POLITECNICO DI TORINO
Repository ISTITUZIONALE

Emulsion Polymerization of Dihydroeugenol-, Eugenol-, and Isoeugenol-Derived Methacrylates

Original
Emulsion Polymerization of Dihydroeugenol-, Eugenol-, and Isoeugenol-Derived Methacrylates / Molina-Gutierrez, S., Ladmiral, V., Bongiovanni, R., Caillol, S., Lacroix-Desmazes, P.. - In: INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH. - ISSN 0888-5885. - STAMPA. - 58:46(2019), pp. 21155-21164. [10.1021/acs.iecr.9b02338]

Availability:
This version is available at: 11583/2833772 since: 2020-06-08T17:16:48Z

Publisher:
American Chemical Society

Published
DOI:10.1021/acs.iecr.9b02338

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright
GENERICO -- per es. Nature : semplice rinvio dal preprint/submitted, o postprint/AAM [ex default]

(Article begins on next page)

19 November 2026

Emulsion polymerization of dihydroeugenol, eugenol and isoeugenol derived methacrylates

Samantha Molina-Gutiérrez,[a,b] *Vincent Ladmiral,**[a] *Roberta Bongiovanni,*[b] *Sylvain Caillol,*[a] *and Patrick Lacroix-Desmazes**[a]

[a] ICGM, CNRS, ENSCM, University of Montpellier, Montpellier, France.

[b] DISAT, Politecnico di Torino, Torino, Italy

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.[28,29,38–42,30–37] 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.[33,43] 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]

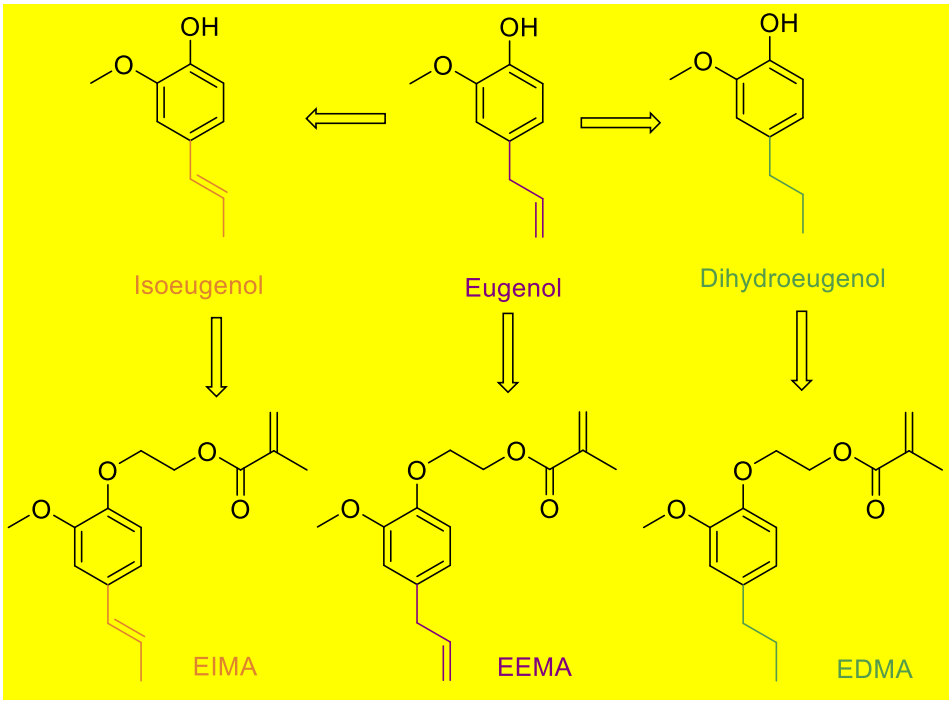
In the present work, aqueous emulsion polymerization of biobased methacrylate monomers derived from eugenol, isoeugenol and dihydroeugenol (named EEMA, EIMA and EDMA respectively, 

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

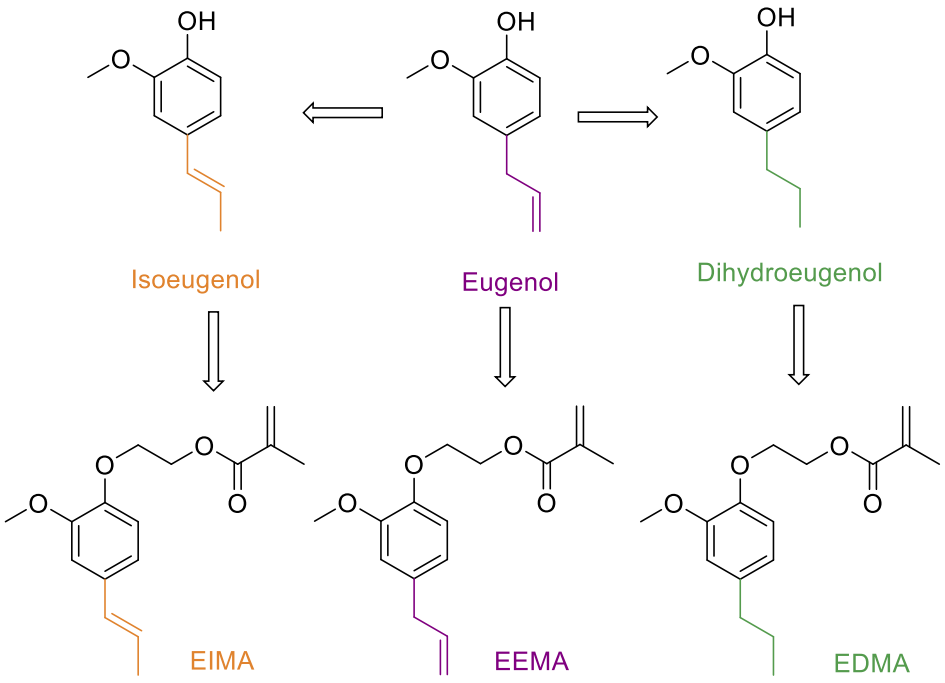


Figure 1. Eugenol-derived methacrylates

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, Table 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 DIW, 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 DIW (out of the 31.6 g of DIW 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.

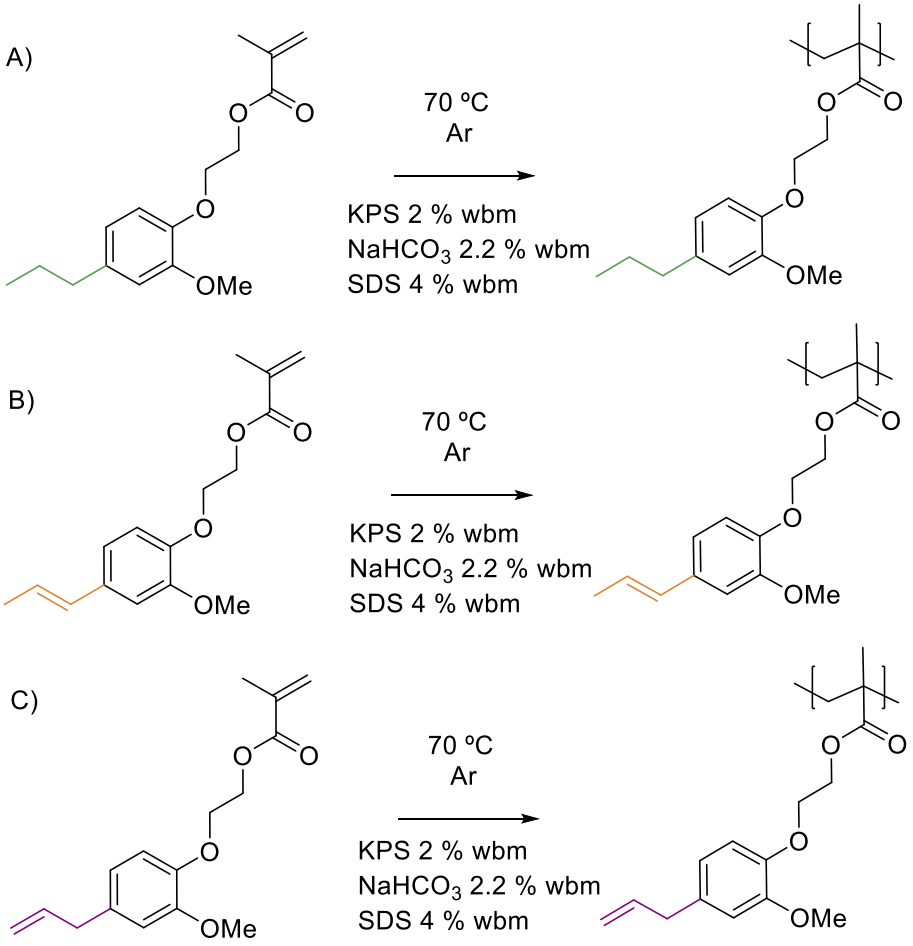
Table 1. Polymerization recipe for KPS thermal initiated emulsion polymerization

Ingredient	Weight (g)	mmol	% wbm
Monomer	4.18	15.00	100.00
Surfactant (SDS)	0.17	0.58	4.00
Initiator (KPS)	0.08	0.31	2.00
Buffer ($NaHCO_3$)	0.09	1.07	2.20
Deionized water	31.62		

Emulsion polymerization of EDMA with thermal initiation using KPS. EDMA (4.183 g, 15 mmol), DIW (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), DIW(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), DIW (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, Table 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 DIW were 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.

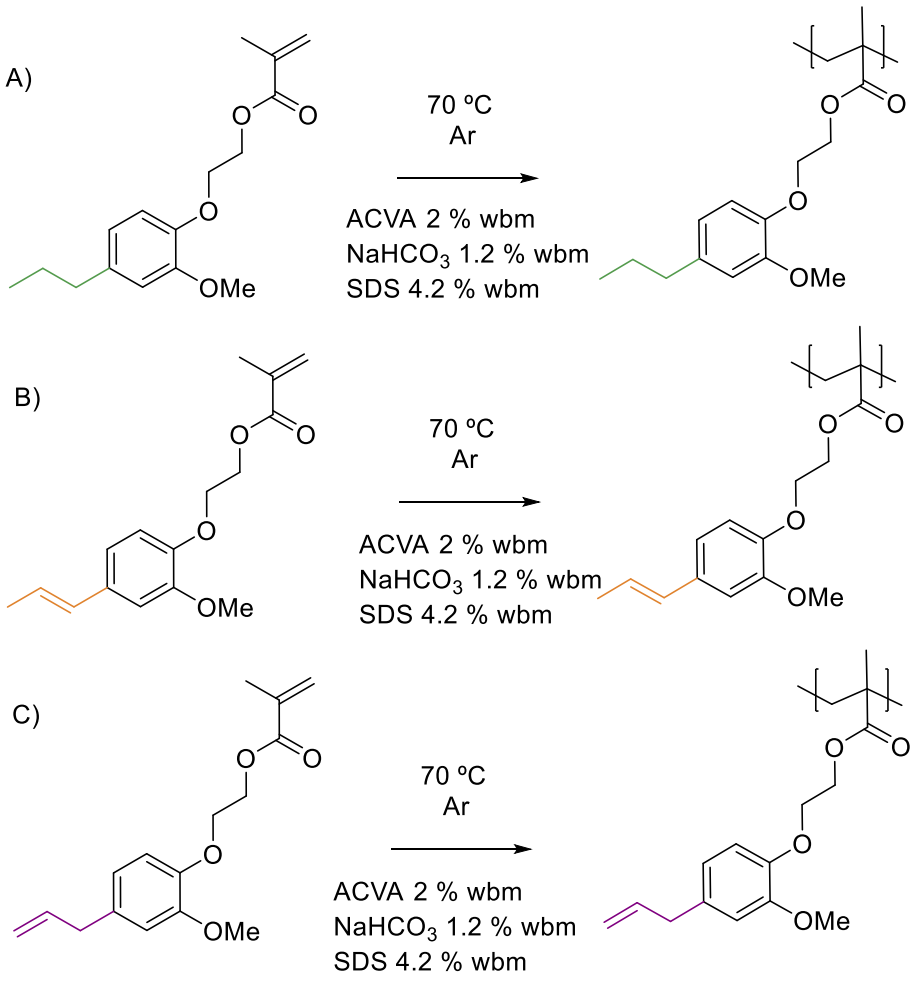
Table 2. Polymerization recipe for ACVA thermal initiated emulsion polymerization

Ingredient	Weight (g)	mmol	% wbm
Monomer	4.18	15.00	100.00
Surfactant (SDS)	0.18	0.61	4.20
Initiator (ACVA)	0.08	0.30	2.00
Buffer ($NaHCO_3$)	0.05	0.60	1.20
Deionized water	31.39		

Emulsion polymerization of EDMA with thermal initiation using ACVA. EDMA (4.170 g, 15 mmol), DIW(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), DIW (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), DIW (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, Table 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 DIW 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 DIW 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).

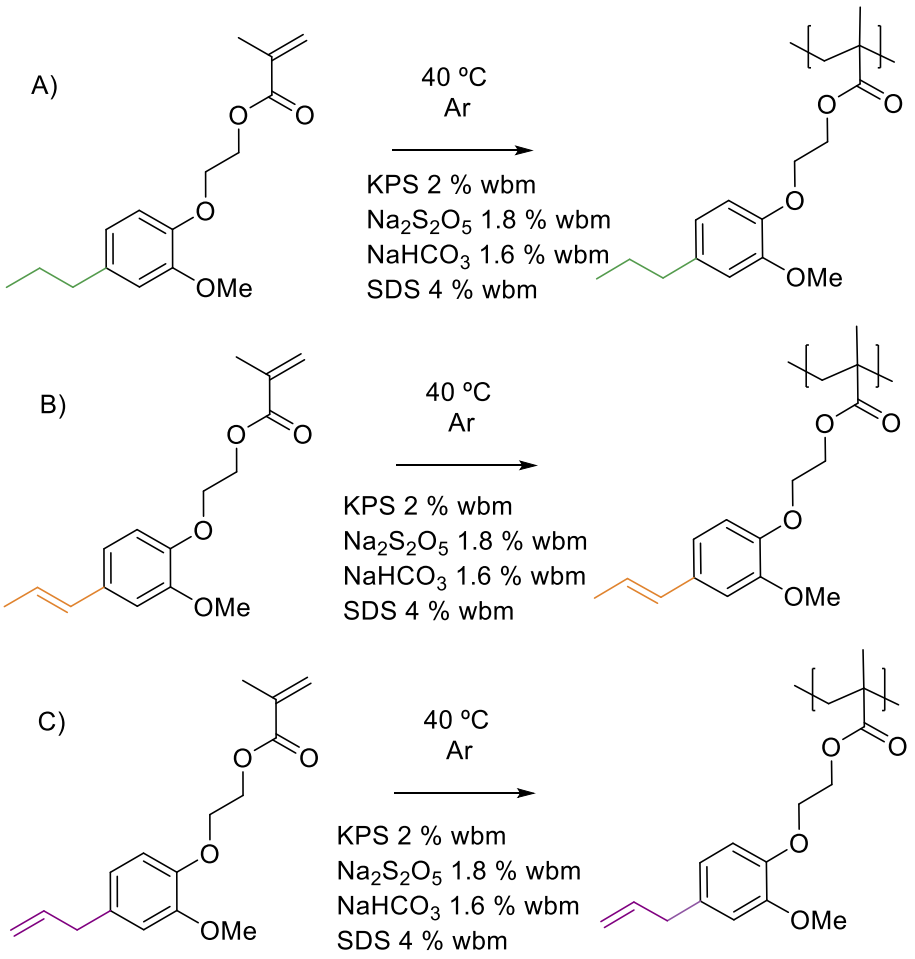
Table 3. Polymerization recipe for SMB:KPS redox initiated emulsion polymerization

Ingredient	Weight (g)	mmol	% wbm
Monomer	4.18	15.00	100.00
Surfactant (SDS)	0.17	0.58	4.00
Initiator oxidant (KPS)	0.08	0.31	2.00
Initiator reductant (sodium metabisulfite)	0.08	0.40	1.83
Buffer ($NaHCO_3$)	0.07	0.80	1.62
Deionized water	32.02		

Emulsion polymerization of EDMA with redox initiation. EDMA (4.177 g, 15 mmol), DIW (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), DIW (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), DIW (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. DIW, 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 DIW (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), DIW (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 ^1H 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 DIW. 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°C to 170ºC 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.

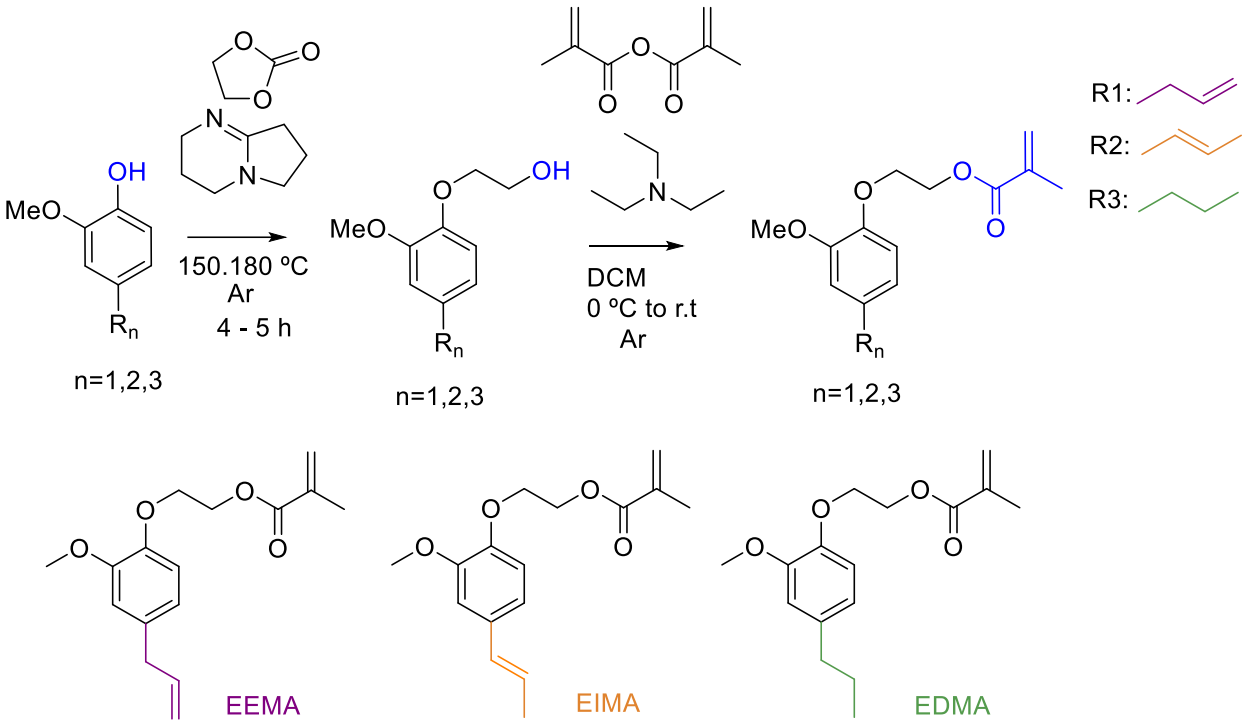
$$Gel\ content(\%) = \frac{W_f \times 100}{W_i} \qquad Eq.(1)$$

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),[44] 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,[45] and $NaHCO_3$ as a buffer according to the initiator used (1.2 to 2.2 % wbm). The monomer conversion was monitored only by ^1H 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 5 h (**Figure 2**), although it showed a rather long induction period (3 h). Induction periods have already been observed with highly hydrophobic monomers. Indeed, the low concentration of monomer in the aqueous phase, due to the low monomer solubility in water, leads to radical termination rather than propagation. This in turn leads to a low concentration of oligoradicals in the aqueous phase, which decreases the probability of oligoradical entry events into the monomer-swollen micelles (micellar nucleation), therefore retarding the nucleation.[46,47] The capture of radicals by the monomer-swollen micelles can be improved by reducing the electrostatic repulsion between the radicals (due to initiator charge, e.g. sulfate group of the KPS) and the surface of the monomer-swollen micelles (due to

surfactant charge, e.g. sulfate group of SDS).[48] Thus, using weakly anionic surfactants (e.g. carboxylic acid-based surfactants) or even non-ionic surfactants (e.g. poly(ethylene oxide)-based surfactants) instead of anionic surfactants (e.g. SDS) can help to increase radical entry and shorten induction period.[49] Nevertheless, the use of weakly anionic surfactants results in latexes with lower colloidal stability (sensitivity to *pH*) and the use of non-ionic surfactants can lead to bigger particles and/or bimodal populations[50] due to a second nucleation period.[51] Moreover, undesired radical transfer to non-ionic surfactants has also been observed.[52] For all these reasons, the use of weakly anionic or non-ionic surfactants was not considered in this work to reduce the induction period. Efforts were instead focused on testing different initiating systems as detailed below. Using KPS as initiator and SDS as surfactant, a stable latex with a particle diameter size of ca. 63 nm was obtained (Table S1, Figure S1a).

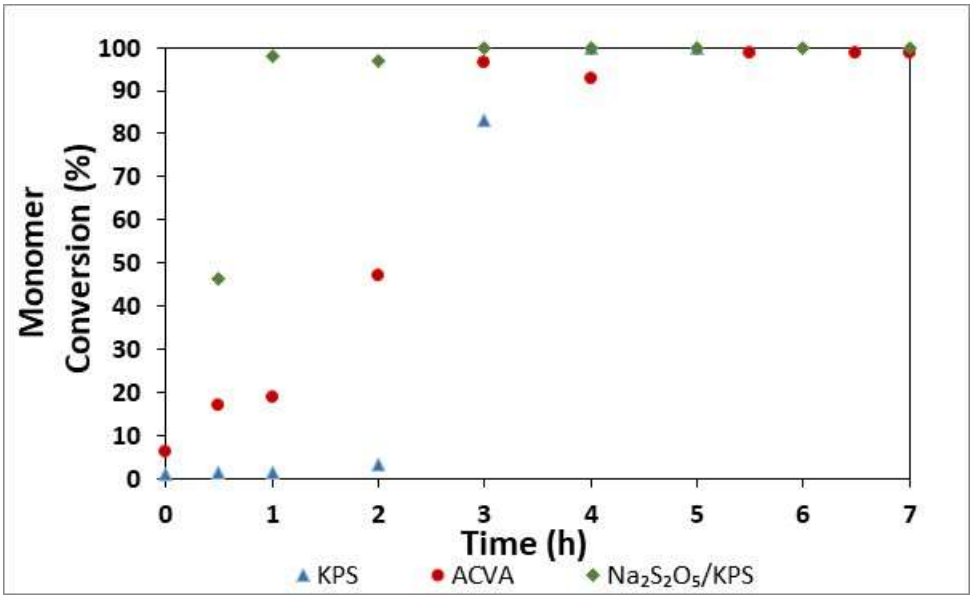


Figure 2. Monomer conversion versus time of emulsion homopolymerization of EDMA

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 4**). High gel content and insoluble polymers limited the possibility to quantify propenyl and allylic double bonds consumption as the measurements were done by ^{1}H NMR. Therefore, we directed some of our efforts to prevent gel formation, aiming to minimize consumption of allylic and propenyl double bonds, as well as the formation of insoluble polymer. In addition, after two weeks, the latex derived from EIMA coagulated, whilst that derived from EEMA sedimented. Gel content (polymer fraction insoluble in THF) should not be confused with flocculation and coagulation processes, which refer to the aggregation of the latex particles (in aqueous medium) in a reversible and irreversible manner respectively. [47] 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.[53,54] Emulsion polymerization using this initiation system was first performed with EDMA (**Figure 2**). In this case, there was no induction period. The latex particle size and thus the number of latex particles is very similar using KPS (63 nm) or ACVA (64 nm); so, the particle size is not the parameter that distinguishes these two systems. A higher radical flux would result in a higher extent of radical entry into the monomer-swollen micelles, thus leading to a shorter induction period. However, dissociation rate constants of KPS and ACVA are not significantly different in the present experimental conditions (approximately 4.3×10^{-5} s^{-1} for KPS and 3.6×10^{-5} s^{-1} for ACVA

at 70°C).[42,53] Thus, in the case of ACVA, it is not a higher radical flux that eliminates the induction period. Instead, the chemical nature of ACVA, as a weakly charged initiator (carboxylic acid for ACVA instead of sulfate group for KPS), leads to a higher probability of radical entry into the negatively charged monomer-swollen micelles (sulfate groups of SDS), hence promoting micellar nucleation and shortening the induction period.[48,55,56] Using ACVA as initiator and SDS as surfactant, 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). Due to the high T_g value of this latex (63°C) and its good colloidal stability, in addition to the measurement of the particle average hydrodynamic diameter by DLS, it was also possible to perform transmission electron microscopy (TEM) analysis without major coalescence of the polymer particles under the electron beam. 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.[57,58]

Moreover, as a higher T_g was measured 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 considered that the extent of the secondary reactions led to a higher crosslink density[59] for PEIMA compared to PEEMA. EIMA may undergo mainly cross-propagation through its propenyl double bond, leading to highly crosslinked polymers (as this cross-propagation reaction is not diminished using ACVA, resulting in a high T_g), while EEMA may undergo 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.[40,60] As for the KPS-initiated polymerizations, the first monomer to be tested was EDMA. In this case, the polymerization reached full conversion after 3 h and no induction period was observed (**Figure 2**, Figure S23). Slightly bigger and thus fewer latex particles are produced using $Na_2S_2O_5$/KPS redox system (71 nm) compared to KPS thermal

initiation system (63 nm). Slower kinetics are expected for the redox system on the basis of the particle size, although the redox polymerization turned out to be faster. The chemical nature of the radicals produced by this $Na_2S_2O_5$/KPS redox system (sulfonate and sulfate radicals) is similar to the radicals produced by KPS thermal initiation (sulfate radicals). Therefore, contrary to the ACVA system, the nature of the produced radicals by this redox system is not responsible for the faster kinetics. The important feature of this system is that one-third of the KPS oxidant was added in one shot to start the polymerization (the remaining two-third of KPS was added semi-continuously), generating a high flux of radicals by the reduction-oxidation reaction between hydrogen sulfite and persulfate, thus reducing significantly any induction period.[40,61] Using $Na_2S_2O_5$/KPS redox system as initiator and SDS as surfactant, 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**).

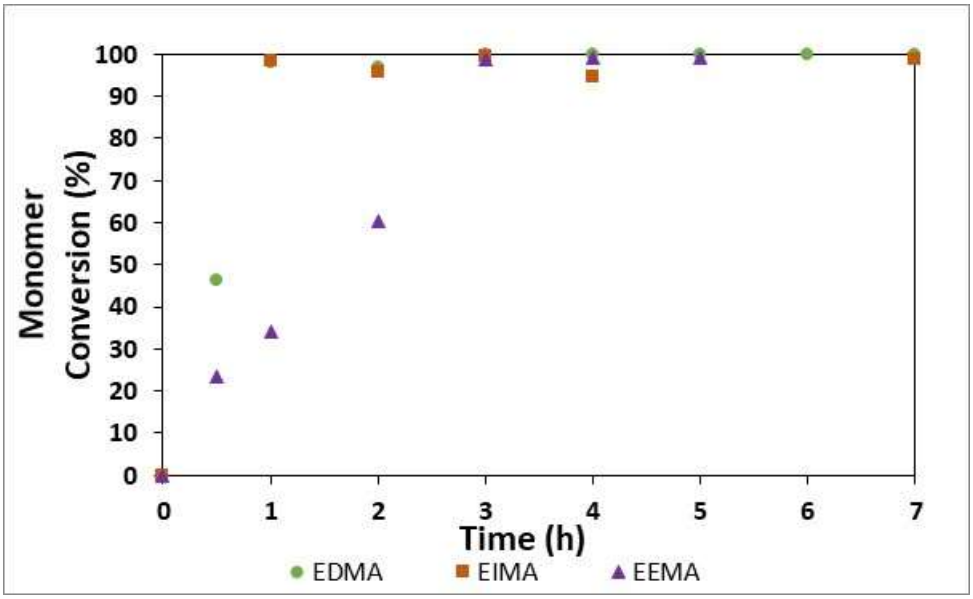


Figure 3. Monomer conversion versus time of eugenol-derived methacrylates in aqueous emulsion homopolymerization using redox $Na_2S_2O_5$/KPS initiation at 40°C.

These polymerization conditions with SMB/KPS redox initiation resulted in quantitative conversions (Figures S21-S22) but high gel content (**Table 4**), 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. Note that the high gel content (>89 % for PEEMA) is not synonymous to high crosslink density. Modification of the T_g value is related to the crosslink density and not solely to the presence of gel content or crosslinked polymers. The relationship between the T_g and the crosslink density is given in the Supporting Information. The rather low T_g values for PEEMA reflects that, although the product is insoluble (high gel content), the crosslinking density in PEEMA latexes is not as high as in the PEIMA latexes (T_g PEIMA ca. 60°C, Figure S16 and Figure S19).[59,62]

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,[63,64] thus higher crosslinking due to secondary reactions would be expected from emulsion polymerization using KPS at 70 °C as stated above.

Table 4. 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[65] and T_g(PEDMA)= 26°C (this work, **Table 4**).

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

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 (due to intermolecular chain transfer to polymer in the case of acrylate polymerization).[66,67] 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.[68] 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.

AUTHOR INFORMATION

* Corresponding author: patrick.lacroix-desmazes@enscm.fr, vincent.ladmiral@enscm.fr

ACKNOWLEDGMENT

This work was funded through a SINCHEM Grant. SINCHEM is a Joint Doctorate program selected under the Erasmus Mundus Action 1 Programme (FPA 2013-0037). The authors also thank Synthomer (UK) Ltd for financial support of their research on biobased polymers as well as for fruitful discussions (Dr. Peter Shaw and Dr. Renaud Perrin).

SYNOPSIS

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



REFERENCES

(1) Williams, C.; Hillmyer, M. Polymers from Renewable Resources: A Perspective for a Special Issue of Polymer Reviews. *Polym. Rev.* **2008**, *48*, 1.

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

(3) 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.

(4) Gandini, A. Polymers from Renewable Resources: A Challenge for the Future of Macromolecular Materials. *Macromolecules* **2008**, *41*, 9491.

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

(6) Ca, V.; Lligadas, G.; Ronda, J. C.; Galia, M.; Galià, M.; Cádiz, V. Renewable Polymeric Materials from Vegetable Oils: A Perspective. *Mater. Today* **2013**, *16*, 337.

(7) Harmsen, P. F. H.; Hackmann, M. M.; Bos, H. L. Green Building Blocks for Bio-Based Plastics. *Biofuels, Bioprod. Biorefining* **2014**, *8*, 306.

(8) Fujisawa, S.; Kadoma, Y. Action of Eugenol as a Retarder against Polymerization of Methyl Methacrylate by Benzoyl Peroxide. *Biomaterials* **1997**, *18*, 701.

(9) Lomège, J.; Lapinte, V.; Negrell, C.; Robin, J.-J.; Caillol, S. Fatty Acid-Based Radically Polymerizable Monomers: From Novel Poly(Meth)Acrylates to Cutting-Edge Properties. *Biomacromolecules* **2019**, *20*, 4.

(10) Bunker, S. P.; Wool, R. P. Synthesis and Characterization of Monomers and Polymers for Adhesives from Methyl Oleate. *J. Polym. Sci. Part A Polym. Chem.* **2002**, *40*, 451.

(11) Ladmiral, V.; Jeannin, R.; Fernandes Lizarazu, K.; Lai-Kee-Him, J.; Bron, P.; Lacroix-Desmazes, P.; Caillol, S. Aromatic Biobased Polymer Latex from Cardanol. *Eur. Polym. J.* **2017**, *93*, 785.

(12) Li, W. S. J.; Negrell, C.; Ladmiral, V.; Lai-Kee-Him, J.; Bron, P.; Lacroix-Desmazes, P.; Joly-Duhamel, C.; Caillol, S. Cardanol-Based Polymer Latex by Radical Aqueous Miniemulsion Polymerization. *Polym. Chem.* **2018**, *9*, 2468.

(13) 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.

(14) Sheldon, R. A. Green and Sustainable Manufacture of Chemicals from Biomass: State of the Art. *Green Chem.* **2014**, *16*, 950.

(15) 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.

(16) Sakai, K.; Takeuti, H.; Mun, S. P.; Imamura, H. Formation of Isoeugenol and Eugenol during the Cleavage of β-Aryl Ethers in Lignin by Alcohol-Bisulfite Treatment. *J. Wood Chem. Technol.* **1988**, *8*, 29.

(17) Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. From Lignin-Derived Aromatic Compounds to Novel Biobased Polymers. *Macromol. Rapid Commun.* **2016**, *37*, 9.

(18) Varanasi, P.; Singh, P.; Auer, M.; Adams, P. D.; Simmons, B. A.; Singh, S. Survey of Renewable Chemicals Produced from Lignocellulosic Biomass during Ionic Liquid Pretreatment. *Biotechnol. Biofuels* **2013**, *6*, 14.

(19) Song, Y.; Mobley, J. K.; Motagamwala, A. H.; Isaacs, M.; Dumesic, J. A.; Ralph, J.; Lee,

A. F.; Wilson, K.; Crocker, M. Gold-Catalyzed Conversion of Lignin to Low Molecular Weight Aromatics. *Chem. Sci.* **2018**, *9*, 8127.

(20) Rojo, L.; Vazquez, B.; Parra, J.; López Bravo, A.; Deb, S.; San Roman, J. From Natural Products to Polymeric Derivatives of "Eugenol": A New Approach for Preparation of Dental Composites and Orthopedic Bone Cements. *Biomacromolecules* **2006**, *7*, 2751.

(21) Deng, J.; Yang, B.; Chen, C.; Liang, J. Renewable Eugenol-Based Polymeric Oil-Absorbent Microspheres: Preparation and Oil Absorption Ability. *ACS Sustain. Chem. Eng.* **2015**, *3*, 599.

(22) Zhao, L.; Xie, Y.; Chen, L.; Xu, X.; Zhao, C. X.; Cheng, F. Efficient Biotransformation of Isoeugenol to Vanillin in Recombinant Strains of Escherichia Coli by Using Engineered Isoeugenol Monooxygenase and Sol-Gel Chitosan Membrane. *Process Biochem.* **2018**, *71*, 76.

(23) Wang, L.; Zhang, R.; Li, J.; Guo, L.; Yang, H.; Ma, F.; Yu, H. Comparative Study of the Fast Pyrolysis Behavior of Ginkgo, Poplar, and Wheat Straw Lignin at Different Temperatures. *Ind. Crops Prod.* **2018**, *122*, 465.

(24) Alupei, V.; Ritter, H. Mikrowellensynthesen Unter Normaldruck. *Nachrichten aus der Chemie* **2005**, *53*, 518.

(25) 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**, in press, https://doi.org/10.1002/macp.201900179.

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

(27) Anastas, P. T.; Zimmerman, J. B. Peer Reviewed: Design Through the 12 Principles of Green Engineering. *Environ. Sci. Technol.* **2003**, *37*, 94A.

(28) Ugelstad, J.; El-Aasser, M. S.; Vanderhoff, J. W. Emulsion Polymerization: Initiation of Polymerization in Monomer Droplets. *J. Polym. Sci. Polym. Lett. Ed.* **1973**, *11*, 503.

(29) Sáenz, J. M.; Asua, J. M. Dispersion Polymerization in Polar Solvents. *J. Polym. Sci. Part A Polym. Chem.* **1995**, *33*, 1511.

(30) Aslamazova, T. R. Emulsifier-Free Latexes and Polymers on Their Base. *Prog. Org. Coatings* **1995**, *25*, 109.

(31) *Emulsion Polymerization and Emulsion Polymers*; Lovell, P. A., El-Aasser, M. S., Eds.; John Wiley & Sons Ltd: Sussex, 1997.

(32) Antonietti, M.; Landfester, K. Polyreactions in Miniemulsions. *Prog. Polym. Sci.* **2002**, *27*, 689.

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

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

(35) Chern, C. S. Emulsion Polymerization Mechanisms and Kinetics. *Prog. Polym. Sci.* **2006**, *31*, 443.

(36) Save, M.; Guillaneuf, Y.; Gilbert, R. G. Controlled Radical Polymerization in Aqueous Dispersed Media. *Aust. J. Chem.* **2006**, *59*, 693.

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

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

(39) Brooks, B. Suspension Polymerization Processes. *Chem. Eng. Technol.* **2010**, *33*, 1737.

(40) Garnier, J.; Dufils, P.-E.; Vinas, J.; Vanderveken, Y.; van Herk, A.; Lacroix-Desmazes, P. Synthesis of Poly(Vinylidene Chloride)-Based Composite Latexes by Emulsion Polymerization from Epoxy Functional Seeds for Improved Thermal Stability. *Polym. Degrad. Stab.* **2012**, *97*, 170.

(41) Pinto, M. C. C.; Santos, J. G. F.; Machado, F.; Pinto, J. C. Suspension Polymerization Processes. In *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2013.

(42) Zhou, Y.; Zhang, Z.; Postma, A.; Moad, G. Kinetics and Mechanism for Thermal and Photochemical Decomposition of 4,4′ -Azobis(4-Cyanopentanoic Acid) in Aqueous Media. *Polym. Chem.* **2019**, 3.

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

(44) Wang, F.; Finnin, J.; Tait, C.; Quirk, S.; Chekhtman, I.; Donohue, A. C.; Ng, S.; D'Souza, A.; Tait, R.; Prankerd, R. The Hydrolysis of Diclofenac Esters: Synthetic Prodrug Building Blocks for Biodegradable Drug-Polymer Conjugates. *J. Pharm. Sci.* **2016**, *105*, 773.

(45) Cifuentes, A.; Bernal, J. L.; Diez-Masa, J. C. Determination of Critical Micelle Concentration Values Using Capillary Electrophoresis Instrumentation. *Anal. Chem.* **1997**, *69*, 4271.

(46) Matsumoto, A.; Murakami, N.; Aota, H.; Ikeda, J.; Capek, I. Emulsion Polymerization of Lauryl Methacrylate and Its Copolymerization with Trimethylolpropane Trimethacrylate. *Polymer (Guildf).* **1999**, *40*, 5687.

(47) Van Herk, A. M. *Chemistry and Technology of Emulsion Polymerisation*; van Herk, A. M.,

Ed.; John Wiley & Sons Ltd: Oxford, UK, 2013.

(48) Thickett, S. C.; Gilbert, R. G. Mechanism of Radical Entry in Electrosterically Stabilized Emulsion Polymerization Systems. *Macromolecules* **2006**, *39*, 6495.

(49) Emelie, B.; Pichot, C.; Guillot, J. Batch Emulsion Copolymerization of N-Butyl Acrylate and Methyl Methacrylate in the Presence of a Nonionic Surfactant. *Die Makromol. Chemie* **1985**, *10*, 43.

(50) Piirma, I.; Chang, M. Emulsion Polymerization of Styrene: Nucleation Studies with Nonionic Emulsifier. *J. Polym. Sci. Polym. Chem. Ed.* **1982**, *20*, 489.

(51) Asua, M.; Zangi, R. Shedding Light on the Different Behavior of Ionic and Nonionic Surfactants in Emulsion Polymerization : From Atomistic Simulations to Experimental Observations †. **2017**, 31692.

(52) Wu, X. Q.; Schork, F. J. Kinetics of Miniemulsion Polymerization of Vinyl Acetate with Nonionic and Anionic Surfactants. *J. Appl. Polym. Sci.* **2001**, *81*, 1691.

(53) 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.

(54) Hioe, J.; Zipse, H. Radical Stability and Its Role in Synthesis and Catalysis. *Org. Biomol. Chem.* **2010**, *8*, 3609.

(55) Coen, E. M.; Lyons, R. A.; Gilbert, R. G. Effects of Poly(Acrylic Acid) Electrosteric Stabilizer on Entry and Exit in Emulsion Polymerization. *Macromolecules* **1996**, *29*, 5128.

(56) Cheong, I. W.; Kim, J. H. Investigation of Seeded Emulsion Polymerization Using a Calorimetric Method: Effects of the Surface Charge Density on Polymerization Rate and Average Number of Radicals per Particle. *Colloids Surfaces A Physicochem. Eng. Asp.*

1999, *153*, 137.

(57) Mallégol, J.; Lemaire, J.; Gardette, J. Drier Influence on the Curing of Linseed Oil. *Prog. Org. Coatings* **2000**, *39*, 107.

(58) Soucek, M. D.; Khattab, T.; Wu, J. Review of Autoxidation and Driers. *Prog. Org. Coatings* **2012**, *73*, 435.

(59) Stutz, H.; Illers, K. -H; Mertes, J. A Generalized Theory for the Glass Transition Temperature of Crosslinked and Uncrosslinked Polymers. *J. Polym. Sci. Part B Polym. Phys.* **1990**, *28*, 1483.

(60) Graillat, C.; Pichot, C.; Guyot, A. Preparation and Characterization of Low Size Polystyrene Latex Particles with Various Strong Acid Surface Charges. *Colloids and Surfaces* **1991**, *56*, 189.

(61) Wang, S.; Daniels, E. S.; Sudol, E. D.; Klein, A.; El-Aasser, M. S. Isothermal Emulsion Polymerization of n -Butyl Methacrylate with KPS and Redox Initiators: Kinetic Study at Different Surfactant/Initiator Concentrations and Reaction Temperature. *J. Appl. Polym. Sci.* **2016**, *133*, n/a.

(62) Bandzierz, K.; Reuvekamp, L.; Dryzek, J.; Dierkes, W.; Blume, A.; Bielinski, D. Influence of Network Structure on Glass Transition Temperature of Elastomers. *Materials (Basel).* **2016**, *9*, 607.

(63) Levchik, G. F.; Si, K.; Levchik, S. V.; Camino, G.; Wilkie, C. A. Correlation between Cross-Linking and Thermal Stability: Cross-Linked Polystyrenes and Polymethacrylates. *Polym. Degrad. Stab.* **1999**, *65*, 395.

(64) Uhl, F. M.; Levchik, G. F.; Levchik, S. V.; Dick, C.; Liggat, J. J.; Snape, C. E.; Wilkie, C. A. Thermal Stability of Cross-Linked Polymers: Methyl Methacrylate with Divinylbenzene

and Styrene with Dimethacrylates. *Polym. Degrad. Stab.* **2001**, *71*, 317.

(65) Misra, S. C.; Pichot, C.; El-Aasser, M. S.; Vanderhoff, J. W. Batch and Semicontinuous Emulsion Copolymerization of Vinyl Acetate–Butyl Acrylate. II. Morphological and Mechanical Properties of Copolymer Latex Films. *J. Polym. Sci. Polym. Chem. Ed.* **2003**, *21*, 2383.

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

(67) Plessis, C.; Arzamendi, G.; Alberdi, J. M.; Agnely, M.; Leiza, J. R.; Asua, J. M. Intramolecular Chain Transfer to Polymer in the Emulsion Polymerization of 2-Ethylhexyl Acrylate. *Macromolecules* **2001**, *34*, 6138.

(68) Boscán, F.; Paulis, M.; Barandiaran, M. J. J. Towards the Production of High Performance Lauryl Methacrylate Based Polymers through Emulsion Polymerization. *Eur. Polym. J.* **2017**, *93*, 44.