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Emulsion polymerization of dihydroeugenol, eugenol and isoeugenol derived methacrylates

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KEYWORDS: eugenol, emulsion polymerization, biobased latex, crosslinking

ABSTRACT

The use of biobased monomers in emulsion polymerization arises as an attractive option for the synthesis of green polymers. Eugenol, a naturally occurring phenol, currently mainly produced from clove oil, but which could be also obtained by depolymerization of lignin, is an interesting molecule for the preparation of biobased monomers and polymers. Readily polymerizable functional groups can be easily introduced into its chemical structure through modification of the phenol group. In the present work, eugenol-based methacrylates have been used as monomers in emulsion radical polymerization with different initiation systems. Stable latexes of poly(ethoxy dihydroeugenyl methacrylate), poly(ethoxy eugenyl methacrylate) and poly(ethoxy isoeugenyl methacrylate) with particle diameter size in the range 45 nm - 71 nm were successfully obtained.

Glass transition temperatures of the resulting polymers ranged between 20 and 72°C. This study opens the way to the use of these new biobased monomers into latexes formulation for adhesives and coatings applications.

INTRODUCTION

Due to current environmental concerns and regulations, the use of biobased molecules derived from renewable sources to replace petroleum-based ones for the production of materials is strongly encouraged.[1,2] Several recent reviews dealing with the use of such molecules in polymerization for the production of novel materials have been published.[3–7] In many cases, the modification of the chemical structure of the biobased molecules is necessary to enhance their reactivity or permit their polymerization. For example, with regards to radical polymerization, it has been demonstrated that the double bonds present in certain fatty acids are not reactive enough and that phenol groups in tannins or lignin-based monomers act as inhibitors.[8,9] Thus, several modifications have been performed to introduce radically polymerizable groups which are not widely present in biobased molecules.[10–13]

Molecules derived from readily available and renewable biomass feedstock are of great advantage. One can indeed select building blocks from a vast array of functional molecules such as terpenes, vegetable oils, lipids, carbohydrates, proteins or lignin derivatives.[14] Eugenol, is a naturally occurring phenol, obtained from several plants including clove buds, cinnamon bark, tulsi leaves, turmeric, pepper, ginger, oregano and thyme.[15] It can also be obtained by depolymerization of lignin.[16,17] Although depolymerization of lignin is not yet an efficient process, significant research efforts have been conducted in this field as it would offer the possibility to produce highly valuable molecules such as vanillin and eugenol in large quantities and with cost-efficient procedures.[18,19]

Due to the presence of several functional groups within its structure, eugenol is an attractive building block for biobased monomers. Readily polymerizable groups such as (meth)acrylates can easily be introduced in its chemical structure by modification of the phenol functional group, as previously reported by Rojo et al.,[20] who functionalized eugenol to produce methacrylate derivatives for orthopedic and dental cements. These methacrylic eugenol-derived monomers were synthesized in two ways: first, via the incorporation of the methacrylic group directly onto the phenol by reaction with methacryloyl chloride leading to eugenyl methacrylate, and secondly, by introduction of an ethoxy spacer group to produce ethoxy eugenyl methacrylate. Both monomers were polymerized in toluene solution with 2,2'-azobisisobutyronitrile (AIBN) as the initiator. The resulting homopolymers were only soluble in organic solvent at low conversion (<10% monomer conversion). The polymerization proceeded primarily through the methacrylic double bond, but partial participation of the allylic double bond to the polymerization produced insoluble crosslinked polymers at higher conversion. Soluble copolymers of ethoxyeugenyl methacrylate and eugenyl methacrylate with ethyl methacrylate were also produced at low conversion. Deng et al. used eugenyl methacrylate in aqueous suspension polymerization using poly(vinyl alcohol) as stabilizer and AIBN as the initiator.[21] In their work, the authors took advantage of the allylic double bond present in eugenyl methacrylate, which was envisioned as a difunctional monomer able to polymerize and crosslink the resulting polymer chains simultaneously. Microspheres with diameter ranging from 500 to 800 μm were obtained and their oil absorbency properties were studied for applications in environmental protection.

Equally, isoeugenol and dihydroeugenol (the hydrogenated form of eugenol) are also interesting molecules for the development of biobased monomers, using the same strategy to introduce (meth)acrylate groups. Isoeugenol can be also obtained from clove oil[22] and lignin.[23] It

can also be synthesized via eugenol isomerization.[24] As natural phenols, these molecules are potential substitutes for aromatic monomers. Recently, the synthesis of a platform of radically polymerizable (meth)acrylates derived from eugenol, isoeugenol and dihydroeugenol, has been reported by our group, and their solution homopolymerization was studied in toluene.[25]

We believe that green chemistry principles should be implemented in the pursuit of sustainable biobased polymers. Not only the design of less toxic monomers and the use of renewable feedstock must be achieved, but less hazardous chemical synthesis and processes involving the use of safer solvents and reactants must also be implemented.[26,27] The reduction of volatile organic compounds (VOCs) can be attained through environmentally friendly polymerization methods such as aqueous emulsion or suspension polymerizations. The use of water as the continuous phase has several advantages: it is an innocuous and non-flammable solvent; it reduces the viscosity of the reaction medium and improves heat transfer enabling easier reaction temperature control. Polymerization in aqueous dispersed media involves several related processes such as: emulsion polymerization, miniemulsion polymerization, microemulsion polymerization, dispersion polymerization, and suspension polymerization.[28–40] Emulsion and suspension polymerizations processes are used at an industrial scale, whilst miniemulsion polymerization offers an alternative approach for very hydrophobic monomers; however, this technique has several constraints which hinders its wider industrial exploitation.[31,41] Hence, emulsion polymerization of biobased monomers is gaining increasing interest in both the academic and the industrial communities and has recently been reviewed by our team.[13]

In the present work, aqueous emulsion polymerization of biobased methacrylate monomers derived from eugenol, isoeugenol and dihydroeugenol (named EEMA, EIMA and EDMA

respectively, **Figure 1**) is explored for the first time as a greener route to biobased aromatic polymer latexes.

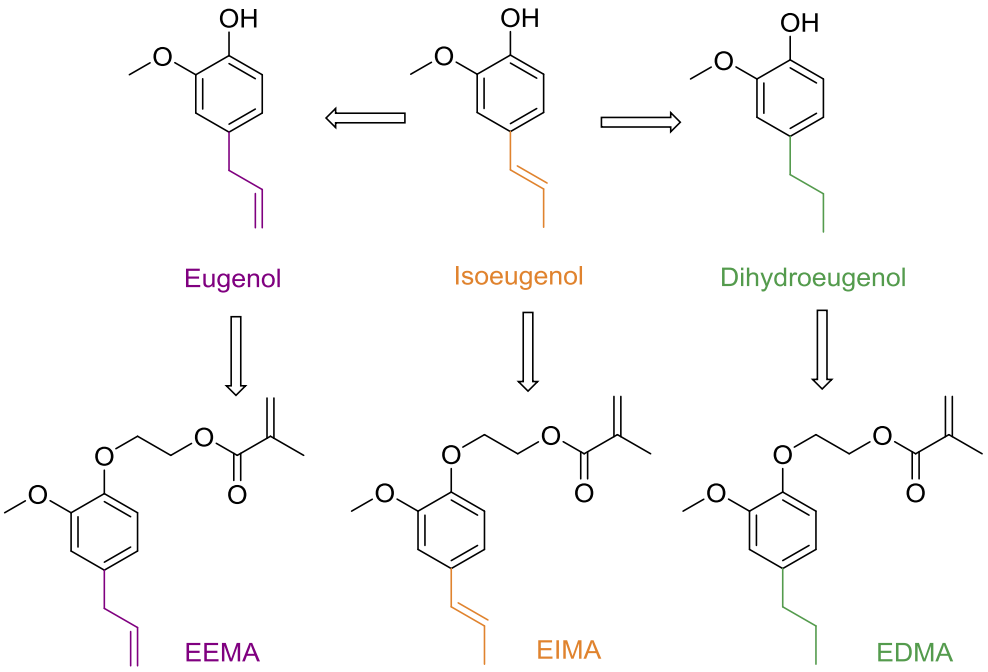


Figure 1. Eugenol-derived methacrylates

To the best of our knowledge, none of the monomers reported herein have been previously synthesized using the proposed synthetic pathway nor used in aqueous emulsion polymerization. Indeed, not only the synthesis of radically polymerizable biobased monomers was targeted but also their application in environmentally friendly processes such as aqueous emulsion radical polymerization. This study was conducted to assess the feasibility of this process with such biobased monomers under different experimental conditions, targeting potential applications in coatings and adhesives.

EXPERIMENTAL

Materials

Potassium persulfate (KPS, ≥99.0%, Aldrich), 4,4′-azobis(4-cyanovaleric acid) (ACVA, ≥98.0%, Fluka), sodium dodecyl sulfate (SDS, >99%, Aldrich), 1,4-bis(trimethylsilyl)benzene (BTB, 96%, Aldrich), sodium metabisulfite $Na_2S_2O_5$ (SMB, 99%, Aldrich), $NaHCO_3$ (99.7%, Aldrich) were used as received. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%, Fluka) was purified by recrystallization in methanol and dried under vacuum before use. Butyl acrylate (BA, ≥99.0%, Aldrich) was distilled under vacuum prior to use. Deionized water (DIW) (1 μS cm^{-1}) was obtained using a D8 ion exchange demineralizer from A2E Affinage de L'Eau. EDMA, EIMA and EEMA monomers were synthesized as described in a previous article from our group.[25]

Methods

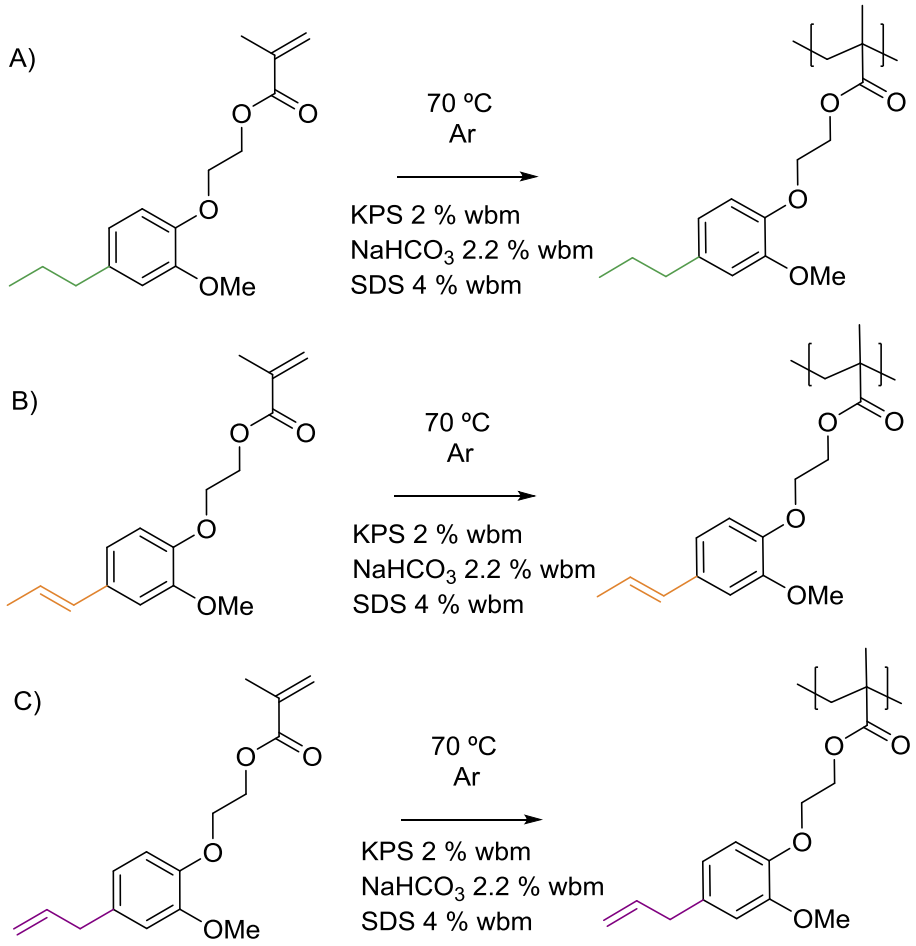
General procedure for emulsion polymerization with thermal initiation using KPS at 70°C (Scheme 1). The emulsion polymerization by thermal initiation was carried out in a 50 mL double-walled jacketed glass reactor with a U-shaped glass stirring rod. For a latex at 12.5-13.7 wt% solids content, eugenol derived methacrylate (15 mmol) was placed in a glass vial and purged with argon for 15 minutes. 31.6 g of DI water, SDS (4 % wbm, weight based on monomer) and $NaHCO_3$ (2.2 % wbm, 1:3.5 molar ratio KPS:$NaHCO_3$), were placed in the reactor and degassed with argon for 30 min. The reactor was heated to 70°C. The degassed monomer was added to the reactor using a syringe and a degassed solution of KPS (2 % wbm) in 4 g of DI water (out of the 31.6 g of DI water previously degassed with argon) was finally added. The reaction mixture was kept under a small flux of argon and mechanical stirring at 250 rpm.

Monomer conversion was followed through ^{1}H-NMR using $CDCl_3$ as deuterated solvent. 1,4-bis(trimethylsilyl)benzene (BTB) was added as internal standard in the case of EEMA.

Emulsion polymerization of EDMA with thermal initiation using KPS. EDMA (4.183 g, 15 mmol), DI water (31.642 g), SDS (0.168 g, 4 % wbm) and $NaHCO_3$ (0.092 g, 2.2 % wbm) and KPS (0.084 g, 2 % wbm). 13.4 % solids content.

Emulsion polymerization of EIMA with thermal initiation using KPS. EIMA (4.179 g, 15 mmol), DI water (31.647 g), SDS (0.167 g, 4% wbm) and $NaHCO_3$ (0.093 g, 2.2 % wbm of monomer) and KPS (0.084g, 2 % wbm). 13.7 % solids content.

Emulsion polymerization of EEMA with thermal initiation using KPS. EEMA (4.152 g, 15 mmol), DI water (31.679 g), SDS (0.177 g, 4.2% wbm) and $NaHCO_3$ (0.092 g, 2.2 % wbm of monomer), BTB (0.181 g, 4.3 %wbm) and KPS (0.084g, 2 % wbm). 12.5 % solids content.



Scheme 1. Emulsion homopolymerization of eugenol-derived methacrylates using KPS thermal initiation at 70°C: A) EDMA, B) EIMA, C) EEMA.

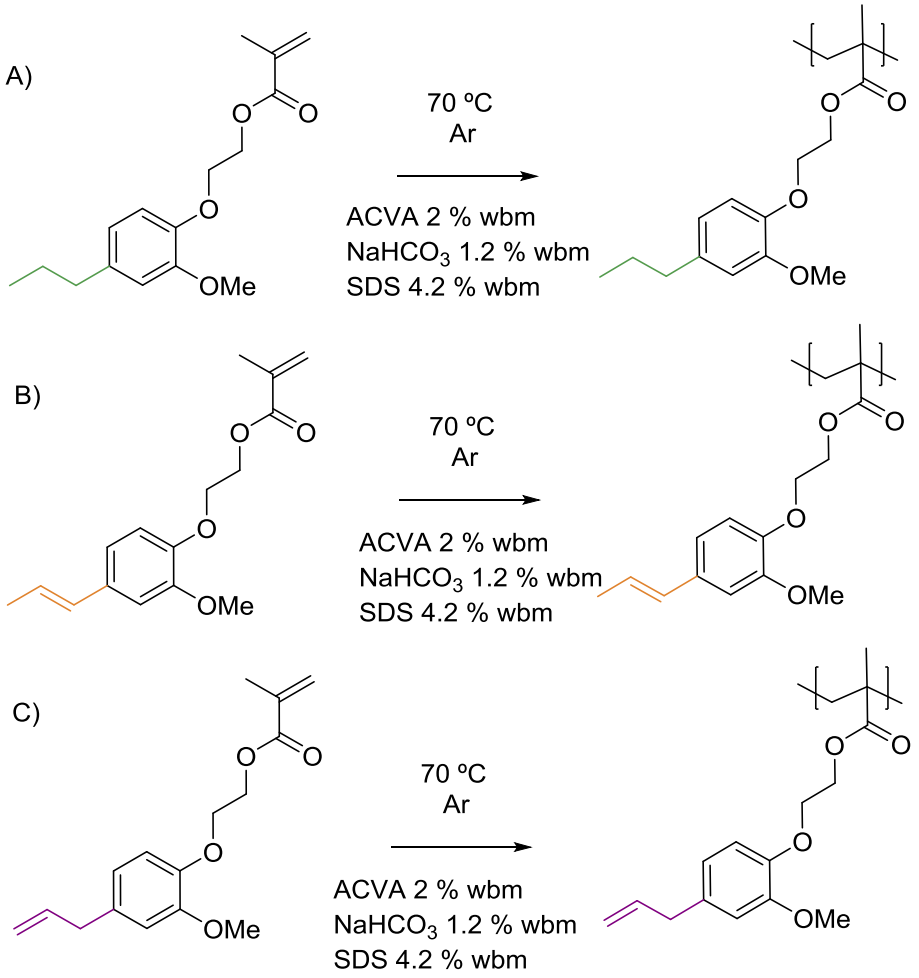
General procedure for emulsion polymerization with thermal initiation using ACVA at 70°C (Scheme 2). The emulsion polymerization was carried out in a 50 mL double-walled jacketed glass reactor with a U-shaped glass stirring rod. For a latex at 12.5 wt% solids, the eugenol derived methacrylate (15 mmol) was placed in a glass vial and purged with argon for 15 minutes. 31 g of DI water was mixed with $NaHCO_3$ (1.2 % wbm, 1:2 molar ratio ACVA:$NaHCO_3$) and 5 mL of the mixture were used to dissolve ACVA (2 % wbm). The remainder was mixed with SDS (4.2 % wbm), placed in the reactor and degassed with argon for 30 min. The reactor was heated to 70°C. The degassed monomer was added to the reactor

through a syringe and ACVA was finally added. The reaction mixture was kept under a small flux of argon and mechanical stirring at 250 rpm. Monomer conversion was followed through ^{1}H NMR using $CDCl_3$ as deuterated solvent. 1,4-bis(trimethylsilyl)benzene (BTB) was added as internal standard in the case of EEMA.

Emulsion polymerization of EDMA with thermal initiation using ACVA. EDMA (4.170 g, 15 mmol), DI water (31.859 g), SDS (0.175 g, 4.2 % wbm) and $NaHCO_3$ (0.051 g, 1.2 % wbm) and ACVA (0.083 g, 2.0 % wbm). 12.5 % solids content.

Emulsion polymerization of EIMA with thermal initiation using ACVA. EIMA (4.142 g, 15 mmol), DI water (31.104 g), SDS (0.177 g, 4.1 % wbm) and $NaHCO_3$ (0.050 g, 1.2 % wbm) and ACVA (0.083g, 2.0 % wbm). 12.5 % solids content.

Emulsion polymerization of EEMA with thermal initiation using ACVA. EEMA (4.150 g, 15 mmol), DI water (31.127 g), SDS (0.174g, 4.2 % wbm) and $NaHCO_3$ (0.052 g, 1.2 % wbm), BTB (0.034 g, 0.83 % wbm) and ACVA (0.084g, 2.0 % wbm). 12.5 % solids content.



Scheme 2. Emulsion homopolymerization of eugenol-derived methacrylates using thermal ACVA initiation at 70°C: A) EDMA, B) EIMA, C) EEMA.

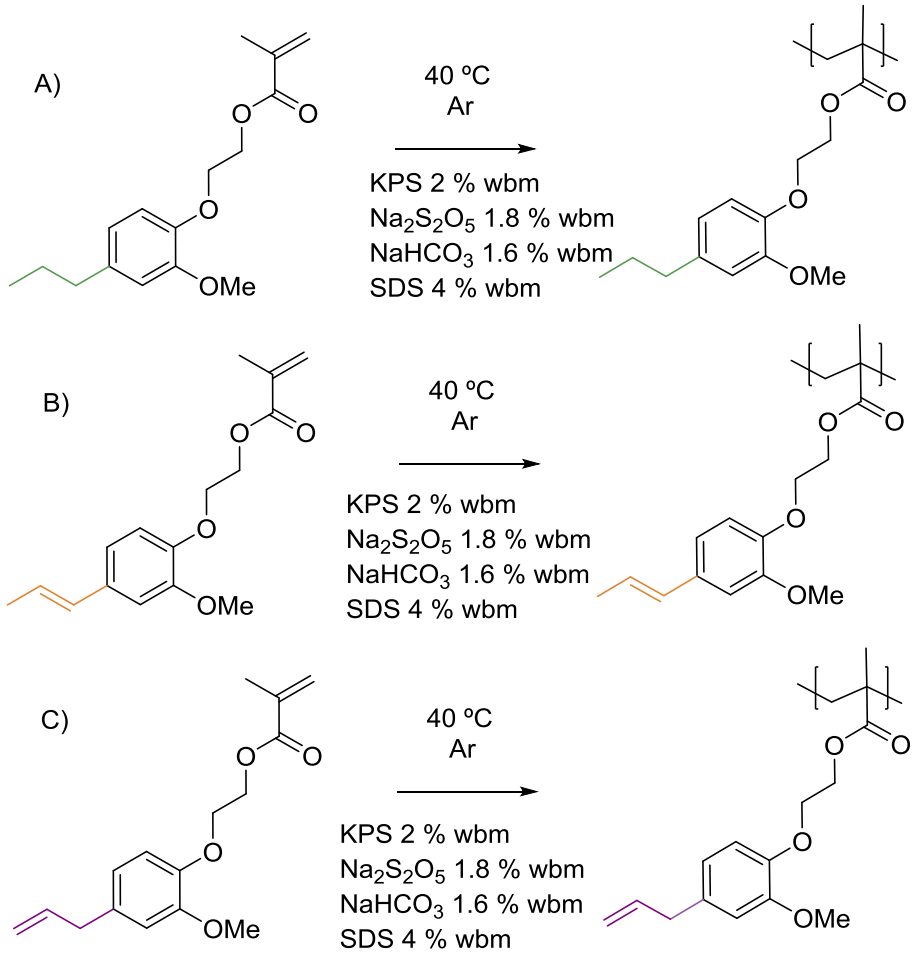
General procedure for emulsion polymerization with redox initiation at 40°C (Scheme 3). The emulsion polymerization was carried out in a 50 mL double-walled jacketed glass reactor with a U-shaped glass stirring rod. Eugenol-derived methacrylate (15 mmol) was purged with argon for 15 min. KPS (2 % wbm) was dissolved in 12 mL of the DI water and placed aside. SDS (4.0 % wbm), $NaHCO_3$ (1.6 % wbm, 1:2 molar ratio $Na_2S_2O_5$:$NaHCO_3$), $Na_2S_2O_5$ (1.8 % wbm, 1.3 SMB/KPS molar ratio) and the rest of the water were mixed, placed in the reactor, and

purged with argon for 30 min. The reactor was heated to 40°C and the eugenol derived monomer was added. Finally, 4 mL of the previously prepared solution of KPS were added in one shot and this was considered as t = 0. The rest of the KPS was added over four hours at 2 mL/h. The polymerization proceeded under mechanical stirring at 250 rpm. Monomer conversion was monitored by ^{1}H NMR using $CDCl_3$ as deuterated solvent (50 μL of latex were mixed with 0.5 mL of $CDCl_3$ and 20 μL of solution 0.05 M of BTB used as external standard in deuterated chloroform).

Emulsion polymerization of EDMA with redox initiation. EDMA (4.177 g, 15 mmol), DI water (32.00 g), SDS (0.168 g, 4.0 % wbm), $Na_2S_2O_5$ (0.077 g, 1.8 % wbm) and $NaHCO_3$ (0.068 g, 1.6 % wbm) and KPS (0.084 g, 2.0 % wbm). 12.5 % solids content.

Emulsion polymerization of EIMA with thermal initiation with redox initiation. EIMA (4.147 g, 15 mmol), DI water (31.761 g), SDS (0.166 g, 4.0 % wbm), $Na_2S_2O_5$ (0.075 g, 1.8 % wbm) and $NaHCO_3$ (0.0686 g, 1.6 % wbm) and KPS (0.083 g, 2.0 % wbm). 12.5 % solids content.

Emulsion polymerization of EEMA with thermal initiation with redox initiation. EEMA (4.159 g, 15 mmol), DI water (31.759 g), SDS (0.166 g, 4.0 % wbm), $Na_2S_2O_5$ (0.076 g, 1.8 % wbm) and $NaHCO_3$ (0.067 g, 1.6 % wbm) and KPS (0.083 g, 2.0 % wbm). 12.5 % solids content.



Scheme 3. Emulsion homopolymerization of eugenol-derived methacrylates using $Na_2S_2O_5$/KPS redox initiation at 40°C: A) EDMA, B) EIMA, C) EEMA.

Emulsion copolymerization of EDMA with butyl acrylate at 30 % solids content.

The emulsion polymerization by thermal initiation was carried out in a 50 mL double-walled jacketed glass reactor with a U-shaped glass stirring rod. For a latex at 30 wt% solids, EDMA and BA were placed in a glass vial and purged with argon for 15 minutes. DI water, SDS (1.3 % wbm) and $NaHCO_3$ (1.1 % wbm, 1:3.5 molar ratio KPS:$NaHCO_3$), were placed in the reactor and degassed with argon for 30 min. The reactor was heated to 70°C. The degassed monomer was added to the reactor through a syringe and KPS (1 % wbm), previously dissolved in 4 g of

DI water (from the total weight) was finally added. The reaction mixture was kept under a small flux or argon and mechanical stirring at 250 rpm.

Emulsion polymerization of 38 % wbm EDMA and 62 % butyl acrylate with thermal initiation with KPS. EDMA (4.1753 g, 38 % wbm), butyl acrylate (6.8123g, 62 % wbm), DI water (26.50 g), SDS (0.1428 g, 1.3 % wbm) and $NaHCO_3$ (0.1212 g, 1.1 % wbm) and KPS (0.1099 g, 1 % wbm). 30 % solids content.

CHARACTERIZATION

Nuclear magnetic resonance spectroscopy (NMR). Monomer conversions were determined through the monitoring of the methacrylate double bond by ^{1}H NMR spectroscopy with a Bruker Avance 400 MHz spectrometer at room temperature. The spectra were recorded by dissolving 0.1 mL of latex in 0.5 mL of $CDCl_3$ (when not indicated otherwise). 1,4-bis(trimethylsilyl)benzene (BTB) was used as internal standard.

Dynamic light scattering (DLS). 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 deionized water. The laser power, time interval, and number of channels were adjusted for each sample to obtain a good ACF (autocorrelation function). The presented results are the average of 5-10 measurements.

Thermogravimetric Analysis (TGA). Thermogravimetric analysis was performed on 10–15 mg samples on a TGA Q50 apparatus from TA Instruments from 20 °C to 590 °C, in an aluminum pan, at a heating rate of 10 °C/min, under nitrogen. Analyses were also performed with a PERSEUS® TGA 209 F1 Libra® from Netzch using a temperature ramp of 20°C/min from 20°C to 620°C under nitrogen flow of 40 mL/min in an alumina crucible.

Differential Scanning Calorimetry. 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 -40°C at 10 °C/min, isotherm plateau at−40 °C for 10 min, first heating ramp from −40 °C to 170 °C at 20 °C/min, cooling stage from 170 °C to−40 °C at 10 °C/min, isotherm plateau at−40 °C for 10 min, second heating ramp from −40 °C to 170 °C at 20 °C/min, cooling stage from 170 °C to−40 °C at 10 °C/min, isotherm plateau at−40 °C for 10 min, third heating ramp from -40 to 170º C and last cooling stage from 170 °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.

Gel content measurements. The gel content of the polymers was measured by placing approximately 50 mg of dried polymer in a Teflon pocket which was subsequently immersed in 10 mL of THF for 24 hours, then dried in a ventilated oven at 50°C for 4 hours. The gel content was calculated based on the initial (W_i) and final (W_f) polymer mass according to Eq. (1) below.

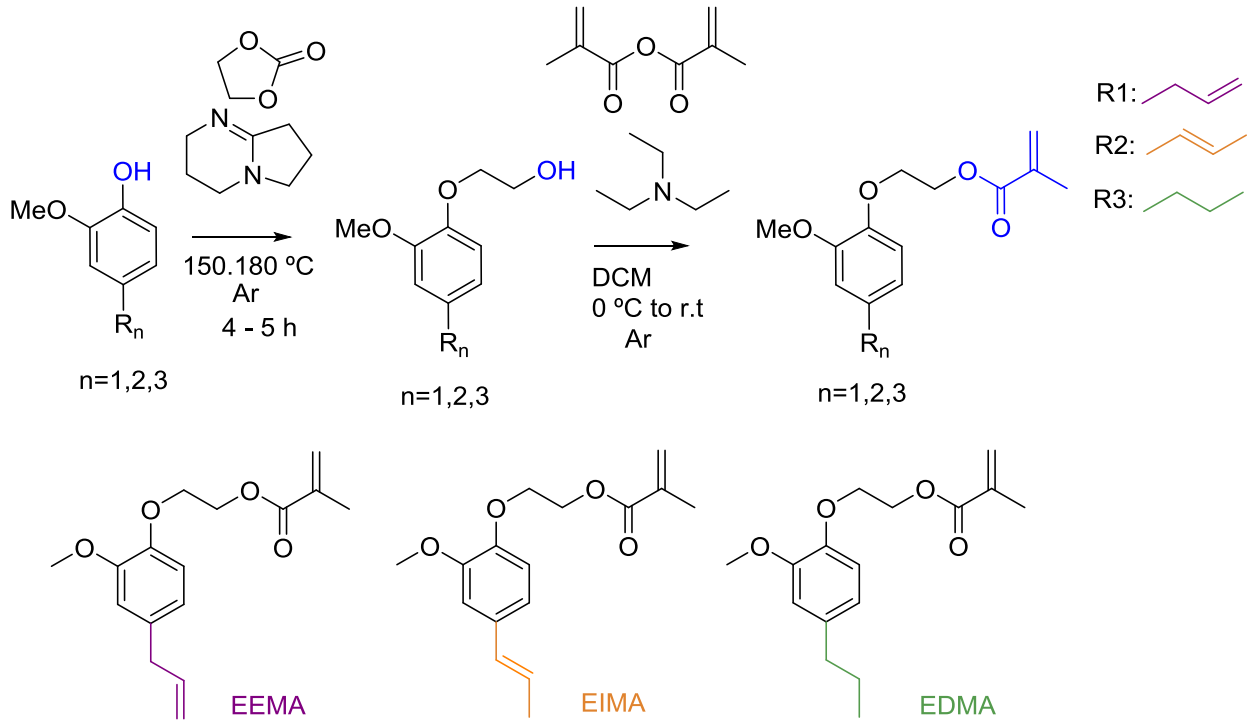
$$Gel\ content(\%) = \frac{W_f \times 100}{W_i} \qquad Eq.(1)$$

RESULTS AND DISCUSSION

Synthesis of eugenol derived methacrylated monomers.

Recently our team reported the synthesis of three eugenol-derived methacrylates and the results of their conventional radical polymerization in solution. The monomers were obtained in good yields (>70 %, up to 88 %) from a two-step synthesis consisting in the introduction of an ethoxy spacer group on the phenol of the molecule to increase the stability of the ester group of the methacrylate function (the direct eugenyl methacrylate is more prone to hydrolysis than the

ethoxyeugenyl methacrylate),[42] followed by methacrylation using methacrylic anhydride at 25 ºC (**Scheme 4**). This synthesis pathway was adapted from our previous work on the functionalization of cardanol.[12]



Scheme 4. Synthesis of eugenol-derived methacrylates

Emulsion homopolymerization of eugenol-derived methacrylates.

The formulations were designed to have 2 % wbm of initiator (either KPS thermal peroxide initiation, ACVA thermal azo initiation, or SMB/KPS redox initiation), approximately 4-4.2 % wbm of surfactant (SDS), targeting approximately twice the value of the critical micelle concentration of SDS,[43] and $NaHCO_3$ as a buffer according to the initiator used (1.2 to 2.2 % wbm). The monomer conversion was monitored only by ^{1}H NMR spectroscopy because thermogravimetric measurements were not suitable due to the high boiling point of the monomers.

As previously observed in our studies on the solution polymerization of the eugenol- and isoeugenol-derived methacrylates,[25] the pendent chain comprising the allylic and propenyl groups were involved in secondary reactions during the course of radical polymerization, such as hydrogen abstraction (benzylic protons –Ar-**CH_2**-CH=CH_2 and propenyl protons –Ar-CH=CH-**CH_3**) and cross-propagation (allylic –Ar-CH_2-**CH=CH_2** and propenyl –Ar-**CH=CH**-CH_3 double bonds). However, in solution homopolymerization in toluene, we observed that high percentages of allylic and propenyl double bonds (91% and 85% respectively) were preserved.[25] Here, keeping the highest amount of unreacted double bonds would also be beneficial to avoid extensive crosslinking during polymerization and to obtain functional latexes that could further undergo chemical reactions such as being photocured using thiol-ene chemistry for instance. This would allow tuning the properties of the coatings/adhesives after the synthesis of the latexes.

The study of the behavior of the dihydroeugenol-derived methacrylate (EDMA) monomer in emulsion polymerization was thus carried out first as this monomer does not possess any double bond, leaving only benzylic protons –Ar-**CH_2**-CH_2-CH_3 able to undergo degradative intramolecular or intermolecular chain transfer, thus limiting the risk of premature crosslinking.

The first aqueous emulsion polymerization was performed using a thermal persulfate initiation (KPS, 70°C). The reaction reached 98% conversion after 5h (**Figure 2**), although it showed a rather long induction period (3h). This has been previously observed for hydrophobic monomers, that are in low concentration in the aqueous phase, leading the oligomeric radicals to undergo recombination or termination. Thus, radical entry rate coefficient is low, resulting in the induction period. This effect was reduced with non-ionic surfactants.[44] A stable latex with a particle diameter size of ca. 63 nm was obtained (Table S1, Figure S1a).

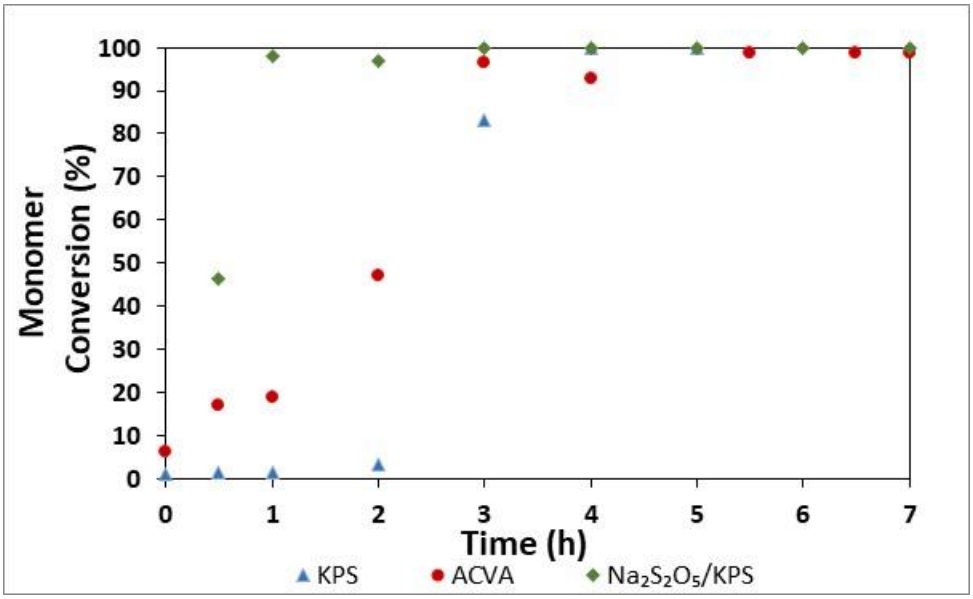


Figure 2. Monomer conversion versus time of emulsion homopolymerization of EDMA

After confirming the feasibility of emulsion polymerization with the monofunctional EDMA, the difunctional EIMA and EEMA monomers were polymerized following the same procedure. The final EEMA conversion was high, as checked by using BTB as internal standard. Both PEIMA and PEEMA homopolymers prepared by emulsion polymerization using KPS thermal initiation were crosslinked and insoluble in organic solvents (gel content > 96%, **Table 1**). In addition, after two weeks, the latex derived from EIMA coagulated, whilst that derived from EEMA sedimented. The particle diameter size of these latexes prior to coagulation and sedimentation was 70 nm and 104 nm for PEIMA and PEEMA respectively (Table S1, Figure S1b-S1c). The colloidal instability of these latexes was not further investigated.

To minimize the secondary reactions that led to crosslinked polymers, a water-soluble azo initiator (ACVA) was used. Carbon-centered radicals produced by azo initiators are less likely to abstract hydrogen atoms than oxygen-centered radicals produced by thermal decomposition of KPS.[45,46] Emulsion polymerization using this initiation system was first performed with EDMA

(**Figure 2**). In this case, there was no induction period. The resulting PEDMA latex was stable and the particle diameter was about 64 nm (Table S1, Figure S4a). The same procedure was carried out with EIMA and EEMA. However, under these conditions, EIMA polymerization also led to organic solvents-insoluble polymer as with KPS initiation, indicating pronounced crosslinking, due to secondary reactions such as cross-propagation reaction between methacrylate and propenyl double bonds. The resultant PEIMA latex was stable with a particle size of 45 nm (Table S1, Figure S4b, Figures S10-S11). In contrast, the emulsion polymerization of EEMA with ACVA showed a soluble fraction of PEEMA in $CDCl_3$ during the ^{1}H-NMR monitoring. However, a high gel content of 98% was obtained. The PEEMA latex was stable with a particle diameter size of 57 nm (Figure S4c).

In our previous studies, it was observed that the solution homopolymerization in toluene of EIMA proceeded faster than that of EEMA, and that EIMA propenyl double bonds were also more reactive than EEMA allylic double bonds.[25] In spite of the secondary reactions, a high percentage of propenyl (85%) and allylic (91%) double bonds were left unreacted in solution polymerization.

The presence of soluble polymer during the EEMA emulsion polymerization with ACVA and its lower T_g =27°C (Figure S17) in comparison to the T_g= 48°C (Figure S14) of the polymer obtained using KPS as initiator, suggest that the secondary reactions producing the crosslinking are not the same or do not occur in the same proportion with each initiator. This implied that the use of ACVA diminishes the secondary reactions leading to crosslinking. However, after drying, the latex displayed a gel content value of 98 %. Thus, the polymer suffers from further crosslinking, likely caused by the oxidation of the residual double bonds, as it was observed in vegetable oils previously.[47,48]

Moreover, as high gel content was obtained for EIMA emulsion polymerization using ACVA as initiator (with a T_g of more than 60°C for PEIMA with either KPS or ACVA, Figure S13 and S16), it could be equally considered that the extent of the secondary reactions leading to crosslinked polymers is not the same for EIMA and EEMA. It could be proposed that EIMA undergoes mainly cross-propagation through its propenyl double bond, leading to highly crosslinked polymers (as this cross-propagation reaction is not diminished using ACVA), while EEMA undergoes mainly allylic hydrogen abstraction (which is less favored with carbon-centered radical from ACVA compared to oxygen-centered radicals from KPS as initiator).

Furthermore, a redox initiation system was used at lower temperature, to avoid high temperatures likely promoting the secondary reactions which may lead to the crosslinking of the polymers. Thus, sodium metabisulfite and KPS at 40°C (as EIMA m.p.: 36°C) in a molar ratio of 1:1.3 KPS/$Na_2S_2O_5$ was used.[49,50] As for the KPS-initiated polymerizations, the first monomer to be tested was EDMA. In this case, the polymerization reached full conversion after 3h and no induction period was observed (**Figure 2**, Figure S23). A stable latex with particle diameter size of 71 nm (Table S1, Figure S7a) was obtained. The same experimental conditions were then used with EIMA and EEMA. The polymerization proceeded to quantitative monomer conversion for the three monomers in 3 h, but the polymerization rate was slower for EEMA (**Figure 3**).

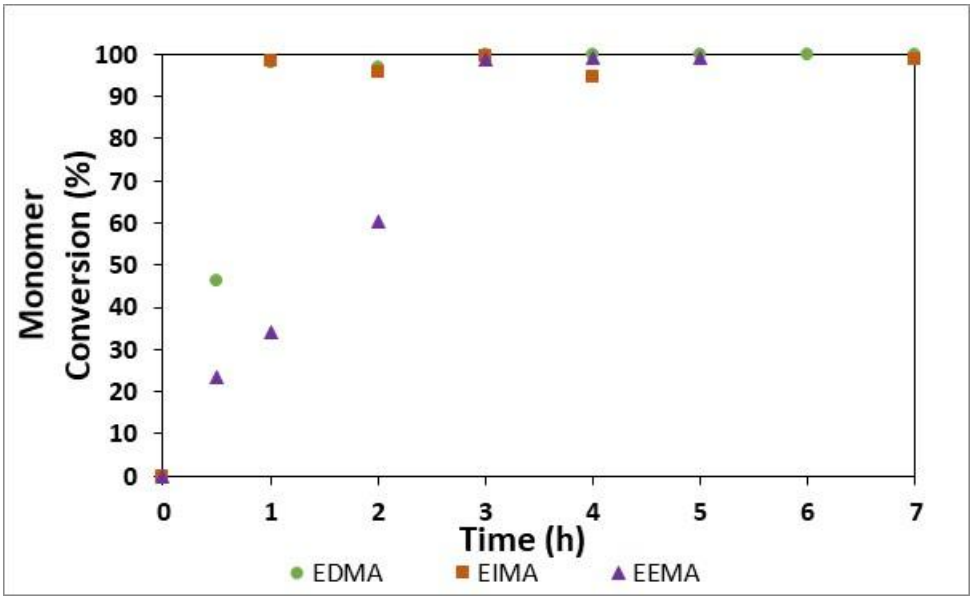


Figure 3. Monomer conversion versus time of eugenol-derived methacrylates in aqueous emulsion homopolymerization using redox $Na_2S_2O_5$/KPS initiation at 40°C.

These polymerization conditions with SMB/KPS redox initiation resulted in quantitative conversions (Figures S21-S22) but high gel content (**Table 1**), with particle diameter of 163 nm for PEIMA (Figure S7b) and 53 nm for PEEMA (Figure S7c). Due to the high gel content, it was not possible to quantify the consumption of abstractable protons nor the consumption of the propenyl or allylic double bonds of EIMA and EEMA respectively. The polymerization of EIMA proceeded at a similar rate to that of EDMA while that of EEMA was much slower. This suggests that a degradative chain transfer reaction (decrease of the number of propagating radicals) occurred in the case of EEMA and that such transfer reaction did not occur (or to a much lower extent) in the case of EIMA. It is important to note that the radical formed by hydrogen abstraction of the allylic protons of EEMA is very poorly reactive as it is highly stabilized through resonance. Both PEEMA obtained with ACVA and $Na_2S_2O_5$/KPS initiation system showed a low T_g=27°C (Figure S17) and T_g=23°C (Figure S20) respectively. This reflects

that, although the product is insoluble, the crosslinking density is not as high as in the PEIMA latexes (T_g PEIMA ca. 60°C, Figure S16 and Figure S19).[51,52]

Furthermore, thermogravimetric analyses show that the decomposition temperatures $T_{d,5\%}$ for PEIMA and PEEMA (Figures S25-S26), according to the initiation systems, decrease in the following order: KPS > ACVA > $Na_2S_2O_5$/KPS. The thermal stability of polymers has been proved to increase as crosslinking density increases,[53,54] thus higher crosslinking due to secondary reactions would be expected from emulsion polymerization using KPS at 70 °C as stated above.

Table 1. Polymer characterization

Monomer	Initiator	Monomer conversion (%)	pH	Particle diameter D_i (nm)	Colloidal stability	Gel Content (%)	T_g (°C)	$T_{d,5\%}$ (°C)
EDMA	KPS (70°C)	100	8.9	63	Yes	1	26	247
	ACVA (70°C)	99	6.3	64	Yes	0	20	265
	NaS_2O_5/KPS (40°C)	100	2.4	71	Yes	0	28	284
EIMA	KPS (70°C)	ND	9.7	70	No	99	72	293
	ACVA (70°C)	ND	6.4	45	Yes	74	63	289
	NaS_2O_5/KPS (40°C)	99	2.4	163	No	99	61	237
EEMA	KPS (70°C)	79	8.9	104	No	96	48	297
	ACVA (70°C)	ND	8.5	57	Yes	98	27	265
	NaS_2O_5/KPS (40°C)	99	3.8	53	Yes	89	23	229

A latex with a higher solids content (30%) was also synthesized. The comonomer used was butyl acrylate. The Fox equation (Eq. 2) was used to calculate the proportion of monomers to be used in the formulation to reach a T_g of -28°C, considering T_g (PBA)=- 53°C[55] and T_g(PEDMA)= 26°C (this work, **Table 1**).

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \qquad Eq.(2)$$

From a monomer mixture of 38 wt % EDMA - 62 wt % BA, a stable latex was obtained with a particle diameter size of 112 nm. After 2 h of reaction, the poly(EDMA-*co*-BA) copolymer was insoluble in organic solvents, as usual for acrylate based latexes. A film forming latex was obtained with a T_g=-23 °C.

CONCLUSIONS

The aqueous emulsion radical homopolymerizations of ethoxy dihydroeugenyl methacrylate (EDMA), ethoxy eugenyl methacrylate (EEMA) and ethoxy isoeugenyl methacrylate (EIMA) were successfully carried out and yielded colloidally stable biobased latexes of particle diameters of about 45-71 nm. These emulsion polymerizations did not require the use of large quantities of surfactants or of low CMC surfactants as is sometimes required for very hydrophobic monomers.[56] Emulsion polymerization with ACVA resulted in stable latexes for the three monomers. Moreover, it was possible to observe a decrease in the T_g of PEEMA prepared using ACVA (T_g= 23 °C) in comparison to the PEEMA obtained using KPS as the initiator (T_g = 48 °C). This indicates that ACVA as the initiator could decrease the secondary reactions leading to crosslinking. During SMB/KPS redox emulsion polymerization at 40 °C, EEMA presented the lowest rate of polymerization compared to EDMA and EIMA, possibly due to hydrogen

abstraction as secondary reaction, leading to a very stable allylic radical not prone to propagate. Moreover, although quantitative conversion was reached for all monomers, the lower T_g values for PEEMA compared to PEIMA (23 ºC and 61 ºC respectively) suggested that the main secondary reaction in the case of EIMA is cross-propagation, leading to highly crosslinked PEIMA polymers while a degradative chain transfer reaction is the main secondary reaction during EEMA redox polymerization, leading to less crosslinked PEEMA polymers.

A stable poly(EDMA-*co*-BA) copolymer latex at 30 % solids content, with film-forming properties (T_g = -23 °C), has also been successfully synthesized. These results open the way to aqueous emulsion copolymerizations of EEMA or EIMA (bearing an allylic or propenyl double bond, respectively) with commercial monomers to produce functional biobased reactive latexes for adhesives and coatings formulations.

ASSOCIATED CONTENT

DLS measurements, TEM measurements, DSC analyses, monomer conversion determination procedure, and TGA analyses are given in the Supporting Information.

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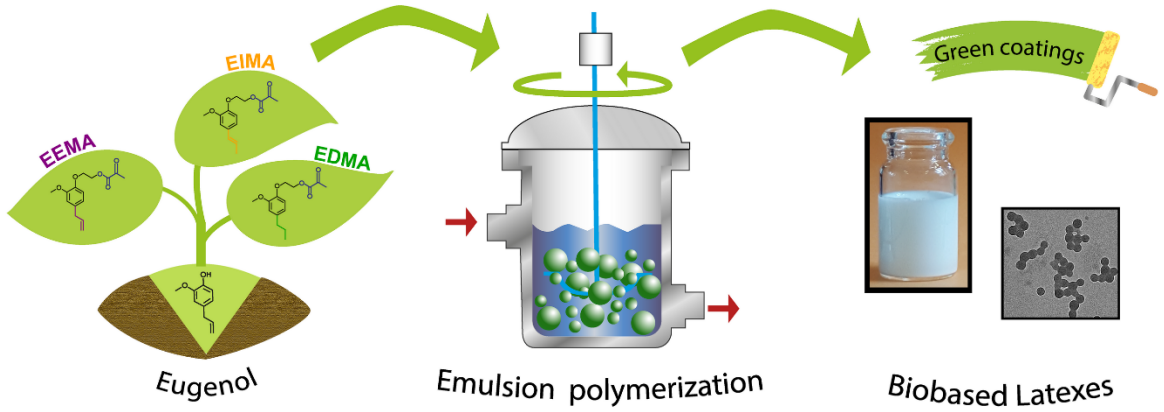
SYNOPSIS

The article presents the aqueous radical emulsion polymerization of three eugenol-derived monomers as an option to produce biobased latexes.



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