of the films prepared from different latex formulations.

| Formulation | | Peel average value (N/cm)[a] | | Peel maximum value (N/cm)[a] | | Loop Tack (N) | |
|---|---|---|---|---|---|---|---|
| | | Value | Std[b] | Value | Std[b] | Value | Std[b] |
| BA:MMA:MAA (87:12:1) | F1 | 3.76 | 0.14 | 4.34 | 0.19 | 9.35 | 0.44 |
| BA:MMA:EDMA: MAA (87:6:6:1) | F2 | 2.49 | 0.10 | 3.08 | 0.12 | 6.39 | 1.34 |
| BA:EDMA: MAA (87:12:1) | F3 | 3.18 | 0.08 | 3.54 | 0.04 | 6.26 | 0.00 |
| BA:EDMA:EEMA MAA (87:11:1:1) | F4 | 0.35 | ND | 0.45 | ND | 2.75 | 0.17 |
| Scotch Magic™ Tape | | 2.00 | 0.061 | 2.31 | 0.09 | 4.81 | 0.03 |

[a] The peel force is normalized by the tape width 1.9 cm.
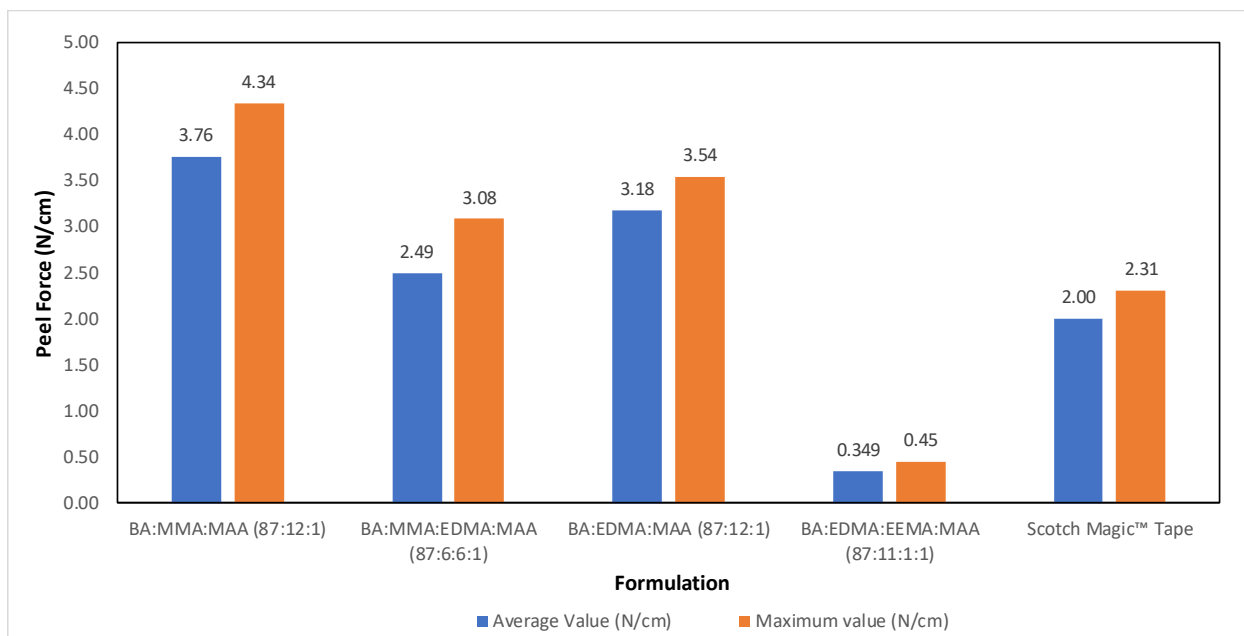
[b] Std: standard deviation.

**Figure 5.** Peel averages and maximum forces of the films prepared from different latex formulations (the peel force is normalized by the tape width 1.9 cm).
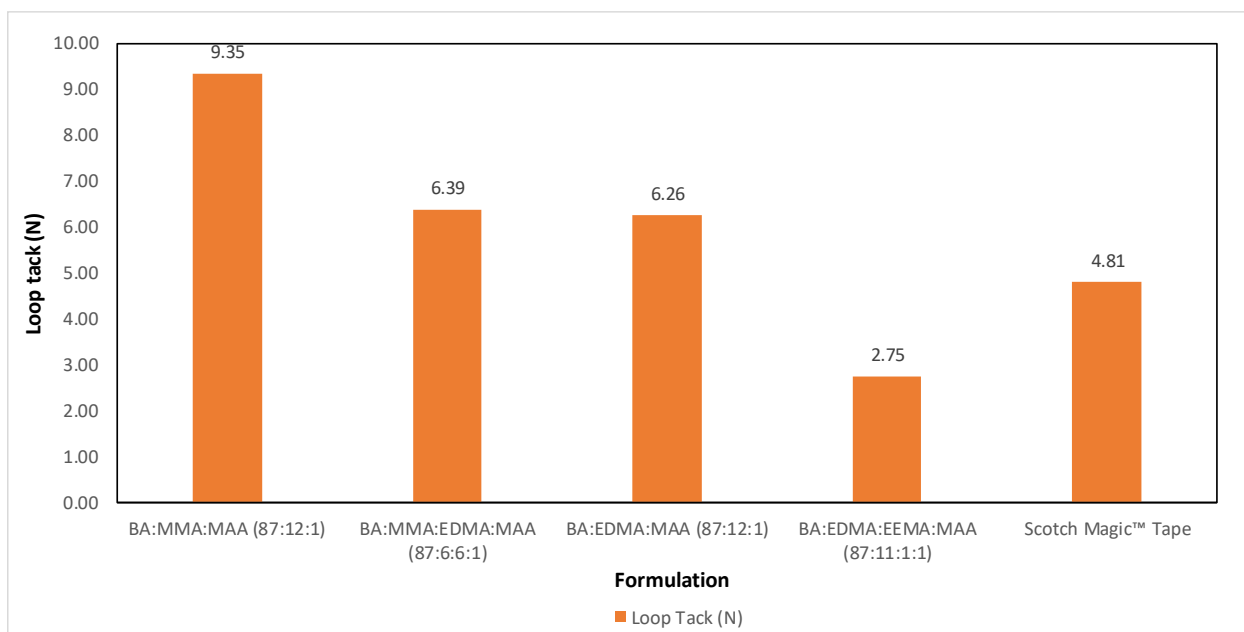


**Figure 6.** Tack forces of the films prepared from different latex formulations.

## CONCLUSIONS

Latexes containing up to 12% wbm of ethoxy dihydroeugenyl methacrylate (EDMA) and 50% total solids content, suitable for application as adhesives, were successfully prepared. The latexes were synthesized using a semi-batch process, which is suitable for scale-up. All formulations provided latexes with good colloidal stability and with particle sizes ranging from 159 to 178 nm in diameter. The copolymers remained stable up to 324°C under air and their $T_g$ ranged between −28 and −32°C, in good agreement with the values estimated with the Fox equation. The adhesive properties of the polymers were tested and the peel and tack forces were shown to be superior to those measured for a commercial product. Thus, the formulations containing EDMA could be suitable for adhesive applications. Fine-tuning of the partial replacement of petroleum-based monomers with monomers derived from biobased building blocks is a first but essential approach in paving the way to more sustainable and greener adhesives.

## ASSOCIATED CONTENT

Supporting information contains calculations of reactivity ratios for the copolymerization of EDMA with MMA, DLS, monomer conversions in emulsion polymerizations, TGA, DSC thermograms, SEC measurements, and 180º peel and loop tack measurements.

## AUTHOR INFORMATION

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REFERENCES

(1)     Gallezot, P. Conversion of Biomass to Selected Chemical Products. *Chem. Soc. Rev.* **2012**, *41*, 1538–1558.

(2)     Gandini, A. The Irruption of Polymers from Renewable Resources on the Scene of Macromolecular Science and Technology. *Green Chem.* **2011**, *13*, 1061.

(3)     Gandini, A.; Lacerda, T. M. From Monomers to Polymers from Renewable Resources: Recent Advances. *Prog. Polym. Sci.* **2015**, *48*, 1–39.

(4)     Gandini, A.; Lacerda, T. M.; Carvalho, A. J. F. F.; Trovatti, E. Progress of Polymers from Renewable Resources: Furans, Vegetable Oils, and Polysaccharides. *Chem. Rev.* **2016**, *116*, 1637–1669.

(5)     Kristufek, S. L.; Wacker, K. T.; Tsao, Y.-Y. T. Y. T.; Su, L.; Wooley, K. L. Monomer Design Strategies to Create Natural Product-Based Polymer Materials. *Nat. Prod. Rep.* **2017**, *34*, 433–459.

(6)     Anastas, P.; Eghbali, N. Green Chemistry: Principles and Practice. *Chem. Soc. Rev.* **2010**, *39*, 301–312.

(7)     Asua, J. M. Emulsion Polymerization: From Fundamental Mechanisms to Process Developments. *J. Polym. Sci. Part A Polym. Chem.* **2004**, *42*, 1025–1041.

(8)     Thickett, S. C.; Gilbert, R. G. Emulsion Polymerization: State of the Art in Kinetics and Mechanisms. *Polymer (Guildf).* **2007**, *48*, 6965–6991.

(9)    Daniel, J.-C.; Pichot, C. *Les Latex Synthétiques: Élaboration et Applications*; Daniel, J.-C., Pichot, C., Eds.; Tec&Doc-Lavoisier: Paris, 2006.

(10)   MarketWatch. *Synthetic Rubber Industry 2020 Global Market Research Report*; NY, 2020.

(11)   Molina-Gutiérrez, S.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Radical Polymerization of Biobased Monomers in Aqueous Dispersed Media. *Green Chem.* **2019**, *21*, 36–53.

(12)   Thames, S. F.; Rawlins, J. W.; Mendon, S. K. Miniemulsion Polymerization of Vegetable Oil Macromonomers. In *Miniemulsion Polymerization Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2010; Vol. 57, pp 139–171.

(13)   Moreno, M.; Lampard, C.; Williams, N.; Lago, E.; Emmett, S.; Goikoetxea, M.; Barandiaran, M. J. Eco-Paints from Bio-Based Fatty Acid Derivative Latexes. *Prog. Org. Coatings* **2015**, *81*, 101–106.

(14)   Demchuk, Z.; Kohut, A.; Voronov, S.; Voronov, A. Versatile Platform for Controlling Properties of Plant Oil-Based Latex Polymer Networks. *ACS Sustain. Chem. Eng.* **2018**, *6*, 2780–2786.

(15)   Asua, J. M. Miniemulsion Polymerization. *Prog. Polym. Sci.* **2002**, *27*, 1283–1346.

(16)   Asua, J. M. Challenges for Industrialization of Miniemulsion Polymerization. *Prog. Polym. Sci.* **2014**, *39*, 1797–1826.

(17)   Wool, R. P.; Bunker, S. P. Pressure Sensitive Adhesives from Plant Oils. 6,646,033 B2, 2003.

(18)    Bunker, S.; Staller, C.; Willenbacher, N.; Wool, R. Miniemulsion Polymerization of Acrylated Methyl Oleate for Pressure Sensitive Adhesives. *Int. J. Adhes. Adhes.* **2003**, *23*, 29–38.

(19)    Badía, A.; Movellan, J.; Barandiaran, M. J.; Leiza, J. R. High Biobased Content Latexes for Development of Sustainable Pressure Sensitive Adhesives. *Ind. Eng. Chem. Res.* **2018**, *57*, 14509–14516.

(20)    Kingsley, K.; Shevchuk, O.; Demchuk, Z.; Voronov, S.; Voronov, A. The Features of Emulsion Copolymerization for Plant Oil-Based Vinyl Monomers and Styrene. *Ind. Crops Prod.* **2017**, *109*, 274–280.

(21)    Moreno, M.; Goikoetxea, M.; Barandiaran, M. J. Biobased-Waterborne Homopolymers from Oleic Acid Derivatives. *J. Polym. Sci. Part A Polym. Chem.* **2012**, *50*, 4628–4637.

(22)    Delatte, D.; Kaya, E.; Kolibal, L. G.; Mendon, S. K.; Rawlins, J. W.; Thames, S. F. Synthesis and Characterization of a Soybean Oil-Based Macromonomer. *J. Appl. Polym. Sci.* **2014**, *131*, 40249.

(23)    Zhang, L.; Cao, Y.; Wang, L.; Shao, L.; Bai, Y. Polyacrylate Emulsion Containing IBOMA for Removable Pressure Sensitive Adhesives. *J. Appl. Polym. Sci.* **2016**, *133*, 42886.

(24)    Ren, S.; Trevino, E.; Dubé, M. A. Copolymerization of Limonene with n -Butyl Acrylate. *Macromol. React. Eng.* **2015**, *9*, 339–349.

(25)    Bloembergen, S. US 6,242,593 B1, Environmentally Friendly Sugar-Based Vinyl Monomer Useful in Repulpable Adhesives and Other Applications, 2001.

(26)    Wang, S.; Shuai, L.; Saha, B.; Vlachos, D. G.; Epps, T. H. From Tree to Tape: Direct

Synthesis of Pressure Sensitive Adhesives from Depolymerized Raw Lignocellulosic Biomass. *ACS Cent. Sci.* **2018**, *4*, 701–708.

(27)    Molina-Gutiérrez, S.; Manseri, A.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Eugenol: A Promising Building Block for Synthesis of Radically Polymerizable Monomers. *Macromol. Chem. Phys.* **2019**, *220*, 1900179.

(28)    Khalil, A. A.; Rahman, U. ur; Khan, M. R.; Sahar, A.; Mehmood, T.; Khan, M. Essential Oil Eugenol: Sources, Extraction Techniques and Nutraceutical Perspectives. *RSC Adv.* **2017**, *7*, 32669–32681.

(29)    Azadi, P.; Inderwildi, O. R.; Farnood, R.; King, D. A. Liquid Fuels, Hydrogen and Chemicals from Lignin: A Critical Review. *Renew. Sustain. Energy Rev.* **2013**, *21*, 506–523.

(30)    Molina-Gutiérrez, S.; Ladmiral, V.; Bongiovanni, R.; Caillol, S.; Lacroix-Desmazes, P. Emulsion Polymerization of Dihydroeugenol-, Eugenol-, and Isoeugenol-Derived Methacrylates. *Ind. Eng. Chem. Res.* **2019**, *58*, 21155–21164.

(31)    Jovanović, R.; Dubé, M. A. Emulsion-Based Pressure-Sensitive Adhesives: A Review. *J. Macromol. Sci. Part C Polym. Rev.* **2004**, *44*, 1–51.

(32)    Kelen, T.; Tüdös, F. Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. I. A New Improved Linear Graphic Method. *J. Macromol. Sci. Part A - Chem.* **1975**, *9*, 1–27.

(33)    Van Den Brink, M.; Van Herk, A. M.; German, A. L. Nonlinear Regression by Visualization of the Sum of Residual Space Applied to the Integrated Copolymerization Equation with

Errors in All Variables. I. Introduction of the Model, Simulations and Design of Experiments. *J. Polym. Sci. Part A Polym. Chem.* **1999**, *37*, 3793–3803.

(34)   Moré, J. J. The Levenberg-Marquardt Algorithm: Implementation and Theory. In *Numerical Analysis. Lecture Notes in Mathematics*; Watson, G.A., Ed.; Springer, Berlin, Heidelberg, 1978; Vol. 630, pp 105–116.

(35)   Mishra, S.; Singh, J.; Choudhary, V. Synthesis and Characterization of Butyl Acrylate/Methyl Methacrylate/Glycidyl Methacrylate Latexes. *J. Appl. Polym. Sci.* **2010**, *115*, 549–557.

(36)   Fox, T. G.; Loshaek, S. Influence of Molecular Weight and Degree of Crosslinking on the Specific Volume and Glass Temperature of Polymers. *J. Polym. Sci.* **1955**, *15*, 371–390.

(37)   Penzel, E.; Rieger, J.; Schneider, H. A. The Glass Transition Temperature of Random Copolymers: 1. Experimental Data and the Gordon-Taylor Equation. *Polymer (Guildf).* **1997**, *38*, 325–337.

(38)   Jones, J. A.; Novo, N.; Flagler, K.; Pagnucco, C. D.; Carew, S.; Cheong, C.; Kong, X. Z.; Burke, N. A. D.; Stöver, H. D. H. Thermoresponsive Copolymers of Methacrylic Acid and Poly(Ethylene Glycol) Methyl Ether Methacrylate. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43*, 6095–6104.

(39)   Li, B.; Brooks, B. W. Semi-Batch Processes for Emulsion Polymerisation. *Polym. Int.* **1992**, *29*, 41–46.

(40)   Van Herk, A. M. *Chemistry and Technology of Emulsion Polymerisation*; van Herk, A. M., Ed.; John Wiley & Sons Ltd: Oxford, UK, 2013.

(41)     Santos, A. M.; Vindevoghel, P.; Graillat, C.; Guyot, A.; Guillot, J. Study of the Thermal Decomposition of Potassium Persulfate by Potentiometry and Capillary Electrophoresis. *J. Polym. Sci. Part A Polym. Chem.* **1996**, *34*, 1271–1281.

(42)     Britton, D. J.; Lovell, P. A.; Heatley, F.; Venkatesh, R. Chain Transfer to Polymer in Emulsion Copolymerizations. *Macromol. Symp.* **2001**, *175*, 95–104.

(43)     Chauvet, J.; Asua, J. M.; Leiza, J. R. Independent Control of Sol Molar Mass and Gel Content in Acrylate Polymer/Latexes. *Polymer (Guildf).* **2005**, *46*, 9555–9561.

(44)     González, I.; Leiza, J. R.; Asua, J. M. Exploring the Limits of Branching and Gel Content in the Emulsion Polymerization of n -BA. *Macromolecules* **2006**, *39*, 5015–5020.

(45)     Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry Part A: Structure and Mechanisms*, 5º Ed.; Springer, Ed.; New York, 2008.

(46)     Zhou, C.-W.; Simmie, J. M.; Somers, K. P.; Goldsmith, C. F.; Curran, H. J. Chemical Kinetics of Hydrogen Atom Abstraction from Allylic Sites by $3 O 2$; Implications for Combustion Modeling and Simulation. *J. Phys. Chem. A* **2017**, *121*, 1890–1899.

(47)     Porter, N. A.; Caldwell, S. E.; Mills, K. A. Mechanisms of Free Radical Oxidation of Unsaturated Lipids. *Lipids* **1995**, *30*, 277–290.

(48)     Lee, J.-H.; Lee, T.-H.; Shim, K.-S.; Park, J.-W.; Kim, H.-J.; Kim, Y.; Jung, S. Effect of Crosslinking Density on Adhesion Performance and Flexibility Properties of Acrylic Pressure Sensitive Adhesives for Flexible Display Applications. *Int. J. Adhes. Adhes.* **2017**, *74*, 137–143.

SYNOPSIS

The article presents the emulsion copolymerization of eugenol and dihydroeugenol-derived methacrylates to produce latexes for adhesive applications

FOR TABLE OF CONTENTS ONLY

Manuscript title: Radical aqueous emulsion copolymerization of eugenol-derived monomers for adhesive applications

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Eugenol-derived methacrylates → Emulsion Polymerization → Biobased adhesives