

## Biobased Latexes from Natural Oil Derivatives

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### Abstract

Vinyl monomers from eugenol (EBM) and guaiacol (GBM) were copolymerized in miniemulsion process with high oleic soybean oil-based (HOSBM) counterpart to yield latexes with higher biobased content. Fully renewable monomer feed yields a broad range of new emulsion polymers with the number-average molecular weight varying at 25,000 – 650,000 g/mol. Increasing GBM/EBM content in the reactive feed leads to increasing latex molecular weight due to the decreasing unsaturation degree (lower content of HOSBM). Monomer feed unsaturation effect found to be more pronounced for latexes from EBM and HOSBM, since GBM shows higher reactivity in free radical polymerization if compared to GBM. Presence of oil-derived unsaturated fragments in emulsion polymers provides an opportunity to crosslink latexes in a controlled way and adjust the resulting polymer networks mechanical properties. Biobased latexes from 25 - 90 wt.% of GBM/EBM and 10 – 75 wt.% of HOSBM were synthesized, characterized and tested in terms of thermomechanical properties of latex crosslinked films and coatings. It is demonstrated that characteristics of latex films and coatings are determined by nature and ratio of aliphatic oil residues of HOSBM and aromatic fragments of EBM/GBM in the macromolecular backbone. Incorporation of rigid fragments of GBM/EBM enhances Young's modulus of the films, whereas the soft plant oil-based units contribute to flexibility of films and coatings. All crosslinked latex films exhibited decent properties and performance in terms of hardness, impact resistance, as well as adhesion to the steel substrate. By combination of aliphatic fatty acid fragments of HOSBM with aromatic GBM/EBM structure, durable latexes can be synthesized with ability to balance thermomechanical properties of the latex polymer networks in a broad range.

## Introduction

Biobased polymers and polymeric materials can provide a broad range of application possibilities, including coatings, plastics, adhesives, composites, etc., with properties and performance which can compete and sometimes outperform the commodity petroleum-based counterparts.<sup>1-3</sup> Using polymers from renewables addresses concerns of global lowering of the oil feedstock, as well as has positive environmental impact, due to the inherent safety and potential biodegradability of the biobased polymeric materials.<sup>4</sup> Extensive research studies are being performed on the synthesis of renewable monomers for free radical polymerization, including from vegetable oils, cardanol, vanillin, eugenol, terpenes, etc.<sup>5-7</sup>

Free radical polymerization in emulsion is the process for producing emulsion polymers (latexes), one of the most advanced polymeric materials, widely used for making coatings, paints, adhesives etc.<sup>8</sup> Because of high hydrophobicity of majority of currently considered in synthesis of renewable monomers plant-based chemicals, their incorporation in commercial latex polymerization at high levels remains a challenge.<sup>9,10</sup> Nevertheless, synthesizing latexes with high biobased content becomes an attractive alternative approach for replacing petroleum-based counterparts in commercial polymeric materials.<sup>11-14</sup>

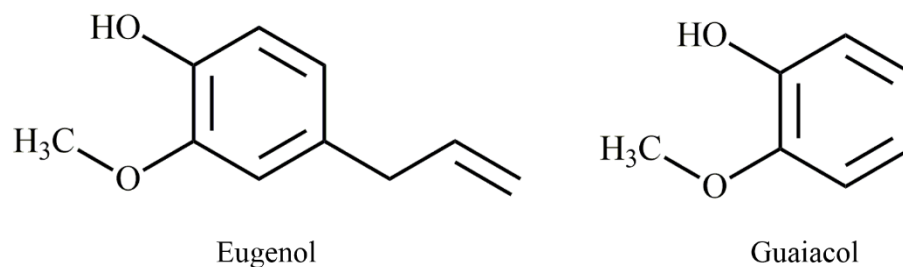
In this regard, Kaya et al. reported synthesis of latexes with varying amounts of soybean oil-based macromonomers in copolymerization with methyl methacrylate.<sup>15</sup> Moreno et al. used miniemulsion polymerization to polymerize monomer synthesized by incorporation of methacrylic functionality into linoleic acid.<sup>16</sup> Fully renewable polymer latexes based on naturally occurring  $\alpha$ -methylene- $\gamma$ -butyrolactone were synthesized in miniemulsion in.<sup>1</sup> Both miniemulsion<sup>17,18</sup> and emulsion<sup>19-22</sup> polymerization processes were successfully attempted for synthesis of latex adhesives based on various renewable biomass sources.

Despite the reported advances, high biobased content latexes are not widely employed for making industrial coatings based on polymers and copolymers from plant derivatives, predominantly due to the limited availability of the respective monomers that can be applied in free radical polymerization.<sup>23-25</sup>

In our recent study, vinyl monomers derived from cardanol (CBM) and high oleic soybean oil (HOSBM) were successfully (co)polymerized in miniemulsion to yield biobased stable latexes with varying CBM and HOSBM content.<sup>14</sup> Both biobased fragments contribute to the

mechanical properties of the resulting crosslinked latex films, when incorporation of aromatic CBM fragments enhances Young's modulus, whereas the aliphatic fatty acid HOSBM constituents make films softer and more flexible. Resulted biobased latex polymer networks demonstrated promising performance in terms of mechanical properties, water and solvent resistance, and adhesion.

Although, the obtained results clearly indicate the potential of both CBM and HOSBM in latexes with high biobased content, synthesis of high molecular weight emulsion polymers from this monomeric pair is challenging due to the fatty acid unsaturated fragments presented in chemical structure of both monomers. Those functional groups trigger the allylic termination when chain propagation coexists with effective degradative chain transfer, extensively occurring during copolymerization of HOSBM and CBM and diminishing degree of polymerization. To overcome this challenge, aromatic renewable monomers with minimized chain transfer impact on latex polymers properties need to be considered.



**Figure 1.** Chemical structures of Eugenol and Guaiacol.

Eugenol is naturally occurring phenol derived from clove oil, also lignin breakdown product, found to be a promising aromatic building block for the synthesis of novel molecular structures (**Figure 1**). Due to the high functionality, eugenol can be converted into a range of biobased reactive monomers used in the formation of renewable thermoplastics and thermosets.[8] Guaiacol is another aromatic derivative, found in all types of lignin (**Figure 1**). The utilization of guaiacol as a renewable building block was reported for synthesis of benzoxazines for the development of thermoset systems.[9] Due to the presence of the hydroxyl group, guaiacol molecules can be functionalized by attaching the vinyl group and converted into the monomer for free radical polymerization.

We hypothesized that synthesis of emulsion polymers from combination of eugenol/guaiacol - and plant oil-based monomers might provide an opportunity to increase molecular weight of biobased latex polymers with properties and performance, still affected by softer plant oil residues and rigid aromatic fragments of either eugenol or guaiacol derivatives in the resulted copolymers. With this in mind, this study combines eugenol-based (EBM), as well as newly synthesized from guaiacol (GBM) vinyl monomers with HOSBM in miniemulsion to yield latex copolymers with various ratios of GBM/EBM and HOSBM. It is expected that this fully renewable monomer feed yields a broad range of new emulsion polymers with higher molecular weight. Additionally, the presence of HOSBM unsaturated fragments provides an opportunity to crosslink latex films in a controlled manner to adjust mechanical properties of the biobased polymer network. A range of new latex polymers with properties and performance determined by soft HOSBM residues and rigid EBM/GBM fragments is expected as a result of benefits from renewable monomers chemical structure and their ability to undergo radical polymerization and yield emulsion polymers.

## **Materials and Methods**

*Materials.* Dihydroeugenol (2-methoxy-4-propylphenol, 98%, Aldrich), ethylene carbonate (98%, Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98%, Aldrich), triethylamine (99.5%, Aldrich), methacrylic anhydride (94%, Aldrich), 2-methoxy-4-vinylphenol (4VG,  $\geq 98\%$ , Aldrich), chlorotriethylsilane (TESCl,  $\geq 98\%$ , Alfa Aesar), imidazole ( $\geq 99\%$ , Aldrich), sodium hydroxide (NaOH, 98%, Aldrich), dichloromethane (DCM,  $>99\%$ , VWR), ethyl acetate ( $>99\%$ , VWR), *n*-heptane ( $>99\%$ , VWR), tetrahydrofuran (THF,  $>99\%$ , VWR), high oleic soybean oil (Perdue Agribusiness LLC, Salisbury, MD), N-(hydroxyethyl) acrylamide (TCI America, Portland, OR), triethylamine (99.5%, Aldrich), potassium hydroxide (98%, Alfa Aesar, Ward Hill, MA), magnesium sulfate (99%, Aldrich), sodium dodecyl sulfate (VWR, Radnor, PA), sodium chloride (ACS grade, VWR, Radnor, PA) were used as received. 2,2'-Azobis(2-methylpropionitrile) (AIBN, Sigma-Aldrich, St. Louis, MO) was purified with recrystallization from methanol. All solvents (tetrahydrofuran, dichloromethane, methanol) were reagent grade or better and were used as received. Deionized water (DI) was used for all reactions (Milli-Q, 18 M $\Omega$ ).

*High Oleic Soybean Oil-Based Monomer (HOSBM) Synthesis.* Monomer from high oleic soybean oil was synthesized using direct transesterification reaction of crude high oleic soybean oil with N-hydroxyethyl acrylamide (HEAA) in the presence of the catalytic amount of NaOH (1 % wt.). Detailed procedure of the HOSBM synthesis and purification can be found in.<sup>10,11</sup>

*Synthesis of Eugenol-Based Monomer (EBM). Step 1. Synthesis of 2-(2-methoxy-4-propylphenoxy) ethan-1-ol.* A 2-neck round-bottom flask was charged with dihydroeugenol (79 g, 480 mmol, 1 equiv.) and ethylene carbonate (47 g, 528 mmol, 1.1 equiv.) with a reflux condenser. The mixture was stirred for 30 min at 150°C, under inert gas. Then, DBN (0.18 g, 1.47 mmol, 0.003 equiv.) was added dropwise into the reaction mixture. After 30 min of reaction at 150°C, the bath temperature was increased to 180°C for 4 hours. Then, the reaction crude was dissolved in 500 mL of DCM and extracted with DI water. The organic phase was dried, filtered and then the solvent was removed on a rotary evaporator. A slightly green solid was obtained (98%).

*Step 2. Synthesis of 2-(2-methoxy-4-propylphenoxy) ethyl methacrylate.* 2-(2-methoxy-4-propylphenoxy) ethan-1-ol (1 equiv.) was placed in a sealed round-bottom flask in dichloromethane under inert gas. Triethylamine (2.4 equiv.) was then added. Methacrylic anhydride (1.1 equiv.) was added dropwise, at 0°C. The reaction crude was stirred for 18 hours at room temperature, washed with 1 M NaOH solution and with DI. Finally, ethyl acetate was used to extract the final product. The organic phase was dried, filtered, and the solvent was removed at 30°C on a rotary evaporator. A slightly yellow liquid was obtained (95%).

*Synthesis of Guaiacol-Based Monomer (GBM) - triethyl(2-methoxy-4-vinylphenoxy) silane.* 4-vinyl guaiacol (45.0 mL, 0.333 mol) and imidazole (56.5 g, 0.830 mol) were dissolved in THF (175 mL). Then, TESC1 (67.0 mL, 0.400 mol) was added dropwise at 0°C under stirring. Afterward, the reaction crude was stirring at room temperature for 18 h, and then diluted with *n*-hexane and washed with DI. The organic phase was dried and the solvent was removed on a rotary evaporator. A colorless liquid was obtained (95%).

*Characterization of HOSBM, EBM, and GBM.* Synthesized HOSBM, EBM and GBM were characterized using <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopy (AVANCE III HDTM 400 high-performance digital NMR spectrometer, BRUKER, Billerica, MA), as well as FTIR spectroscopy to confirm the chemical structure of the monomers. Additionally, GBM and EBM

were characterized using High-Resolution Mass Spectrometry to determine the molecular mass of the resulted monomers.

*Free Radical Polymerization of EBM and GBM in Solution.* For homopolymerization, 1 M of EBM/GBM and AIBN (0.02 - 0.06 M) were dissolved in toluene, the solution was stirred and purged under a nitrogen blanket at room temperature for 5 min following by heating to 60°C for 5 h (total monomer conversion of 87 ÷ 95%). Small samples (0.5 g) of the reaction mixture were taken over polymerization time to determine the monomer conversion. The EBM and GBM homopolymerization rate was determined by plotting the monomer conversion vs. time at a linear region at the lower conversion values (up to 25%). The resulting homopolymer was precipitated in a large excess of methanol and purified 3-4 times by reprecipitation. The purified homopolymer samples were dried at room temperature until constant mass. The average number and weight molecular weight of the homopolymers synthesized in the presence of various AIBN concentrations were determined by gel permeation chromatography (GPC). Then, utilizing Mayo method, chain transfer constants on EBM/GBM were determined by plotting the reciprocal value of the degree of polymerization vs. polymerization rate for both monomers, and extrapolating to zero rate.

*Free-Radical Copolymerization of EBM and GBM with Styrene.*

To determine reactivity of EBM/GBM in chain copolymerization, various ratios of each monomer (0.2 – 1.2 g; 0.15 - 0.85 mole part), and styrene (0.05 – 0.4 g; 0.85 - 0.15 mole part, total monomer concentration 1 M), and AIBN (0.037 - 0.04 g, 0.038 M) were dissolved in toluene. The reaction mixture was purged with nitrogen at room temperature for 5 min and heated under an argon blanket at 75°C for 1.5 - 2 h until a total monomer conversion of 10 - 25% was reached. The aliquots of 0.5 g of the reaction mixture were taken from the reactor every 15 - 25 min to monitor the progress of monomer conversion during the copolymerization using a gravimetric method after precipitation of the copolymer in a large excess of methanol (1:10). The resulting copolymers were purified three times by reprecipitation, dried under a nitrogen blanket at room temperature (for NMR study) and at 100°C (to determine total monomer conversion) until constant mass. The chemical structure and composition of the copolymers were determined by <sup>1</sup>H NMR spectroscopy. For this, 12 mg of the copolymer sample was dissolved in chloroform-d<sub>1</sub> and tested using JEOL ECA 400 MHz NMR Spectrometer.

The data on resulted copolymers composition were applied for determination of EBM/GBM reactivity ratios in copolymerization with styrene ( $r_1, r_2$ ), For this purpose, Finemann-Ross method and equation (1) yielding a straight line plot with slope  $r_1$  and intercept  $r_2$  were employed:

$$\frac{f(1-F)}{F} = r_2 - \frac{f^2}{F} r_1 \quad (1)$$

where  $f$ - a molar fraction of monomer in feed;  $F$ -molar fraction of monomer fragments in copolymer;  $r_1, r_2$  -reactivity ratios of EBM/GBM and styrene, respectively.

For each comonomer pair, feed composition  $F_i = [M_1]_i/[M_2]_i$  and copolymer composition  $f_i = [m_1]_i/[m_2]_i$  where  $[M_1]$  and  $[M_2]$  are each monomer's concentration in a feed and  $[m_1]$  and  $[m_2]$  are each monomer's content in resulted copolymers, were calculated.

Utilizing the determined reactivity ratios and the  $Q$ - $e$  parameters for styrene, the  $Q$ - $e$  values of GBM/EBM were calculated using the Alfrey-Price scheme ( Eq.2.1 - 2.2).

$$r_1 = \frac{Q_1}{Q_2} \cdot \exp(-e_1(e_1 - e_2)) \quad (2.1)$$

$$r_2 = \frac{Q_2}{Q_1} \cdot \exp(-e_2(e_2 - e_1)) \quad (2.2)$$

*Biobased latex latex synthesis.* A range of biobased latexes was synthesized using miniemulsion polymerization of HOSBM with GBM or EBM at various monomeric ratios. The miniemulsion process was carried out at 30% solids content, where the oil phase comprised of the mixture of HOSBM and EBM/GBM at certain amounts (15 g total) and AIBN (0.23 g, 1.5 wt.% of oil phase). First, aqueous phase was prepared by dissolving 0.6 g of surfactant (SDS, 4 wt.%) and 0.04 g of sodium chloride (0.02 M) in distilled water under constant stirring at 700 rpm. Next, pre-emulsion was formed by slow drop-wise adding the oil phase to the aqueous phase at a high stirring rate (1000 rpm) and mixing for 45 min. The resulting pre-emulsion was placed in ice bath and sonicated using a Q-Sonica digital sonicator (500 W, 1-inch tip, 20kHz, Newtown, CT) with high energy three pulses of 1 min each.

The formed stable miniemulsions were transferred in a round-bottom flask with an egg-shaped magnetic stirrer, purged with nitrogen for 5 minutes, and polymerized at 75°C for 8 hours under continuous stirring at 300 rpm.

*Characterization of biobased latexes and latex films.* Conversion and solid content of biobased latex polymers were characterized by gravimetric analysis. To quantify the latex polymer yield, the latex sample (0.5 g) was reprecipitated in methanol (5 g) three times, dried in

the oven at 120°C until a constant mass. The latex solids content was measured by placing the latex sample (1 g) on an aluminum dish and drying in the oven at 120°C for 45 min.

The latex copolymers composition was examined using <sup>1</sup>H NMR spectroscopy after dissolving the biobased copolymers in CDCl<sub>3</sub>.

Number- and weight-average molecular weight of latex copolymers was determined by gel permeation chromatography (GPC) using a Waters Corporation modular chromatograph which consists of a Waters 515 HPLC pump, a Waters 2410 Refractive Index Detector, and a set of two 10 μm PL-gel mixed-B columns; the column temperature was set at 40 °C and THF was applied as a carrier with 0.35ml/min of flow rate.

Latex particles size distributions were determined by DLS (Particle Sizing Systems Nicomp 380, Santa Barbara, CA). For DLS measurements, one drop of each latex was diluted by 5 ml of distilled water. The prepared samples were analyzed at a 90° scattering angle for a 5 min running time.

To determine the glass transition temperature (*T<sub>g</sub>*) of latex copolymers, Differential Scanning Calorimetry (DSC) (TA instruments Q 2000 calorimeter) with a heating/cooling/heating regime in the temperature range of -150 to 120°C with a dry nitrogen purge of the sample at 50 ml/min was used. The latex polymer samples (20 mg) were heated/cooled at a rate of 10°C/min.

Biobased latex coatings and free films were prepared by applying 5ml of latex sample, using a drawdown bar with a thickness of 8 μm, on steel panels (for coatings) or glass substrates (for preparing free films) and cured at 135°C for 4 - 5 hours in the oven using autoxidation mechanism without the addition of the catalyst. The resulting biobased films were peeled off from the glass substrate. The thickness of the latex coatings and free films was measured using a Byko-test 8500 coatings thickness gauge.

Crosslinked latex films were characterized using dynamical mechanical analysis (DMA) (TA Instruments Q 800) in the temperature range of -50 to 150°C with a heating rate of 5°C/min and soaking time of 3 min at -50°C. Rectangular-shaped latex films were analyzed in order to evaluate its dynamical mechanical behavior. Then, the crosslink density of latex-free films (*ν*) was determined using the rubber elasticity theory:

$$\nu = \frac{G'}{R \cdot T}, mol/cm^3$$



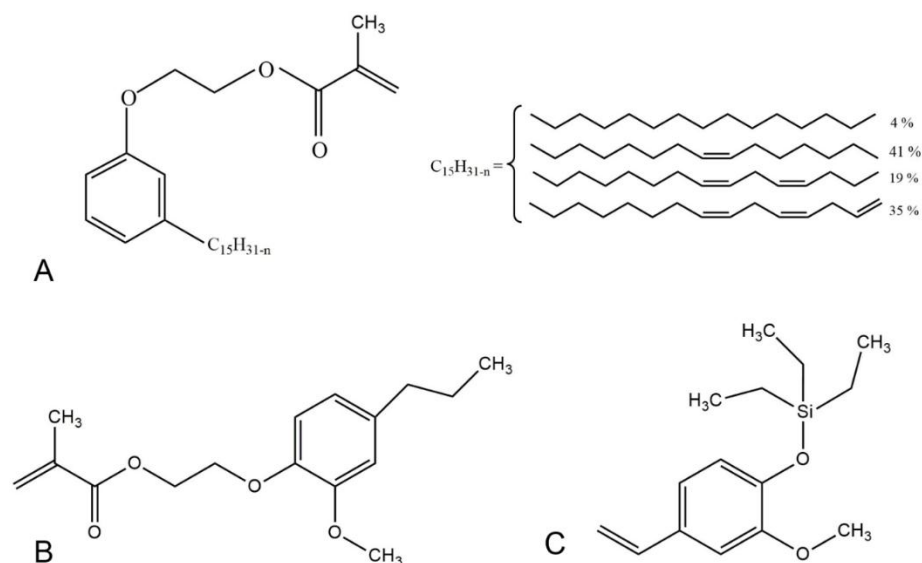
where  $G'$  – storage modulus within the rubbery plateau;  $R$  - gas constant;  $T$  - absolute temperature, K.

Mechanical behavior of biobased latex free films was evaluated using an Instron tensile testing machine (Model 2710-004) with a maximum load of 500 N. The tested films had a rectangular shape with a constant width of 5 mm. The dimensions of latex free films were evaluated before each measurement.[12-14]

Biobased latex coatings performance was characterized by measuring the hardness, flexibility, and adhesion to the metal substrate of each selected coating. The hardness of the latex coatings was evaluated using pencil and pendulum hardness tests according to ASTM D3363-05 and ASTM D4366-16 standards respectively. Latex coating flexibility was determined using an impact test (ASTM D2794) which demonstrates the ability of a tested coating to “absorb” an attack from external impact without forming cracks on the surface. The adhesion of the biobased latex coatings to the metal substrate was characterized using ASTM method 3359 by applying and peeling pressure-sensitive tape over the cross-cut made on the coating surface and comparing with ASTM standards.

## **Results and Discussion**

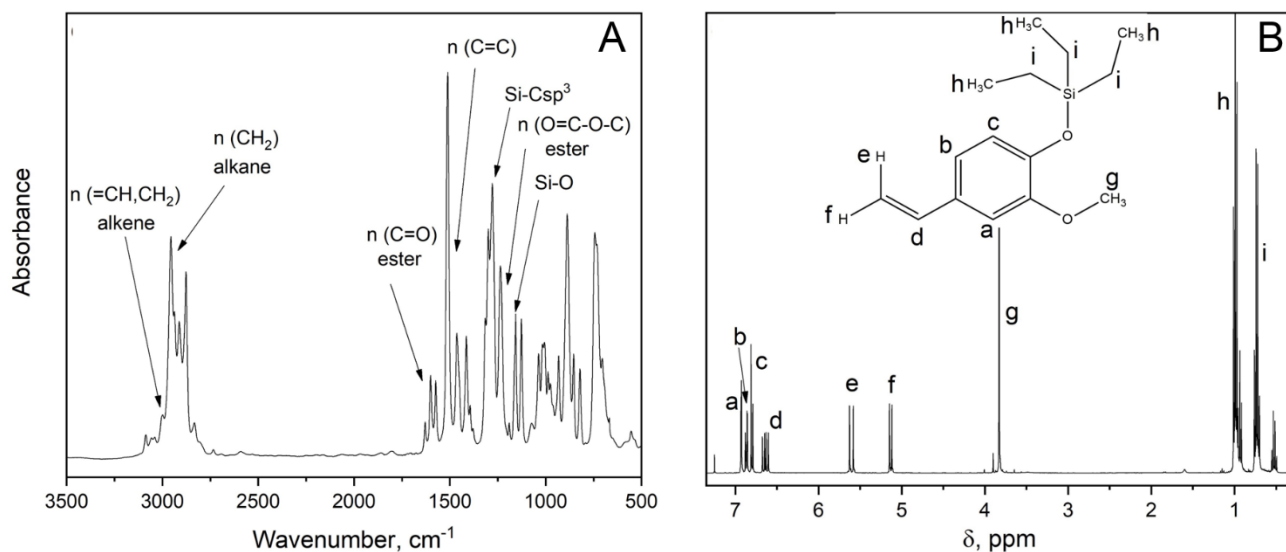
In recent publication, we reported about durable latexes from fully renewable monomer feeds containing aliphatic high oleic soybean oil-based monomer (HOSBM) (**Figure 1A**) and aromatic cardanol-based monomer (CBM).<sup>A</sup> For the biobased emulsion polymers from HOSBM and CBM, the rate of polymerization depends noticeably on fatty acids unsaturation presented in both monomers, causing the retardation effect and diminishing final molecular weight of emulsion polymers. This effect is determined by allylic inhibition, which is a chain transfer reaction to the fatty acid double bonds leading to the chain propagation coexisting during the polymerization with the chain transfer on both monomers. As a result, the latex polymers with lower degree of polymerization are synthesized.



**Figure 1.** Chemical structure of HOSBM (**A**), EBM (**B**) and GBM (**C**).

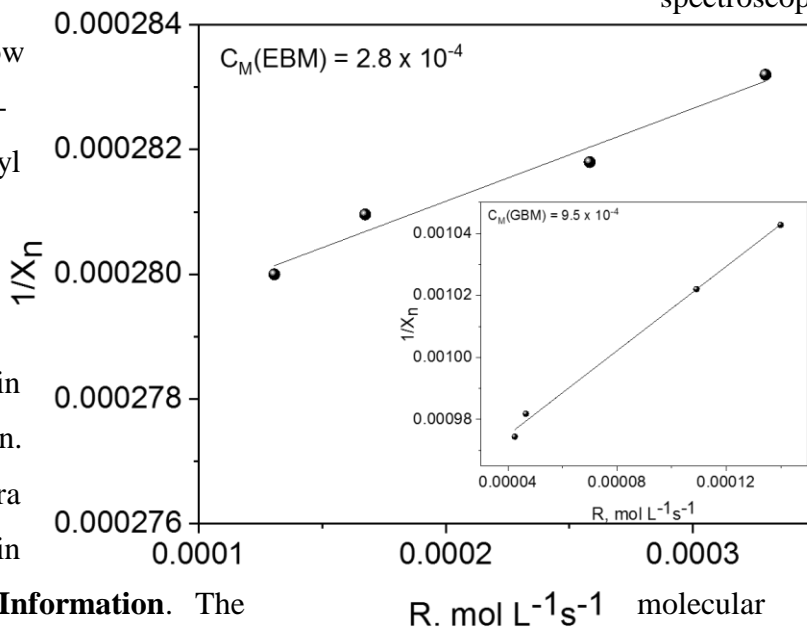
To be able to increase the molecular weight of biobased emulsion polymers without deteriorating the material properties and performance, two newly synthesized biobased monomers – derivatives of eugenol and guaiacol - with no fatty acid unsaturation in the chemical structure were considered in this study as counterparts in miniemulsion process with HOSBM.

Synthesis of eugenol-based monomer (EBM) (**Figure 1B**) as well as its feasibility in free radical copolymerization, including miniemulsion processes, has been reported by our group recently<sup>A,B,C,D</sup>. Synthesis of aromatic renewable monomer from guaiacol (GBM) (**Figure 1C**) was successfully developed in this study. Guaiacol is a naturally occurring lignin derivative biosynthesized by microorganisms, while found in various essential oils eugenol is an allyl chain-substituted guaiacol.



**Figure 2.** FTIR (A) and  $^1\text{H}$  NMR (B) spectra of GBM.

In fact, both these compounds can be considered as natural aromatic oils. Chemical structure of the newly synthesized GBM was confirmed using  $^1\text{H}$  NMR spectroscopy (Figure 2A) and FT-IR spectra show (2-methoxy-4-silane 4-vinyl GBM contain a can provide reactivity in polymerization. FTIR spectra provided in Supporting Information. The monomers was determined using mass-spectrometry, and is in good agreement with the theoretical average molecular weight. Characteristic mass spectra of GBM is provided in Figure S2 in Supporting Information.

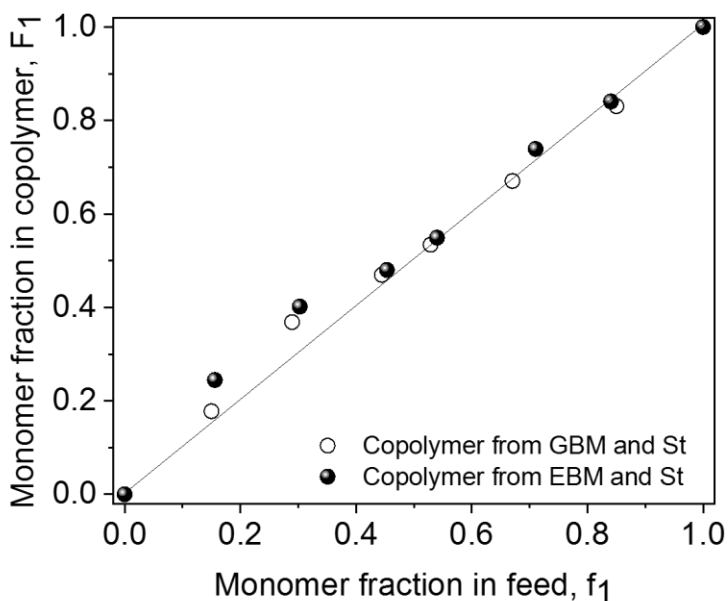


spectroscopy (Figure 2B). The that the triethyl vinylphenoxy) guaiacol, the molecules fragment that monomer chain radical  $^1\text{H}$  NMR and of the EBM are Figure S1 in

**Figure 3.** Monomer chain transfer constant ( $C_M$ ) in the polymerization of EBM and GBM (inset) determined using the Mayo method.

To establish potential effects of GBM and EBM chemical structure on their capability in their free radical reactions, their both homopolymerization was carried out in solution. Using the established Mayo method, we determined the extent of the effect of chain transfer on each monomer on reaction rate by determining the values of  $C_M$  (ratio of the chain transfer and propagation rate constants) in polymerization of GBM and EBM at 75°C. For this purpose, the inverse value of the number-average degree of polymerization was plotted against the polymerization rate, and  $C_M$  was determined by the intercept or by extrapolating to zero rate.<sup>A</sup> For both monomers, the obtained values of  $C_M$  are low ( $9.5 \times 10^{-4}$  for GBM,  $2.8 \times 10^{-4}$  for EBM) (**Figure 3**), thus indicating that chain propagation during polymerization of GBM and EBM is not significantly impacted by effective chain transfer to monomer. To this end, both biobased monomers can be considered as counterparts in copolymerization with HOSBM, yielding latex copolymers with higher molecular weight, if compared to unsaturated CBM previously investigated in our group.

The further step of this study was to evaluate the reactivity of the GBM and EBM in free radical copolymerization by determining their  $Q$ - $e$  values. First, two biobased monomers were copolymerized with styrene (St). Monomer reactivity ratios  $r_1$  and  $r_2$  for two monomer pairs (GBM-St and EBM-St) were calculated using (measured with  $^1\text{H}$  NMR spectroscopy at low monomer conversions of 5–10%) instantaneous copolymer composition (**Figure 4**) and the Kelen–Tudos approach to a solution of the Mayo–Lewis copolymerization equation.<sup>A,B</sup>



**Figure 4.** Experimental biobased content in the GBM-St and EBM-St copolymers vs. biobased content in the initial feed mixture.

Experimental data of feed composition  $F_i = [M_1]_i/[M_2]_i$  and copolymer composition  $f_i = [m_1]_i/[m_2]_i$ ,  $y_i$  values were calculated and plotted vs.  $x_i$  values.<sup>A</sup>  $[M_1]$ ,  $[M_2]$  are each monomer concentration in a feed, and  $[m_1]$ ,  $[m_2]$  are each monomer content in a copolymer.

Experimental data on  $r_1$  and  $r_2$  for GBM-St and EBM-St monomer pairs are shown in **Table 1**.

**Table 1.** Monomer reactivity ratios for copolymerization of GBM and EBM with St.

Comonomer pair	$r_1$	$r_2$
GBM - St	$0.79 \pm 0.05$	$0.65 \pm 0.03$
EBM - St	$0.87 \pm 0.04^*$	$0.32 \pm 0.04$

**Figure S3 in Supporting Information** shows the effect of biobased comonomer chemical structure on copolymerization rate for various ratios of EBM and GBM in monomer feed with St. One can see that copolymerization rate is overall higher for the monomer mixtures which contain EBM and St. This can be explained by the effect of the higher chain transfer on the GBM, as indicated by chain transfer constant values determined using Mayo method.

Based on the  $r_1$  and  $r_2$  shown in **Table 1**, their product equals 0.51 for GBM and St, 0.27 for EBM and St. The obtained data indicate that copolymerization of both comonomer pairs results in random copolymers having the experimental  $r_1$  and  $r_2$  for GBM and St, EBM and St as well as literature data on styrene  $Q$ - $e$  values ( $Q = 1$  and  $e = -0.8$ ),<sup>A</sup> the Alfrey-Price scheme was applied to calculate the  $Q$ - $e$  of the GBM and EBM monomer. This calculation yields  $Q = 1.26 \pm 0.05$  and  $e = 0.33 \pm 0.03$  for the EBM,  $Q = 0.80 \pm 0.06$  and  $e = 0.02 \pm 0.01$  for the GBM.

For a broad variety of polymeric materials applications, replacing petroleum-based ingredients with a natural renewable component in emulsion polymers and synthesizing fully biobased latexes can be beneficial. The latter aspect is a major long-term target of this research study. Latexes from fully biobased monomer mixture containing different levels of GBM and EBM (25-90 wt.%) in combination with HOSBM (10-50 wt.%) were synthesized using miniemulsion polymerization at

75°C under stirring. Synthesized latexes with an average particle size of 50–120 nm exhibit high stability at room temperature within several months. The characteristics of the resulted biobased emulsion polymers are shown in **Table 2**.

**Table 2. Biobased Latex Polymer Properties.**

Feed content, wt%*		Copolymer content, wt%	Conversion, %	$T_g$ , °C	$M_n$ , g/mol
EBM	HOSBM				
50	50	56:44	84.0	-19	139,100
75	25	84:16	93.5	-12	203,700
85	15	89:11	97.0	5	108,900
90	10	96:4	97.5	13.4	125,900
GBM	HOSBM				
25	75	30:70	71.5	-85	24,300
50	50	54:46	81.3	6	81,300
75	25	79:21	96.0	9	93,300
90	10	90:10	98.0	28	66,400

The obtained results indicate that the molecular weight of the latex copolymers decreases in a range corresponding to increasing unsaturation in monomer feed (increasing HOSBM content), as we previously reported and explained by the effect of degradative chain transfer on the HOSBM provided by allylic hydrogen atoms in the molecules.<sup>A-C</sup> It is also evident that copolymerization of EBM and HOSBM yields latex polymers with overall higher molecular weight if compared to latexes based on GBM and HOSBM and explained by the more expressed chain transfer reaction in case of GBM, if compared to EBM.

The obtained in DSC measurements  $T_g$  values (**Table 2**) indicate that variation in the biobased monomer feed composition changes, to a large extent, the thermal properties of latex copolymers. As expected, presence of HOSBM fragments decreases the glass transition temperature due to the internal plasticization effect of plant oil-based copolymers, reported in our previous study.<sup>A,B</sup> It can be concluded that combination of the non-polar long fatty acid side chains of HOSBM with aromatic fragments of GBM and EBM impacts intermacromolecular interactions and provides the way for adjusting the  $T_g$  of the resulting materials. This effect is

clearly more pronounced for latex copolymers based on GBM and HOSBM because of differences in emulsion polymers molecular weight.

As it was determined in our previous study, the vast majority of double bonds in HOSBM fatty fragments are retained during the polymerization.<sup>A</sup> The presence of those double bonds makes the resulted latex copolymers suitable for post-polymerization crosslinking reactions.

Crosslinking impacts such mechanical properties, as hardness, elongation at break, Young's modulus making them all essentially dependent on resulting polymer network, particularly crosslink density,  $\nu$ . This is because the mobility of polymer chains in a crosslinked network determines the thermomechanical behavior of polymer materials and is a function of  $\nu$ .

In this study, biobased latex free films and latex coatings were formed by applying latexes to a steel substrate and curing at elevated temperature for a certain period of time. Curing protocols were chosen based on data for the films exhibited an extent of autooxidative crosslinking determined by measuring the gel content in our previous studies.<sup>A,B</sup>

Crosslinked latex films were investigated using dynamic mechanical analysis (DMA) to determine the glass transition temperature and crosslink density. The  $\nu$  of the biobased polymer networks was calculated as described elsewhere<sup>A</sup> using the storage modulus  $E'$  vs. T dependence in the rubber elasticity region (50°C above  $T_g$ ). It is evident that for both monomeric pairs, increasing HOSBM content in the feed increases its unsaturation content, which results in an increased crosslink density of the biobased polymer network (**Table 3**).

**Table 3. Cured Biobased Latex Films Properties.**

Feed content, wt%*		Copolymer content, wt%	$T_g$ , °C	$\nu \times 10^5$ mol/cm <sup>3</sup>	$M_c$	$E$ , MPa	$K \cdot 10^{-4}$ J/m <sup>3</sup>	$\epsilon_b$ , %
<b>EBM HOSBM</b>								
90	10	96:4	33	3.5	30,400	66.5	87.3	427.7
85	15	89:11	32	6.7	15,900	0.34	78.8	462.5
83	17	86:16	???	6.8	15,600	0.21	62.6	487.9
80	20	81:19	???	7.1	15,500	0.14	53.8	322.2
75	25	84:16	26	9.5	11,200	0.11	48.7	442.1
<b>GBM HOSBM</b>								
90	10	90:10	51	5.2	20,500	170.6	73.4	67.3
85	15	86:14	44	6.6	16,100	77.2	76.4	377.1
83	17	83:17	42	9.9	10,800	45.9	86.8	438.2
80	20	82:18	40	11.7	9,100	42.8	136.3	542.5

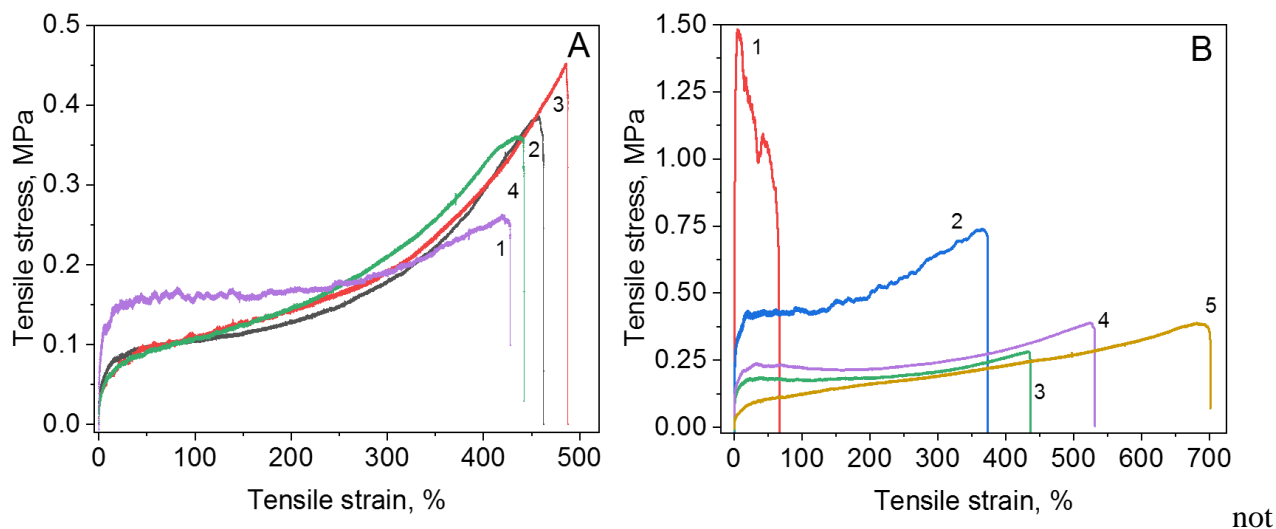
The obtained data show that the incorporation of soft plant oil-based fragments in copolymer decreases the  $T_g$  of latex films. As it can be expected, the effective molecular weight between crosslinking nodes ( $M_c$ ) of cured films (shown in **Table 3**) decreases with an increasing HOSBM content in latex copolymers corresponding to the higher crosslink density of the films. This effect is more pronounced for the films made of latexes based on GBM and HOSBM.

To provide more insights on the effect of different biobased fragments on the mechanical properties of biobased latex films, tensile properties were evaluated at room temperature as a function of latex copolymer composition. Toughness, Young's modulus, and elongation at break were determined for each crosslinked latex film (**Table 3 and Figure 5**).

The obtained results confirm that the incorporation of different amounts of either eugenol- or guaiacol-based fragments in combination with HOSBM enhances the Young's modulus of the films, whereas the plant oil-based constituents made the cross-linked material softer and more flexible.



While Young's modulus increases with an increasing of either EBM or GBM content in both series of experiments, presence of aromatic constituents contributed in a different manner to the changes in toughness of the crosslinked films. Although, overall the presence of HOSBM fragments makes the films more flexible, as the data demonstrates, toughness of the GBM-based materials increases with an increasing HOSBM content, while effect of plant oil-based fragments was almost not noticeable for the films based of EBM (**Figure 5A** and **5B**). In fact, as **Table 3** shows, as crosslinking density increases in the latter films, the elongation at break almost does



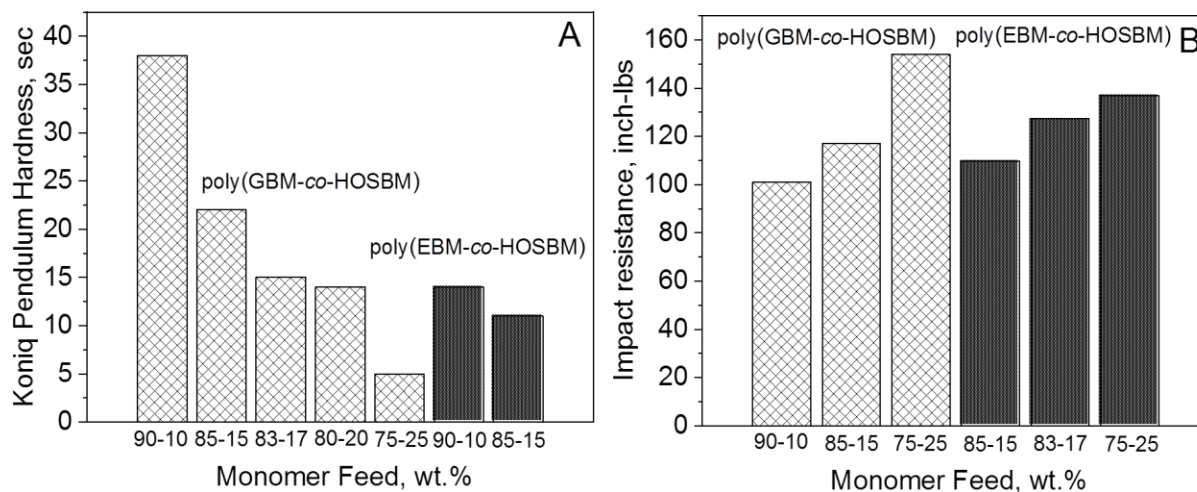
not change, thus even causing slight decrease of the toughness resulting from a fact that Young's modulus of the films decreases.

**Figure 5.** Stress – strain plots for biobased latex films from (A) EBM and HOSBM (A, 10 (1), 15 (2), 17 (3), 25 (4) wt.% of HOSBM), (B) GBM and HOSBM (10 (1), 15 (2), 17 (3), 20 (4), 25 (5) wt.% of HOSBM, respectively).

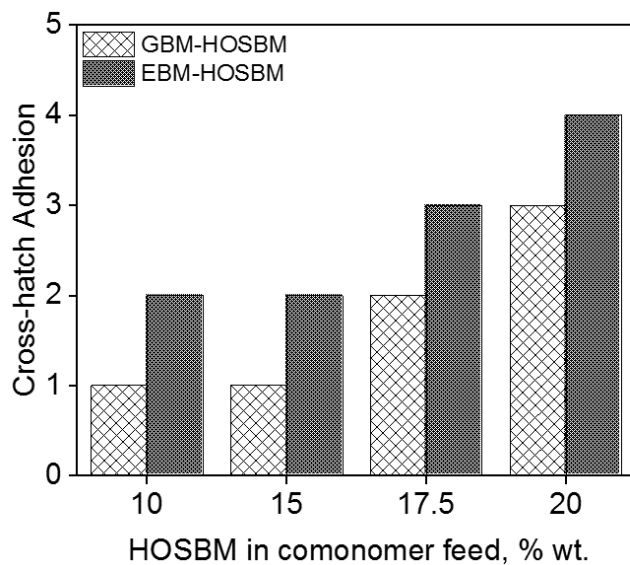
Therefore, mechanical properties of the biobased latex films in this study depend considerably on the crosslinking density and composition of the polymer network, which can be controlled by the ratio of HOSBM and aromatic fragments in latex copolymers.

In addition to tensile properties, latex characteristics can impact hardness, flexibility and adhesion of biobased latex coatings. Using ASTM methods, König pendulum hardness and impact resistance of coatings were evaluated (**Figure 6**). As it can be expected, the obtained hardness is higher for latex coatings made from a higher amount of aromatic renewable

fragments in the crosslinked polymer network (**Figure 6A**) while increasing the plant oil-based fragments content in resulted latexes leads to increasing impact resistance, proportionally to the changes of material crosslinking density (**Figure 6B**).



**Figure 6.** Effect of renewable monomers feed composition on pendulum hardness (**A**) and impact resistance (**B**) of biobased latex coatings.



**Figure 7.** Effect of renewable monomers feed composition adhesion of of biobased latex coatings to the metal substrate.

The adhesion of the biobased latex coatings to the metal substrate was measured by cross-cut adhesion test and found to be impacted by the latex copolymer composition. The data indicated that higher plant oil-based content in latexes enhances polymer coatings adhesion (**Figure 7**).

Overall, the obtained biobased latex coatings show superior behavior in terms of flexibility for all tested copolymer compositions. The provided data indicate that mechanical properties of coatings can be tuned by combination of incorporated fatty acid fragments and aromatic fragments of latex copolymers.

## Conclusions

Vinyl monomers derived from eugenol (EBM) guaiacol (GBM) were successfully (co)polymerized with high oleic soybean oil-based monomer (HOSBM) in miniemulsion in order to demonstrate EBM/GBM feasibility in the synthesis of biobased latexes. To characterize reactivity of GBM and EBM in chain copolymerization,  $Q-e$  values for each aromatic renewable monomer were determined. The obtained results indicate that both monomers are well suited for chain copolymerization

Miniemulsion (co)polymerization of 25 - 90 wt.% of GBM/EBM and 10 – 75 wt.% of HOSBM yields stable aqueous polymer dispersions with latex particle diameters of 50 - 120 nm. The fully renewable monomer feeds yield a broad range of new emulsion polymers with the number-average molecular weight varying at 25,000 – 650,000, overall higher for the copolymerization of EBM and HOSBM. As expected, rate of GBM/EBM copolymerization with HOSBM depends noticeably on the plant oil-based monomer unsaturation due to allylic termination of HOSBM. Increasing GBM/EBM content in the monomer feed corresponds to decreasing degree of unsaturation and leads to increasing molecular weight of latex polymers. The effect of monomer feed unsaturation is more pronounced for latexes from EBM due higher reactivity in free radical polymerization.

Synthesized biobased copolymers are characterized by  $T_g$  in a range of -19 – 35°C, which increases with each aromatic monomer content. Both biobased fragments contribute to the mechanical properties of the resulting polymeric materials. It is demonstrated that latex films and coatings characteristics are determined by nature and ratio of soft oil residues of HOSBM and rigid aromatic fragments of EBM/GBM in the macromolecular backbone. Presence of

unsaturated HOSBM fragments in emulsion polymers provides an opportunity to crosslink latex films to different degrees and control the polymer network mechanical properties. Incorporation of aromatic fragments of GBM/EBM enhances Young's modulus of the films, whereas the plant oil-based units contribute to softer and more flexible films. Tensile testing shows that mechanical properties of crosslinked latex films depend considerably on the polymer network crosslinking density, which can be controlled by varying the ratio of GBM/EBM and HOSBM. All crosslinked latex films from HOSBM and GBM/EBM show decent hardness, impact resistance and adhesion to the steel substrate.

The obtained results demonstrate the potential of vinyl monomers derived from eugenol and guaiacol in copolymerization with high oleic soybean oil-based monomer as candidates for the synthesis of renewable waterborne polymeric materials. By combination of aliphatic fatty acid fragments of HOSBM with aromatic GBM/EBM structure, durable latexes can be synthesized with ability to balance thermomechanical properties of resulting crosslinked latex films in a broad range.

## **Supporting Information**

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### **Notes**

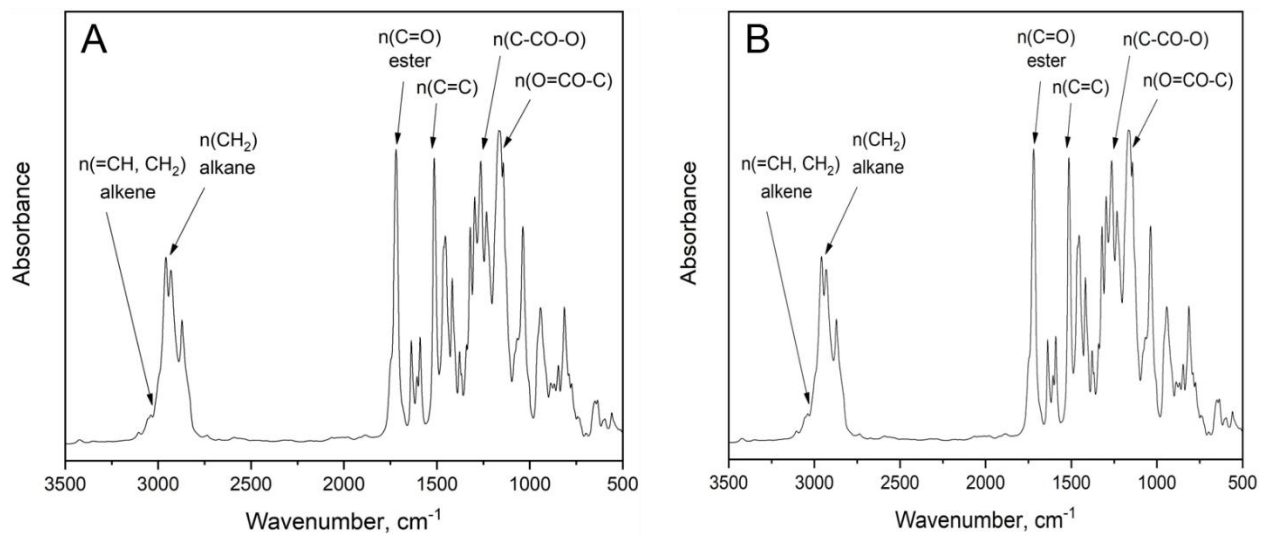
The authors declare no competing financial interests.

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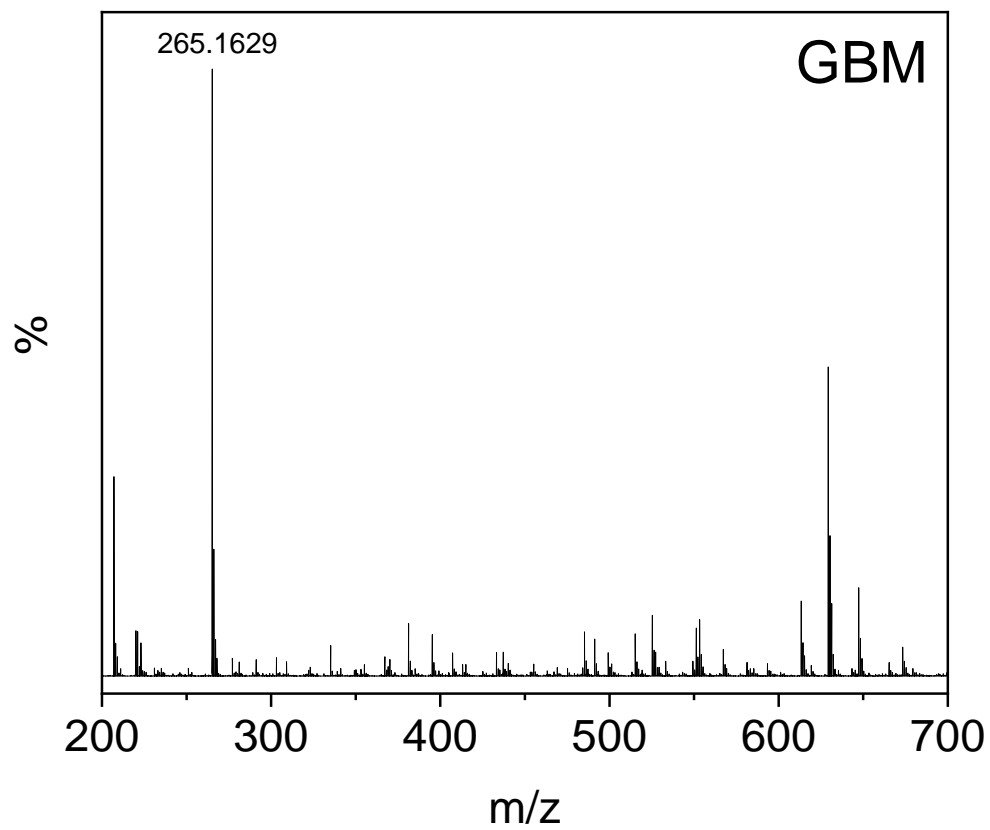
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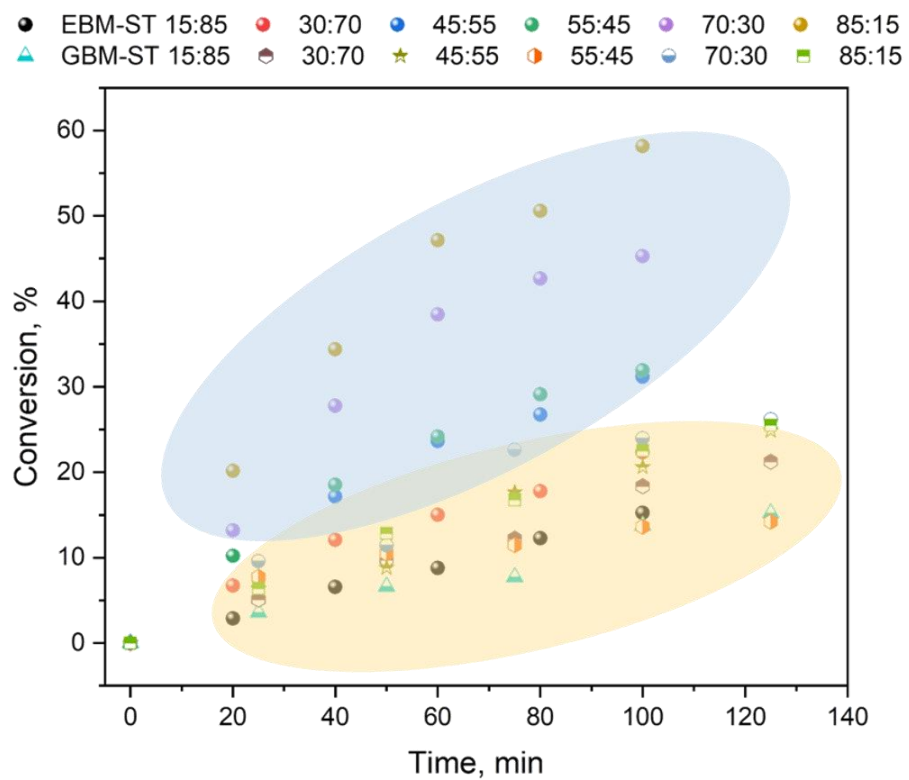
## Supporting Information



**Figure S1.** FTIR (A) and  $^1\text{H}$  NMR (B) spectra of EBM.



**Figure S2.** Characteristic mass spectrum of GBM.





**Figure S3.** Conversion–time changes in copolymerization of St with GBM and EBM in various ratios.