Free-Radical Copolymerization Behavior of Plant-Oil-Based Vinyl Monomers and Their Feasibility in Latex Synthesis

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Supporting Information

ABSTRACT: Vinyl monomers from soybean, sunflower, linseed, and olive oils were copolymerized with styrene (St), methyl methacrylate (MMA), and vinyl acetate (VAc) to determine the reactivity of biobased monomers in radical copolymerization, as well as their feasibility in emulsion processes for the synthesis of biobased latexes. Radical copolymerization of plant-oil-based monomers is described with the classical Mayo–Lewis equation. Using emulsion (or miniemulsion) polymerization with MMA or VAc, stable aqueous polymer dispersions with latex particles measuring 80–160 nm and containing 3–35 wt % of biobased monomer units were successfully synthesized. The number-average molecular weight of the latex copolymers (20 000–150 000) decreases by increasing the degree of unsaturation in monomers and their content in the reaction feed. The presence of plant-oil-based fragments changes the Tg of resulting copolymers from 105 to 79 °C in copolymerization with MMA and from 30 to 11 °C in copolymerization with VAc. As a result, biobased units provide considerable flexibility (elongation at break of about 250%) and improve the toughness of the normally rigid and brittle poly(MMA). Even a small amount (2–5%) of biobased fragments incorporated into the structure of poly(VAc) significantly improves water resistance and provides hydrophobicity to the resulting polymer latex films. The obtained results clearly indicate that the vinyl monomers from plant oils can be considered as good candidates for internal plasticization of polymeric materials through reducing intermolecular interactions in copolymers.

INTRODUCTION

The compositions of most plant oils, including oils from annual crops, consist of a wide range of triglycerides (esters of glycerol and three long-chain fatty acids), varying across different plant species and growth conditions.1 Plant oils represent good renewable sources for oleochemical industrial products, particularly biobased polymers, because their structures are similar to those of petroleum-based long-chain hydrocarbons, with the main difference being that plant oils are much more unsaturated.2−6 These structural differences provide additional opportunities for chemical modifications of plant-oil-based macromolecules and the possibility of developing new types of biobased polymers.

To obtain cross-linked polymers from plant oils, an oxidative mechanism is typically used as the polymerization method for triglycerides with different types of unsaturated fatty acid chains having one or several double bonds.7−10 Cross-linked macromolecules have also been developed by modification of triglycerides with vinyl monomers (e.g., styrenation of unsaturated fatty acid chains) in the presence of radical initiators (benzoyl peroxide, di-tert-butyl peroxide).11,12 To prepare thermosetting polyesters, polyurethanes, polyamides, acrylic resins, and epoxy resins from triglyceride oils, various polycondensation strategies can be used, including polycondensation of diacids, diols, diisocyanates, and epoxy resins via epoxidation of unsaturated fatty acid chains of triglyceride oils.13 Coatings based on water-soluble alkyd resins prepared from maleinized triglyceride oils have been described by Solomon14 and reported in several papers.15−17

Free-radical chain copolymerization is an efficient method for the synthesis of an almost unlimited number of different macromolecules by variation in the nature of and amount of two or more monomers, as well as for tailoring the resulting macromolecules with specifically desired properties.18 In particular, copolymerization of the second monomer into the polymer structure can plasticize the resulting material by...
lowering the intermolecular interactions between the chains, thus softening the polymers and decreasing the glass-transition temperature, or the modulus (internal plasticization).\textsuperscript{19,20} Long nonpolar fragments of bulky comonomers (C\textsubscript{16}−C\textsubscript{18}) included into the macromolecules can be considered good candidates for internal plasticization of polymeric materials. It should be noted that the latter approach is more efficient than external plasticization (a method that provides plasticity through physical mixing of polymers with compounds of low vapor pressure) or mixtures of two or more polymers.\textsuperscript{21}

Recently, we reported on the synthesis and free-radical polymerization behavior of a vinyl monomer from soybean oil triglycerides,\textsuperscript{22} as well as homopolymerization of new monomers based on sunflower, linseed, and olive oils\textsuperscript{23} (Scheme 1). Conventional radical chain polymerization of these monomers yields linear macromolecules, whereas the double bonds of the fatty acid chains remain unaffected and thus capable of postpolymerization oxidative reactions to modify the polymer, if needed.

In radical copolymerization, newly developed monomers with long, nonpolar C\textsubscript{18} fragments of differing unsaturation can act as a specialty monomer (polymer modifier), even at their low content (2−5 wt %), to provide unique properties and performance (flexibility, toughness, water resistance, adhesion, etc.) of resulting polymeric materials in various industrial applications. Particularly, water resistance of coatings and their mechanical properties can be improved by internal plasticization provided by copolymerizing the plant-oil-based monomers.

Emulsion polymerization is a predominant process widely employed in industry for commercial radical copolymerization and for producing waterborne polymeric materials (latexes in particular). Because of the highly hydrophobic nature of triglyceride molecules, using plant oils in this process has been challenging. In the synthesis of most available copolymers from plant oils for making industrial coatings, radical copolymerization, including the emulsion copolymerization technique, is not currently employed due to the absence of the respective monomers.\textsuperscript{24−30} Recently, Tang et al. developed a new strategy for synthesizing fatty monomers from high oleic soybean oil (HOSO) and demonstrated their ability to yield thermoplastic polymers in free-radical polymerization.\textsuperscript{31} As a result, macro-molecules with a wide range of glass-transition temperatures and properties were synthesized from a library of HOSO-based (meth)acrylate monomers.\textsuperscript{32} Polymers exhibiting T\textsubscript{g} in a range of more than 100 °C difference and demonstrating physical properties of materials with viscoelastic and thermoplastic behaviors were obtained. Vilela et al. employed transition-metal-catalyzed transvinylation to obtain vinyl monomers from oleic and linoleic acids and vinyl acetate (VAc).\textsuperscript{33} Variation of resulting fatty acid vinyl ester monomers yielded copolymers with VAc in a range of M\textsubscript{n} = 1000−3000 and glass-transition temperatures between −5 and 16 °C.

Inspired by the feasibility of recently synthesized new vinyl monomers from sunflower (SFM), linseed (LSM), soybean (SBM), and olive (OVM) oils in chain radical polymerization, we report about their copolymerization behavior in reactions with conventional vinyl comonomers. The ability to control the content of plant-oil-based monomer units in the resulting macromolecules using the classical Mayo−Lewis equation was investigated. Another objective of this study was to synthesize latexes from new monomers and evaluate how the fraction of the plant-oil-based monomer units in the resulting macromolecules affects the latex properties, glass-transition temperature (T\textsubscript{g}), and mechanical performance of films and coatings made from the obtained biobased latexes, as well as polymer latex film hydrophobicity.

\section*{RESULTS AND DISCUSSION}

\underline{Radical Copolymerization of Plant-Oil-Based Monomers.} Two reactive sites are present in a plant-oil-based monomer’s structure: a vinyl double bond, CH\textsubscript{2}=CH−C(O), which determines chain propagation, and isolated double bonds in fatty fragments, CH\textsubscript{2}=CH−CH=CH\textsubscript{2} containing allylic hydrogen atoms prone to degradative chain transfer by formation of less active −CH=CH−CH\textsuperscript{−} radicals.\textsuperscript{25} Recently, we reported on the synthesis and free-radical copolymerization behavior of a vinyl monomer from soybean oil triglycerides with methyl methacrylate (MMA).\textsuperscript{22} Nevertheless, growing PMMA radicals are known to undergo chain transfer reactions to a lesser extent.\textsuperscript{27} At the same time, homopolymerization of new monomers based on sunflower,

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
\textbf{Oil Type} & \textbf{Saturated} & \textbf{Unsaturated} & \textbf{Fatty Acids} & & \\
\hline
& Stearic & Palmitic & Oleic & Linoleic & Linolenic \\
\hline
Olive & 7.5−20 & 0.5−5 & 65−85 & 3.5−20 & 0−1.5 \\
Sunflower & 3−6 & 1−3 & 14−35 & 44−75 & 1−2 \\
Soybean & 7−11 & 2−6 & 22−34 & 43−56 & 7−10 \\
Linseed & 4−7 & 2−5 & 12−34 & 17−24 & 35−60 \\
\hline
\end{tabular}
\caption{Typical Chemical Compositions of Plant Oils Used in This Study for Monomer Synthesis

Scheme 1. Chemical Structure of Plant-Oil-Based Monomers and Typical Chemical Compositions of Plant Oils Used in This Study for Monomer Synthesis

\begin{equation}
\begin{aligned}
\text{HN} & \quad \text{O} \\
\text{O} & \quad \text{R}
\end{aligned}
\end{equation}

linseed, and olive oils revealed that (1) the number-average molecular weight of plant-oil-based homopolymers decreases in the range of poly(OVM) > poly(SFM) > poly(SBM) > poly(LSM), corresponding to increasing degree of unsaturation in the monomers; (2) the obtained values of the chain transfer constant on monomer \( C_m \) clearly depend on the monomer structure as follows: \( C_m(\text{LSM}) > C_m(\text{SBM}) > C_m(\text{SFM}) > C_m(\text{OVM}) \). Such a behavior is explained by the presence of differing numbers of allylic hydrogen atoms in the monomer molecules and the corresponding reaction of chain termination through degradative chain transfer on monomers (allylic termination).  

Taking into account that VAc is widely used for the development of industrial aqueous polymer dispersions (latexes), radical copolymerization of LSM, SBM, SFM, and OVM with VAc was explored in this study to evaluate plant-oil-based monomers’ feasibility in the use of copolymerization and ability to vary the biobased content in the resulting macromolecules. Unlike PMMA radicals, growing PVAc radicals show higher reactivity in chain transfer reactions. Hence, one of the experimental goals was to determine whether the chain transfer reactions observed during the homopolymerization of plant-oil-based monomers impact the radical copolymerization behavior of LSM, SBM, OVM, and/or SFM.

First, the \( Q-e \) parameters, which provide a semiquantitative prediction of monomer reactivity ratios of monomers, allowing for description of the behavior of monomers in radical copolymerization, were targeted. For this purpose, in copolymerization of the SBM, LSM, SFM, and OVM with styrene (St), monomer reactivity ratios \( r_1 \) and \( r_2 \) were experimentally determined for each monomer pair by measuring an instantaneous copolymer composition (at low monomer conversions of 5–10%, using \( ^1H \) NMR spectroscopy) (Figure S1 in Supporting Information) and employing the Fineman–Ross method to a solution of the Mayo–Lewis copolymerization equation (Figure 1). Employing a Fineman–Ross equation \(^a\) yields a straight line plot with slope \( r_1 \) and intercept \( r_2 \).

For each monomer pair, the experimental data of the feed composition \( F_i = [M_i]/[M_2] \), and copolymer composition \( f_i = [m_i]/[m_2] \), were calculated, where \([M_i]\) and \([M_2]\) are each monomer’s concentration in a feed and \([m_i]\) and \([m_2]\) are each monomer’s content in a copolymer.

\[
r_2 = Q_2/Q_1 \exp\{-e_2(e_2 - e_1)\}, \\
r_1 = Q_1/Q_2 \exp\{-e_1(e_1 - e_2)\} \\
\]

(1)

Experimental data on \( r_1 \) and \( r_2 \) for monomer pairs are shown in Table 1. It could be concluded that all of the growing plant-oil-based monomer radicals are mainly added to the St monomer \( (r_1 < 1) \). Given the experimental \( r_1 \) and \( r_2 \) values for each monomer pair, as well as literature data on St \( Q-e \) parameters \( (Q = 1 \text{ and } e = -0.8) \), the Alfrey–Price scheme (eq 1) was applied to calculate the \( Q-e \) of the SBM, LSM, SFM, and OVM (Table 2).

\[
\begin{array}{cccc}
\text{comonomer pair} & \text{r}_1 & \text{r}_2 \\
\hline
\text{SBM–St} & 0.35 \pm 0.03 & 1.11 \pm 0.10 \\
\text{LSM–St} & 0.37 \pm 0.06 & 1.10 \pm 0.05 \\
\text{OVM–St} & 0.39 \pm 0.05 & 1.19 \pm 0.28 \\
\text{SFM–St} & 0.37 \pm 0.02 & 0.83 \pm 0.09 \\
\end{array}
\]

Table 1. Monomer Reactivity Ratios for Copolymerization of Plant-Oil-Based Monomers and St

\[
\begin{array}{cccc}
\text{plant-oil-based monomer} & Q & e \\
\hline
\text{SBM} & 0.41 \pm 0.01 & 0.18 \pm 0.06 \\
\text{LSM} & 0.43 \pm 0.06 & 0.15 \pm 0.12 \\
\text{OVM} & 0.42 \pm 0.05 & 0.09 \pm 0.08 \\
\text{SFM} & 0.51 \pm 0.02 & 0.28 \pm 0.05 \\
\end{array}
\]

Table 2. \( Q-e \) Parameters of Plant-Oil-Based Monomers

The obtained results show that both \( Q \) and \( e \) values are similar for all four plant-oil-based monomers. Because in an empirical \( Q-e \) scheme, the \( Q \) value describes the effects of the resonance factor and (to a smaller extent) the steric factor, it appears that both these factors affect plant-oil-based monomer reactivity in copolymerization in a similar way. In the \( Q-e \) approach, the \( e \) value describes the polar factor by defining the role of monomer polarity in copolymerization. The data indicate that among the four monomers, the less unsaturated, thus, less polar, olive oil-based monomer possesses the smallest \( e \) value. Otherwise, polar effects do not seem to have a significant impact on plant-oil-based monomer reactivity in copolymerization. In general, differences between the \( Q-e \) values of the biobased vinyl monomers are small, as might be expected, assuming similarities in the structure of the monomer molecules.

To further demonstrate that experimentally determined \( Q-e \) parameters can be applied to control the composition of copolymers from plant-oil-based monomers, a series of studies on radical copolymerization of LSM, OVM, SFM, and SBM with VAc were carried out.

The chemical composition of each resulting copolymer (10 for each monomer pair) was determined using \( ^1H \) NMR spectroscopy and compared with the theoretical copolymer compositions. The theoretical compositions were assessed using the Alfrey–Price scheme (eq 1) and \( Q-e \) values for VAc \( (Q = 0.026, e = -0.88) \), as well as for plant-oil-based monomers, as shown in Table 3, to determine \( r_1 \) and \( r_2 \) for each monomer pair. In the next step, these \( r_1 \) and \( r_2 \) were applied to calculate each theoretical copolymer composition using the Mayo–Lewis copolymerization equation (eq 2).

![Figure 1. Experimental content of the plant-oil-based monomer in the copolymers with St vs content of the plant-oil-based monomer in the initial feed mixture.](image-url)
It can be seen (Figure 2) that the experimental and calculated plots are in good agreement, indicating that radical copolymerization of both LSM (Figure 2A) and SBM (Figure 2B) with VAc is described by the Mayo–Lewis copolymerization equation. The determined $Q_e$ values can be employed in estimating plant-oil-based monomer reactivity in copolymerization with other monomers to control biobased content in the resulting copolymers. In terms of polymerizability in radical copolymerization, the plant-oil-based monomers LSM, OVM, SFM, and SBM can be classified as vinyl monomers.

**Synthesis and Properties of Biobased Latexes.** Latexes based on VAc and acrylic monomers are widely applied as adhesives and binders in various coatings, as well as in the impregnation of different materials (paper, nonwoven, etc.). Incorporation of small amounts of hydrophobic monomers (e.g., 2-ethylhexyl acrylate) into latex polymers is known to improve their properties and performance (flexibility, toughness, water resistance, and adhesion). VAc and acrylic monomers (particularly, MMA) are known to be moderately soluble in water (2.5 and 1.6 g/100 mL, respectively), whereas plant-oil-based monomers are hydrophobic and almost insoluble in water. The synthesis of latex polymers from highly hydrophobic monomers has been conducted through conventional emulsion polymerization under certain conditions (e.g., higher surfactant concentration).

The miniemulsion (when reaction starts in the monomer droplet) polymerization technique was developed and studied by Ugelstad and Schork. Hydrophilic monomers have been shown to be successfully copolymerized with hydrophobic octadecyl methacrylate using miniemulsion polymerization. Even fluorinated monomers can be easily polymerized and copolymerized using miniemulsions. Special approaches have been used, such as higher shear rate, adding osmotic agents, and using initiators soluble in oleophase (AIBN). Miniemulsion polymerization occurs in nanosized droplets, which can be considered as nanoreactors. The large interfacial area between the aqueous and oil phases facilitates radical reactions at the interface and increases copolymerization feasibility for monomers with a very different aqueous solubility.

In this study, latexes from LSM, SBM, OVM, SFM, and MMA or VAc were synthesized using emulsion and miniemulsion polymerization. Two oil phases, from the plant-oil-based monomer (Oil Phase 1) and from the comonomer (MMA or VAc) and radical initiator (AIBN) (Oil Phase 2), were applied in the miniemulsion process. Each oil phase was miniemulsified in a surfactant-containing aqueous phase to obtain two separate miniemulsions. Polymerization started by slowly adding a miniemulsion, containing a plant-oil-based monomer, into a comonomer-containing one at 60 °C under

| Table 3. Experimental and Calculated Monomer Reactivity Ratios in Copolymerization of Plant-Oil-Based Monomers with VAc |
|-------------------------------|----------------|----------------|----------------|----------------|
| pair                         | SBM: VAc      | LSM: VAc      | OVM: VAc      | SFM: VAc      |
|                              | cal            | exp            | cal            | exp            |
| $r_1$                        | 13.0           | 7.1 ± 0.3      | 14.0           | 10.8 ± 0.7     |
| $r_2$                        | 0.03           | 0.08 ± 0.04    | 0.02           | 0.08 ± 0.03    |

Figure 2. Calculated and experimental plant-oil-based monomer content in LSM-based (A) and SBM-based (B) copolymers with VAc vs plant-oil-based monomer content in the initial feed mixture.

| Table 4. Characteristics of Latexes from Plant-Oil-Based Monomers and MMA Synthesized in the Miniemulsion Process |
|----------------------------------------------------------------------------------------------------------------|
| biobased content (feed), wt % | biobased content (polymer), wt % | conversion, % | latex solid content, % | latex particles size, nm | $M_n$ | $T_g$ |
|-------------------------------|-------------------------------|---------------|------------------------|--------------------------|-------|-------|
| 10OVM                         | 6.5                           | 97            | 38.8                   | 73 ± 18                   | 152 200 | 97    |
| 10SBM                         | 6.9                           | 92            | 36.8                   | 39 ± 16                   | 81 230  | 97    |
| 10SFM                         | 6.4                           | 99            | 40.3                   | 99 ± 14                   | 98 040  | 97    |
| 10LSM                         | 3.5                           | 98            | 39.3                   | 113 ± 15                  | 66 250  | 96    |
| 30OVM                         | 21.2                          | 94            | 28.0                   | 116 ± 38                  | 60 000  | 85    |
| 30SBM                         | 28.0                          | 87            | 22.0                   | 131 ± 37                  | 95 600  | 79    |
| 30SFM                         | 21.7                          | 92            | 27.6                   | 156 ± 39                  | 22 700  | 88    |
| 40SBM                         | 33.8                          | 88            | 22.3                   | 76 ± 21                   | 34 400  | 87    |

$$\frac{[m_1]}{[m_2]} = \left(\frac{[M_1]}{[M_2]}\right) \times \left(\frac{[r_1[M_1] + [M_2]}}{[r_2[M_1] + [M_2]]}\right)$$

It can be seen (Figure 2) that the experimental and calculated plots are in good agreement, indicating that radical copolymerization of both LSM (Figure 2A) and SBM (Figure 2B) with VAc is described by the Mayo–Lewis copolymerization equation. The determined $Q_e$ values can be employed in estimating plant-oil-based monomer reactivity in copolymerization with other monomers to control biobased content in the resulting copolymers. In terms of polymerizability in radical copolymerization, the plant-oil-based monomers LSM, OVM, SFM, and SBM can be classified as vinyl monomers.
Table 5. Characteristics of Latexes from Plant-Oil-Based Monomers and VAc

| biobased content (feed), wt % | biobased content (polymer), wt % | conversion, % | latex solid content, % | latex particle size, nm | $M_n$ | $T_g$ |
|-----------------------------|---------------------------------|----------------|-----------------------|------------------------|--------|------|
| Miniemulsion                |                                 |                |                       |                        |        |      |
| SOVM                        | 13.4                            | 69.0           | 21.0                  | 163 ± 65               | 77 500 | 20   |
| SSBM                        | 7.7                             | 67.5           | 27.0                  | 139 ± 65               | 27 270 | 29   |
| SSMF                        | 6.4                             | 65.6           | 26.2                  | 168 ± 41               | 20 875 | 25   |
| SLSM                        | 9.8                             | 38.3           | 7.5                   | 97 ± 49                | 25 550 | 24   |
| Emulsion                    |                                 |                |                       |                        |        |      |
| SOVM (50)                   | 8.2                             | 79.0           | 42.6                  | 148 ± 16               | 18 330 | 15   |
| SSBM (15)                   | 5.1                             | 70.0           | 35.9                  | 140 ± 52               | 20 950 | 11   |
| SSMF (15)                   | 4.8                             | 69.5           | 36.1                  | 384 ± 94               | 34 950 | 19   |
| SLSM (75)                   | 2.8                             | 87.8           | 45.6                  | 112 ± 42               | 56 250 | 26   |

*Values in brackets: conversion of VAc (wt %) before the plant-oil-based counterpart was added.

Miniemulsion copolymerization of plant-oil-based monomers and MMA was completed within 3 h, during which essentially all monomers were polymerized; the conversion of monomers was about 87–99% (Table 4). The resulting latexes with an average particle size of 80–160 nm and biobased content of 5–35 wt % exhibit high stability at room temperature within several months. The molecular weight of the resulting copolymers decreases as follows: poly(MMA-co-OVM) > poly(MMA-co-SBM) > poly(MMA-co-SFM) > poly(MMA-co-LSM), corresponding to increasing degree of unsaturation in the monomers. An similar effect was observed by increasing the fraction of the plant-oil-monomer in the initial mixture.

Decreasing molecular weight can be explained by the effect of degradative chain transfer on the monomer (allylic termination) provided by differing numbers of allylic hydrogen atoms in the monomer molecules. Analysis of $T_g$ data measured by differential scanning calorimetry (DSC) shows that the presence of biobased fragments in the resulting copolymers decreases the glass-transition temperature in comparison to that of poly(MMA) ($T_g = 105 \degree C$). The obtained data indicate that variation of biobased content in macromolecules changes the thermal properties of the resulting copolymers from MMA and plant-oil-based monomers to a large extent.

After 6 h of miniemulsion copolymerization of plant-oil-based monomers and VAc, the total monomer conversion was about 70%. This can be explained by allylic termination, as well as high reactivity of the VAc radical.18 The increasing unsaturation of plant-oil-based monomers leads to an increase in the number of allylic hydrogen atoms and effective chain transfer reactions and lowers the molecular weight of the resulting polymers. This is confirmed by the fact that the highest molecular weight was detected for VAc copolymers with the least unsaturated OVM.

Using the emulsion technique when the plant-oil-based monomer is fed into the reaction mixture after VAc is partially converted, both conversion and latex solid content can be increased (Table 5). DSC data show that the impact of oil-based fragments (3–13 wt %) on the $T_g$ of copolymers with VAc is more significant than that of copolymers with MMA. For both copolymers from MMA and VAc, biobased fragments make the resulting macromolecules more flexible, as indicated by a decreasing glass-transition temperature. Softening the polymer usually increases the elongation of break at room temperature and toughness and lowers Young’s modulus. These effects are targeted by plasticization of coating or film to facilitate easier processing.

To provide more insights into the plasticizing effect of plant-oil-based fragments, tensile properties of the resulting latex copolymer films with MMA were evaluated at room temperature as a function of the biobased content. The results were obtained for the MMA copolymers with SBM and with less unsaturated OVM (Table 6). Although poly(MMA) does not form a film at 18–25 °C, 40–45 μm latex films were successfully created for testing from copolymers with various biobased contents.

Table 6. Tensile Properties (at Room Temperature) of Latex Films from OVM and SBM Copolymerized with MMA

|                     | $G'(\omega)$, MPa | $E$, MPa | $\sigma$, MPa | $\varepsilon_b$, % | toughness, $10^{-4}$, J/m² |
|---------------------|-------------------|----------|---------------|-------------------|-----------------------------|
| 15OVM               | 1634              | 1429 ± 166 | 10.3          | 0.95               | 3.8                         |
| 35OVM               | 697               | 542 ± 48  | 9.5           | 17.5              | 23                          |
| 40OVM               | 342               | 131 ± 30  | 3.3           | 243               | 180                         |
| 20SBM               | 1615              | 1159 ± 6  | 11.3          | 1.3               | 5.2                         |
| 35SBM               | 916               | 407 ± 26  | 6.6           | 3.2               | 5.8                         |
| 40SBM               | 263               | 171 ± 38  | 3.1           | 68.1              | 6.7                         |

*$G'(\omega)$ is the storage modulus, E is Young’s modulus, $\sigma$ is the tensile strength at break, and $\varepsilon_b$ is the elongation at break.

Table 6 shows that although Young’s modulus and tensile strength decrease by increasing the biobased content in the copolymers with MMA, elongation at break increases significantly for both comonomer pairs. The obtained data indicate that although poly(MMA) is a rigid and brittle material with limited ability for elongation, the presence of the biobased fragments makes the latex films much softer and increases material toughness. The latter behavior is much more pronounced for MMA copolymerized with the less unsaturated OVM than for MMA copolymerized with SBM. The results clearly indicate that the vinyl monomers from plant oils can be considered as good candidates for internal plasticization of polymeric materials through chain copolymerization into the macromolecular structure and reducing intermolecular interactions in copolymers.

In addition to improving mechanical properties, plant-oil-based fragments can provide water resistance and hydrophobicity to latex films (coatings). In particular, poly(VAc) aqueous emulsions often need to be modified because of inherently poor properties with respect to water resistance. Water molecules act as plasticizers in such latex films and worsen their mechanical properties; thus, hydrophobic
additives are often needed to reduce water sensitivity of the polymer.

Table 7 displays the data on the surface energy and water resistance of the latex films from VAc copolymerized with a relatively small amount of plant-oil-based monomers in a reactive mixture. Both water resistance and hydrophobicity of the films increase dramatically in the presence of biobased fragments in the resulting structure of macromolecules. Table S1 shows a similar change in the surface energy of latex films based on MMA copolymerized with plant-oil-based monomers.

Transmission electron microscopy (TEM) analysis of the synthesized latexes indicates that predominantly spherical particles from plant-oil-based monomers and MMA or VAc are formed, possessing unimodal size distributions (Figure S2). In general, TEM results are in agreement with the DLS data recorded for copolymers with various biobased contents (Tables 4 and 5).

**Experimental Section**

**Materials.** Soybean oil (Crisco; The J.M. Smucker Company, Orrville, OH), sunflower oil (Kirlangic; Turkey), olive oil (Bertolli; Houston, TX), linseed oil (Sunnyside Corp., Wheeling, IL), and N-(hydroxyethyl)acrylamide (HEAAm; TCI America) were used as received. 2,2′-Azobis(2-methyl-propiionitrile) (AIBN; Sigma-Aldrich, St. Louis, MO) was purified with recrystallization from methanol. St (Sigma-Aldrich, St. Louis, MO), MMA (TCI America), and VAc (TCI America) monomers were distilled under a vacuum to remove the inhibitor and stored in a refrigerator. Toluene (Sigma-Aldrich, St. Louis, MO) was distilled before use. Other solvents and chemicals, analytical grade or better, were used as received. Deionized water was used for purification purposes (Milli Q, 18 MΩ).

**Plant-Oil-Based Acrylic Monomer Synthesis and Characterization.** Plant-oil-based acrylic monomers were synthesized from soybean, linseed, sunflower, olive oils, and N-(hydroxyethyl)acrylamide using previously reported methods.22,23 The resulting monomers contain one acrylic double bond linked to one fatty chain, which varied between fully saturated, mono-, and polyunsaturated, depending on plant-oil composition (Scheme 2).

Characterization. 1H NMR spectra were recorded on an AVANCE III HDTM 400 high-performance digital NMR spectrometer (Bruker, Billerica, MA) using CDCl3 as a solvent. The electrospray ionization high-resolution mass spectrum of the monomers was obtained using a Bruker Daltonics BioTOF mass spectrometer (Figure S3). The transmission electron microscopy (TEM) analysis of the synthesized latexes indicates that predominantly spherical particles from plant-oil-based monomers and MMA or VAc are formed, possessing unimodal size distributions (Figure S2).

**Conclusions.** Vinyl monomers from soybean, sunflower, linseed, and olive oils were copolymerized with St, MMA, and VAc to determine the reactivity of biobased monomers in radical copolymerization, as well as their feasibility in emulsion processes for the synthesis of biobased latexes. Radical copolymerization of plant-oil-based monomers is described with the classical Mayo–Lewis equation. Both Q (0.41−0.51) and ε (0.09−0.28) values do not essentially depend on the structure of the biobased monomers.

Emulsion (or miniemulsion) polymerization of plant-oil-based monomers with MMA or VAc yields stable aqueous polymer dispersions with latex particle sizes of 80−160 nm, biobased monomer units containing latex polymer macromolecules of 3−35 wt %, and a number-average molecular weight of the resulting copolymers of 20 000−150 000. The molecular weight of the synthesized macromolecules decreases by increasing the degree of unsaturation in the biobased monomers and monomer content in the reaction feed.

Thermal analysis shows that the presence of oil-based fragments in the copolymers decreases glass-transition temperature of both copolymers with MMA and VAc. The tensile properties of latex films indicate that the presence of the biobased fragments increases PMMA toughness (elongation at breakup to about 250%). Small amount of plant-oil-based fragments copolymerized with VAc significantly increases the water resistance and hydrophobicity of the resulting latex films. The results clearly show the potential of vinyl monomers from plant oils as candidates for internal plasticization of polymeric materials through radical copolymerization into a macro-molecular structure and reducing intermolecular interactions in copolymers.

**Scheme 2. Selected Monomer Structure of (Acryloylamino)ethyl Linoleate**

\[
\text{CH}_2=\text{CH}-\text{C}(O)-\text{NH}-\text{CH}_2\text{CH}_2-O-\text{C}(O)-(\text{CH}_2)_3\text{CH}=\text{CH}-\text{CH}-\text{CH}=\text{CH}-(\text{CH}_2)_3\text{CH}_2
\]

**Table 7. Surface Energy of Latex Films from PVA and Copolymers of VAc and Plant-Oil-Based Monomers Synthesized in the Emulsion Polymerization Process**

| sample | film thickness, μm | water resistance (double rubs) | water contact angle, θ, deg | CH$_3$I contact angle, θ, deg | surface energy, N/m | λ\(\text{d}_{1}\), N/m | λ\(\text{d}_{2}\), N/m | λ\(\text{d}_{3}\), N/m |
|-------|-------------------|-----------------------------|-----------------------------|-----------------------------|-------------------|----------------|----------------|----------------|
| SOVM(50) | 42 ± 8 | >400 | 66 ± 2 | 45 ± 2 | 29.2 | 13.5 | 42.7 |
| SSBM(15) | 41 ± 5 | 340 | 59 ± 3 | 47 ± 2 | 26.7 | 18.9 | 45.6 |
| SSFM(15) | 42 ± 6 | 390 | 69 ± 2 | 40 ± 1 | 33.0 | 10.1 | 43.1 |
| SLSM(75) | 44 ± 6 | >400 | 69 ± 2 | 40 ± 2 | 32.9 | 10.3 | 43.2 |
| PVA | 42 ± 8 | 0 | 51 ± 3 | 51 ± 3 | 18.8 | 54.2 | 73.0 |

*Values in in brackets: conversion of VAc (wt %) before the plant-oil-based counterpart was added.

**Free-Radical Copolymerization of Plant-Oil-Based Monomers with St/VAc.** Each plant-oil-based monomer (0.4−2 g; 0.1−0.9 mole part), vinyl monomer (0.1−0.5 g; St or VAc; 0.9−0.1 mole part, total monomer concentration 1−2 M), and AIBN (0.04 g 0.038 M) were dissolved in 5 mL of toluene, and the mixture was stirred. The reaction mixture was purged with argon at room temperature for 30 min. Copolymerization was carried out under an argon blanket at 60 °C for 2 h until a total monomer conversion of 10−15% was reached. Samples (0.6-0.7 g) of the reaction mixture were taken to monitor the progress of the copolymerization reaction using a gravimetric method after precipitation of the copolymer using a large excess of methanol or a methanol/water mixture. The resulting copolymers were purified by multiple precipitations from

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toluene in methanol or in a methanol/water mixture. The purified polymer was dried under a nitrogen blanket at room temperature until it reached a constant weight. The resulting copolymers containing various amounts of plant-oil-based fragments are highly soluble in dichloromethane, chloroform, ethyl acetate, heptane, toluene, dioxane, and tetrahydrofuran (THF) and less soluble in acetone, dimethylformamide, methanol, and water.

**Plant-Oil-Based Copolymer Characterization.** To determine the composition of copolymers from each plant-oil-based monomer and St or VAc, 1H NMR spectra were recorded as described above. The average molecular weight of the copolymers was determined by gel permeation chromatography (GPC) using a Waters Corporation modular chromatograph consisting 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. THF was used as the carrier solvent.

**Synthesis of Plant-Oil-Based Latexes in Miniemulsion.** To synthesize latexes from each plant-oil-based monomer and MMA or VAc in miniemulsion, two oil phases were prepared. Two separate miniemulsions of MMA (or VAc) and plant-oil-based monomers were used instead of emulsifying the monomer mixture to minimize possible chain transfer reactions on the biobased monomer during copolymerization to increase total monomer conversion and, thus, copolymer molecular weight. For Oil Phase 1, a different amount of each plant-oil-based monomer (0.75−6 g) was dissolved in 1-octanol (weight ratio 2:1). Oil Phase 2 was prepared by mixing a different amount of VAc (or MMA) (9−14 g), 1.5 wt % of hexadecane (0.13−0.21 g) (based on VAc/MMA weight) to prevent Ostwald ripening, and 1.5 wt % of initiator AIBN (0.2−0.3 g) (based on monomer weight). For the aqueous phase, 5 wt % sodium dodecyl sulfate (SDS, 0.75 g) (emulsifier) was dissolved in water.

For pre-emulsification, Oil Phase 1 and Oil Phase 2 were added dropwise to the aqueous phase divided into two parts and homogenized using a magnetic stirrer for 45 min at 1200 rpm. Two miniemulsions were prepared by ultrasonating the pre-emulsified mixtures for 180 s at 90% amplitude (digital sonicator 500 Watt, 1/2″ tip, 20 kHz; QSonica, Newtown, CN) at room temperature. VAc- (or MMA)-containing miniemulsion was slowly added dropwise to the aqueous phase divided into two parts dissolved in water.

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**Synthesis of Plant-Oil-Based Latexes Using Emulsion Polymerization with VAc.** A 250 mL reactor equipped with a mechanical stirrer, reflux condenser, nitrogen purge, and feed tubes was filled with 83 g of deionized water, 4.83 g of a 65% aqueous solution of the commercial nonionic surfactant Triton 405 (highly ethoxylated fatty alcohol), 3.25 g of a 20 wt % aqueous solution of SDS, 1.66 g of a 30 wt % aqueous solution of sodium vinyl sulfonate, and 0.19 g of sodium acetate. The aqueous phase was heated up to 65 °C while slowly adding 5 g of VAc. When the temperature reached 65 °C, 1.58 g of a 6.2 wt % aqueous solution of ammonium persulfate (initiator) was added and the temperature was raised to 70 °C. At this point, either 15, 45, or 75 g of VAc and 4.58 g of a 3.3 wt % ammonium persulfate aqueous solution were added to the reaction mixture over 240 min, and the temperature was raised to 75 °C. When VAc conversion reached 15, 50, or 75%, a mixture comprising 5 g of plant-oil-based monomer and 75, 45, or 15 g of VAc, respectively, was added. Subsequently, 1 g of a 9% ammonium persulfate aqueous solution was added, and the temperature was raised to 80 °C and maintained for 60 min.

**Characterization of Plant-Oil-Based Latexes.** The solid content of the synthesized plant-oil-based latexes was determined gravimetrically after drying the samples at 110 °C. The size distribution of latex particles was measured using a Zetasizer Nano-ZS90 (Malvern, Worcestershire, U.K.) at a single scattering angle of 90° and a temperature of 25 °C (for measurement, 50 μL drop of each latex was placed in 5 mL of water). For each latex sample, copolymer composition and average molecular weight were determined using 1H NMR spectroscopy and GPC, as described above.

The morphology of latex particles was observed on a tungsten filament 100 kV transmission electron microscope (TEM) JEOL JEM-100CX II, (JEOL, Peabody, MA). For the TEM measurements, a drop of latex dispersion diluted with deionized water was placed onto a copper mesh covered with a thin carbon film. The samples were characterized after drying.

The glass-transition temperature of the resulting latexes was determined via modulated DSC using a TA Instruments Q1000 calorimeter. Dry nitrogen was purged through the sample at a flow rate of 50 mL/min. The samples were subjected to an underlying heating rate of 5−10 °C/min.

Latex films were prepared using a draw down bar of 6 mm in thickness, which was cleaned by acetone before application of steel substrate QD36 and after drying the films at 105 °C for 2 h. The dynamic mechanical behavior of the latex films was determined using a dynamic mechanical analyzer (TA Instruments Q800) with tensile mode and a heating rate of 5 °C/min. Samples of films with a typical size of 13 mm × 5 mm (length × width) were used.

The mechanical properties of the latex films were determined using an Instron testing machine 2710-004 with a crosshead speed of 5 mm/min, a maximal load of 500 N, and a temperature range of 0−100 °C. Rectangular samples with a size of about 25 mm × 5 mm (length × width) were used. At least five replicates of each latex sample were used to obtain an average value.

To determine the surface energy of latex films with varying biobased contents, water and diiodomethane contact angle measurements were carried out using a contact angle/surface tension analyzer (FTA 125) and the static sessile drop (50 μL) method. An average value of at least five measurements on each film was taken. Surface energy, \( \gamma \), and its components, \( \gamma_d \), \( \gamma_s \), and \( \gamma_h \), were determined using the following formulae:

\[
\gamma = \gamma_d + \gamma_s + \gamma_h
\]

Where \( \gamma_d \) is the dispersive component, \( \gamma_s \) is the specific surface component, and \( \gamma_h \) is the hydrophilic component.

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Where \( \gamma_d \) is the dispersive component, \( \gamma_s \) is the specific surface component, and \( \gamma_h \) is the hydrophilic component.
were estimated using Owens and Wendt expression for modified Young’s equation.\textsuperscript{12}
For selected latex films from copolymers of VAc and plant-oil-based monomers, water resistance (using ASTM D5402-15) was determined.

■ ASSOCIATED CONTENT

\( \text{Supporting Information} \)

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00308.

Experimental details on monomer characterization and copolymer chemical structures (PDF)

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**Notes**

The authors declare no competing financial interest.

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