

Synthesis and Free Radical Copolymerization of a Vinyl Monomer from Soybean Oil

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S Supporting Information

ABSTRACT: A one-step method that converts soybean oil into (acryloylamino)ethyl soyate, a new vinyl monomer of free radical polymerization, was developed. The synthesized monomer combines a vinyl double bond (acryloyl functional group) and nonconjugated (isolated) double bonds of fatty acids. The double bond of the acryloyl group is reactive in a free radical chain polymerization that yields linear macromolecules containing isolated double bonds in side chains. Monomer reactivity ratios (r_1 , r_2) in copolymerization of the new soybean oil-based acrylic monomer (SBA) with styrene, methyl methacrylate, and vinyl acetate, as well as the $Q-e$ parameters of the SBA, were determined. The obtained results indicate that copolymerization can be described with the classical Mayo–Lewis equation. In terms of polymerizability, the SBA can be classified as an acrylic monomer. The double bonds of the fatty acid chains remain mainly unaffected during the free radical polymerization. The remaining unsaturated fragments in the side chains make the resulting macromolecules capable of further oxidative cross-linking and the development of cross-linked polymer coatings.

KEYWORDS: Biobased monomer, Free radical polymerization, Renewable polymers



INTRODUCTION

The design of biobased polymers from renewable resources is a promising platform to provide new materials with industrially viable properties and a positive environmental impact.^{1,2} On a cost–performance basis, some of the biobased polymeric materials can even surpass existing petroleum-based polymers in various applications.^{3–5} Because of their abundant availability, vegetable oils have recently become the most important renewable feedstock in the chemical industry, particularly in the production of biobased polymers.^{6–10}

Vegetable oils consist predominantly of triglycerides. Conceptually different strategies were used to prepare polymers, such as oxypolymerized oils, polyesters, polyurethanes, polyamides, acrylic resins, and epoxy resins, from triglyceride oils.⁷ The oxidative mechanism is one of the most common methods for polymerization of the triglycerides with different types of unsaturated fatty acid chains with one or several double bonds (isolated or conjugated), to obtain cross-linked polymers.^{11–14} Cross-linked macromolecules have also been developed by modification of triglycerides with vinyl monomers (for example, styrenation of unsaturated fatty acid chains) in the presence of radical initiators (benzoyl peroxide, di-*tert*-butyl peroxide).^{15,16}

Polyesters, polyurethanes, polyamides, etc. from triglyceride oils can be synthesized via polycondensation of diacids, diols, diisocyanates, and epoxy resins via epoxidation of unsaturated fatty acid chains of triglyceride oils.⁷ However, most currently available syntheses of polymers from triglyceride oils are limited to polycondensation and oxypolymerization. Both mechanisms result in the formation of exclusively cross-linked polymers, widely applicable in industrial coatings.^{17,18} Coatings based on

water-soluble alkyd resins prepared from maleinized triglyceride oils were described by Solomon¹⁹ and reported in several papers.^{20–22}

At the same time, the development of waterborne polymeric materials (latexes, emulsions, dispersions) from vegetable oils remains challenging because of their highly hydrophobic nature.⁷ In fact, converting triglyceride oils into vinyl monomers for synthesizing waterborne polymeric materials (latexes, adhesives, etc.) via classic chain radical copolymerization is not described in the literature.

In this study, we developed a one-step approach for synthesizing a new vinyl monomer of free radical polymerization from naturally occurring triglycerides of soybean oil (Scheme 1).

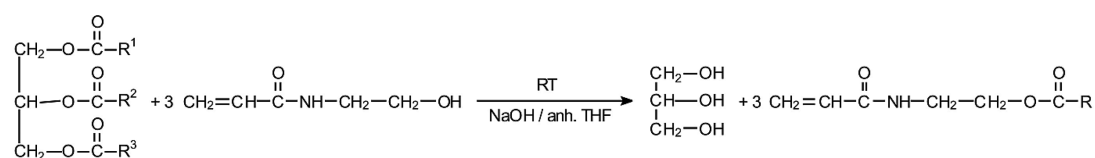
The chemical structure of the SBA combines double bonds with various reactivity in free radical reactions. These are (i) vinyl double bond, $\text{CH}_2=\text{CH}-$, of the acrylic functional group, and (ii) one or several isolated double bonds of fatty acids acyl groups ($-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$, respectively). The vinyl bond is reactive in conventional addition chain polymerization by facilitating macromolecular chain growth. The double bonds of the fatty acid chains are mainly unaffected during the free radical polymerization process that yields linear macromolecules. These unsaturated fatty fragments with double bonds make the resulting macromolecules capable of postpolymerization oxidative reactions to form cross-linked

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Scheme 1. Synthesis of Soy-based Acrylic Monomer via Direct Transesterification Reaction of Triglycerides of Soybean Oil with *N*-(Hydroxyethyl)acrylamide^a



^aR¹, R², R³: saturated or unsaturated fatty acid chains with one or several isolated double bonds.

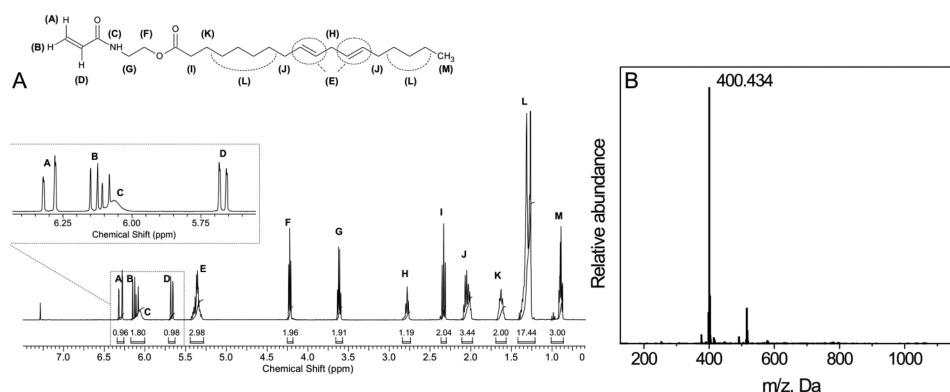


Figure 1. ¹H NMR spectrum (A) and mass spectrum (B) of characteristic SBA.

polymer structures, or of modification of unsaturated fatty acid chains in resulting macromolecules.

MATERIALS AND METHODS

Materials. Soybean oil (Crisco, The J.M. Smucker Company, Orville, OH) and *N*-(hydroxyethyl)acrylamide (HEAAm; TCI America) were used as received. Azobis(isobutyronitrile) (AIBN; Sigma-Aldrich, St. Louis, MO) was purified with recrystallization from methanol. Styrene (St; Sigma-Aldrich, St. Louis, MO), methyl methacrylate (MMA; TCI America), and vinyl acetate (Vac; TCI America) monomers were distilled under vacuum to remove the inhibitor and stored in a refrigerator. Toluene (Sigma-Aldrich, St. Louis, MO) was distilled prior to use. Other solvents and chemicals, analytical grade or better, were used as received. Deionized water was used for purification purposes (Milli-Q, 18 MΩ).

Soy-based Acrylic Monomer (SBA) Synthesis and Characterization. About 115 g of *N*-hydroxyethyl-acrylamide was added to 150 g of soybean oil (acrylamide alcohol to triglyceride molar ratio as 5.9 to 1), 150 mL of tetrahydrofuran, and 0.1 g of 2,6-dimethylphenol in a two-neck 500 mL round-bottomed flask equipped with a mechanical stirrer. The reaction mixture was heated up to 40 °C in the presence of a catalytic amount of ground sodium hydroxide slowly added to the reaction mixture with continuous stirring. The reaction mixture was stirred at 40 °C until complete homogenization (approximately 3 h), and was allowed to remain overnight at room temperature. The synthesized product was diluted with CH₂Cl₂, purified by washing with brine, treated with magnesium sulfate, and dried under vacuum to obtain 170 g of (acryloylamino)ethyl soyate (90% of theoretical).

The resulting SBA contains one acrylic double bond linked to one fatty chain that varies between fully saturated, mono- and polyunsaturated, depending on soybean oil composition. The SBA is mostly represented by (acryloylamino)ethyl linoleate in the case of transesterification of commodity soybean oil.

To confirm the chemical structure of the SBA monomer, (acryloylamino)ethyl soyate, 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 ESI high-resolution mass spectrum of the SBA was obtained using a Bruker Daltonics BioTOF mass spectrometer.

SBA Free Radical Polymerization. SBA (0.5 M) and AIBN (0.024 M) were dissolved in toluene, and the mixture was stirred. The reaction mixture was purged with argon at room temperature for 30 min and heated to 60 °C under an argon blanket for 8 h (total monomer conversion of 65 ÷ 85%). The resulting homopolymer was precipitated using a large excess of hexane and purified with multiple precipitations. The purified polymer was dried under reduced pressure at room temperature until a constant weight was obtained. The average molecular weight of the homopolymer was determined with gel permeation chromatography (*M*_n = 26 380 g/mol, PDI = 1.8), see Figure S2 in the Supporting Information).

Free Radical Copolymerization of SBA with St/MMA/Vac. SBA (0.1 ÷ 0.9 mole part), vinyl monomer (St, MMA or Vac) (0.9 ÷ 0.1 mole part), and AIBN (0.024 M) were dissolved in toluene, and the mixture was stirred. The total concentration of monomers was 1–2 M. 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. Small samples of the reaction mixture were taken to monitor the progress of the copolymerization reaction using a gravimetric method after precipitation of the copolymer. The resulting copolymer was isolated with precipitation in methanol or hexane and purified with multiple precipitations. The purified polymer was dried under reduced pressure at room temperature until a constant weight was obtained. The resulting copolymers containing 20–80 w% of soy-based acrylic units are soluble in acetone, toluene and tetrahydrofuran and nonsoluble in methanol and water. The average molecular weight of the copolymers was determined with gel permeation chromatography (*M*_n = 28 000–37 000 g/mol).

SBA-based Copolymer Characterization. To determine the composition of the SBA–St, SBA–MMA, and SBA–Vac copolymers, ¹H NMR spectra for the homo- and copolymers were recorded on an AVANCE III HDTM 400 high-performance digital NMR spectrometer (Bruker, Billerica, MA) using CDCl₃ as a solvent and phthalic anhydride as an internal reference.

The average molecular weight of the copolymers was determined with 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. Tetrahydrofuran (THF) was used as the carrier solvent.

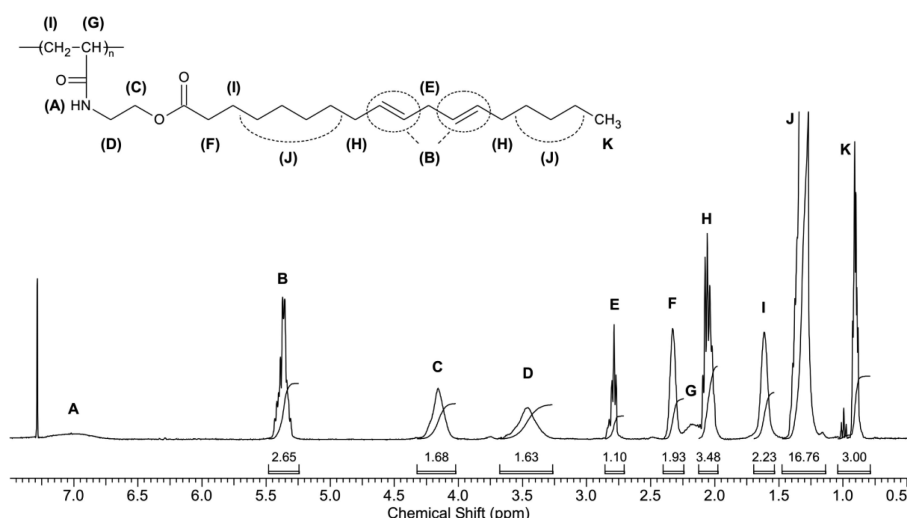


Figure 2. ^1H NMR spectrum of the characteristic poly((acryloylamino)ethyl soyate).

The glass transition temperatures of the SBA homopolymer and the SBA–MMA copolymers were determined via modulated differential scanning calorimetry (MDSC) using a TA Instruments Q1000 calorimeter. Dry nitrogen with a flow rate of 50 mL/min was purged through the sample. The samples were subjected to an underlying heating rate of 10 $^{\circ}\text{C}/\text{min}$.

RESULTS AND DISCUSSION

To the best of our knowledge, vegetable oil-based vinyl monomers with two types of double bonds having different reactivity in radical reactions have not been previously reported.

The main goal of this study was to synthesize the SBA, (acryloylamino)ethyl soyate, using direct transesterification of crude soybean oil with *N*-(hydroxyethyl)acrylamide, and investigate free radical copolymerization of the SBA with commodity vinyl monomers, styrene, methyl methacrylate, and vinyl acetate.

To yield the (acryloylamino)ethyl soyate, crude soybean oil was reacted in one step with *N*-(hydroxyethyl)acrylamide in the presence of a catalytic amount of sodium hydroxide. Among various solvents, tetrahydrofuran is a suitable reaction medium for high-yield synthesis of the targeted SBA monomer, which depends on the initial concentration of the reactants and the ratio of catalyst (NaOH) to reactants.

The anticipated chemical structure of the synthesized monomer was confirmed using ^1H NMR spectroscopy (Figure 1A) and FT-IR spectroscopy (Figure S1 in the Supporting Information). The recorded spectra show that the (acryloylamino)ethyl soyate molecules contain an *N*-acryloyl fragment that provides monomer reactivity in chain radical polymerization. More details concerning the ^1H NMR and FT-IR spectra of the monomer can be found in the Supporting Information. The molecular weight of the SBA monomer determined using mass spectrometry (Figure 1B), after deducing the molecular weight of a sodium atom (377), is a perfect match with the theoretical average SBA molecular weight (375).

To establish the monomer capability of free radical reactions, homopolymerization was carried out in toluene at 60 $^{\circ}\text{C}$, an initial monomer concentration of 0.5 M, and a concentration of free radical initiator AIBN (0.024 M) (see the Supporting Information for more details).

The ^1H NMR spectrum of the homopolymer (Figure 2), as compared with the ^1H NMR spectrum of the SBA (Figure 1A), shows the absence of the vinyl double bond of the acrylic functional group that confirms the formation of macrochains from the SBA monomer links. Hence, the homopolymer spectrum indicates that the polymer backbone is formed through the polymerization of SBA acrylic fragments, while the isolated double bonds of the soy-based monomer remain unaffected during the reaction.

The further focus of this study was to evaluate the reactivity of the SBA acrylic double bond and monomer feasibility in free radical copolymerization. We performed experiments in order to determine the Q - e values for a new soy-based acrylic monomer. For this purpose, in copolymerization of the SBA and styrene (St), the r_1 and r_2 were determined experimentally by measuring an instantaneous copolymer composition (with ^1H NMR spectroscopy at low monomer conversions of 5–10%) (Figure 3) and employing the Kelen–Tudos approach to a solution of the Mayo–Lewis copolymerization equation (eq S1 in the Supporting Information).^{23–25}

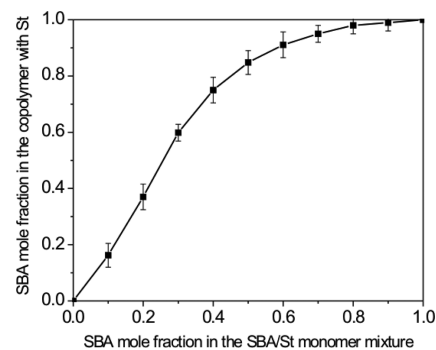


Figure 3. Experimental SBA content in the SBA–St copolymer vs SBA content in the initial feed mixture.

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.²⁴ $[M_1]$, $[M_2]$ 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 SBA and St are shown in Table 1.

Table 1. Monomer Reactivity Ratios for Copolymerization of SBA and MMA, St, Vac

comonomer pair	r_1	r_2
SBA–St	0.18 ± 0.06^a	0.85 ± 0.2^a
SBA–MMA	0.45 ± 0.1^b	2.15 ± 0.4^b
SBA–Vac	9.43 ± 0.7^b	0.06 ± 0.01^b

^aDetermined experimentally. ^bCalculated using the Q – e values. Chemical structure of the copolymers from the soy-based acrylic monomer and MMA, St and Vac are shown in the Supporting Information (Figure S3).

Having the experimental r_1 and r_2 for SBA and St, as well as literature data on styrene Q – e values ($Q = 1$ and $e = -0.8$),²³ the Alfrey–Price scheme (eq S2 in the Supporting Information) was applied to calculate the Q – e of the SBA monomer. This calculation yields $Q = 0.39$ and $e = 0.58$ for the SBA.

To demonstrate that the Q – e values of SBA can be applied to control copolymer composition, additional studies on copolymerization of the soy-based acrylic monomer with methyl methacrylate (MMA) and vinyl acetate (Vac) were performed.

The chemical composition of each resulting SBA–MMA and SBA–Vac copolymer (ten for each monomer pair) was determined experimentally using ¹H NMR spectroscopy and compared to the theoretical copolymer compositions. The theoretical compositions were assessed using the Alfrey–Price scheme (eq S2 in the Supporting Information) and the Q – e values for MMA ($Q = 0.78$, $e = 0.4$),²³ Vac ($Q = 0.026$, $e = -0.22$),²³ and SBA ($Q = 0.39$, $e = 0.58$) to determine r_1 and r_2 for the SBA–MMA and SBA–Vac monomer pairs. In the next step, these r_1 and r_2 values were applied to calculate each theoretical copolymer composition using the Mayo–Lewis copolymerization equation (eq 1).

$$\frac{[m_1]}{[m_2]} = \frac{[M_1]}{[M_2]} \cdot \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \quad (1)$$

It can be clearly seen in Figure 4 that the experimental and calculated plots are in good agreement, indicating that copolymerization of SBA with Vac (Figure 4A) and MMA (Figure 4B) can be described with the classical Mayo–Lewis copolymerization equation. Additionally, the Q – e values of the

new monomer allow the prediction of SBA reactivity in free radical copolymerization with other monomers.

The SBA unit content in copolymers can vary within a broad range and in a controlled way in terms of feed composition upon the copolymerization of SBA with other vinyl monomers, for instance, styrene, methyl methacrylate, and vinyl acetate. For most free radical copolymerizations, the product $r_1 \cdot r_2$ may be used with discretion for estimating the extent of copolymer randomness.^{23,25,26} On the basis of the r_1 and r_2 values shown in Table 1, their product equals 0.96 for SBA and MMA, 0.15 for SBA and St, and 0.56 for SBA and Vac. The obtained data indicate that there is a tendency toward alternation of fragments in the macromolecular backbone of copolymer from SBA and St (the $r_1 \cdot r_2$ value approaches zero). In contrast, the copolymerization of SBA and MMA results in random copolymers (r_1 and r_2 product approaches 1).

To show that the fraction of the SBA monomer units in the resulting macromolecules affects the copolymers' properties, the glass transition temperature (T_g) of the SBA–MMA copolymers with a varied composition was determined using differential scanning calorimetry (DSC). The DSC data indicate that T_g of the SBA–MMA copolymers changes considerably with increases in the fraction of the soybean oil-derived fragments in the synthesized macromolecules, approaching 22 °C when the copolymer contains 30 mol % of SBA monomer units (Figure S4 in the Supporting Information).

CONCLUSION

To conclude, a one-step method was developed that converts soybean oil into (acryloylamino)ethyl soyate, a new vinyl monomer, via direct transesterification reaction of triglycerides with *N*-(hydroxyethyl)acrylamide. The monomer reactivity ratios (r_1 , r_2) in copolymerization of the new soybean oil-based acrylic monomer (SBA) with styrene, methyl methacrylate, and vinyl acetate, as well as the Q – e parameters of the SBA ($Q = 0.39$ and $e = 0.58$), were determined. The obtained results indicate that copolymerization is described with the classical Mayo–Lewis equation. In terms of polymerizability, the new monomer behaves as a conventional vinyl monomer. Therefore, free radical copolymerization of the biobased acrylic monomer synthesized in this work, (acryloylamino)ethyl soyate, and commodity monomers can become an important and useful tool in designing new polymeric materials. The (acryloylamino)ethyl soyate derived from renewable resources could replace petroleum-based monomers in the production of polymer latexes, adhesives, and other industrial materials

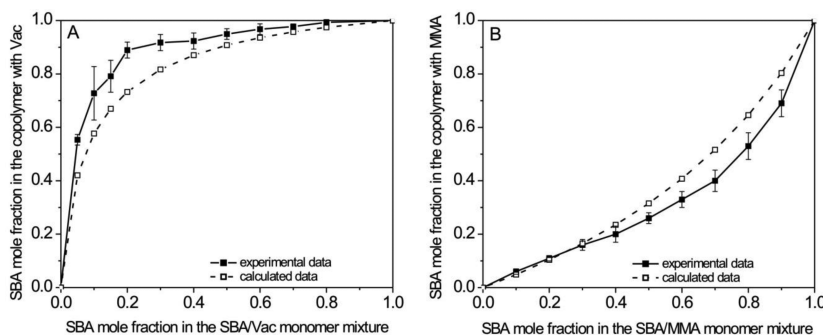


Figure 4. Calculated and experimental SBA content in SBA–Vac (A) and SBA–MMA (B) copolymer composition vs SBA content in the initial feed mixture.

(including dispersion polymerization) that utilize acrylic monomers and polymers.

■ ASSOCIATED CONTENT

📄 Supporting Information

Experimental details on monomer characterization and copolymers chemical structure. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00312.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Belgacem, M. N.; Gandini, A. *Monomers, Polymers and Composites from Renewable Resources*; Elsevier, Amsterdam, 2008.
- (2) Lu, Y.; Larock, R. C. Novel polymeric materials from vegetable oils and vinyl monomers: Preparation, properties and applications. *ChemSusChem* **2009**, *2*, 136–147.
- (3) Williams, C. K.; Hillmeyer, M. A. Polymers from renewable resources: A perspective for a special issue of polymer reviews. *Polym. Rev.* **2008**, *48*, 1–10.
- (4) Gallezot, P. Conversion of biomass to selected chemical products. *Chem. Soc. Rev.* **2012**, *41*, 1538–1558.
- (5) Lligadas, G.; Ronda, J. C.; Galia, M.; Cadiz, V. Renewable polymeric materials from vegetable oils: A perspective. *Mater. Today* **2013**, *16* (9), 337–343.
- (6) Verhe, R. G. Industrial products from lipids and proteins. In *Renewable Bioresources: Scope and Modification for Non-Food Applications*; Stevens, C. V., Verhe, R. G., Eds.; John Wiley & Sons, Ltd: Chichester, U. K., 2004.
- (7) Guner, F. S.; Yagci, Y.; Erciyas, A. T. Polymers from triglyceride oils. *Prog. Polym. Sci.* **2006**, *31*, 633–670.
- (8) Sharma, V.; Kundu, P. P. Addition polymers from natural oils—A Review. *Prog. Polym. Sci.* **2006**, *31*, 983–1008.
- (9) Wool, R. P.; Sun, X. S. *Bio-Based Polymers and Composites*; Elsevier: Amsterdam, 2005.
- (10) Gunstone, F. *Fatty Acid and Lipid Chemistry*; Blackie Academic & Professional: New York, 1996.
- (11) Mallegol, J.; Lemaire, J.; Gardette, J. L. Drier influence on the curing of linseed oil. *Prog. Org. Coat.* **2000**, *39*, 107–113.
- (12) Hess, P. S.; O'Hare, G. A. Oxidation of linseed oil—temperature effects. *Ind. Eng. Chem.* **1950**, *42* (7), 1424–1431.
- (13) Yildiz, G.; Wehling, R. L.; Cuppet, S. L. Method for determining oxidation of vegetable oils by near-infrared spectroscopy. *J. Am. Oil Chem. Soc.* **2001**, *78* (5), 495–502.
- (14) Asadauskas, S.; Erhan, S. Z. Thin-film test to investigate liquid oxypolymerization of nonvolatile analytes: Assessment of vegetable oils and biodegradable lubricants. *J. Am. Oil Chem. Soc.* **2001**, *78* (10), 1029–1035.
- (15) Erkal, F. S.; Erciyas, A. T.; Yagci, Y. Styrenation of triglyceride oils by macromonomer technique. *J. Coat. Technol.* **1993**, *65*, 37–43.
- (16) Kabasakal, O. S.; Guner, F. S.; Erciyas, A. T.; Yagci, Y. Styrenation of oils based on secondary esters of castor oil. *J. Coat. Technol.* **1995**, *67*, 47–51.

(17) Bailey, A. E. *Bailey's Industrial Oil and Fat Products*; Wiley: New York, 1996.

(18) Johnson, R. W.; Fritz, E. E. *Fatty Acids in Industry*; Marcel Dekker: New York, 1989.

(19) Solomon, D. H. *The Chemistry of Organic Film Formers*; Wiley: New York, 1971.

(20) Hofland, A. *Surf. Coat. Int.* **1994**, *7*, 270–281.

(21) Rodstrud, G.; Sutcliffe, J. F. Alkyd emulsions-properties and application. Results from comparative investigations of penetration and aging of alkyds, alkyd emulsions and acrylic disperions. *Surf. Coat. Int.* **1994**, *1*, 7–16.

(22) Aigbodion, A. I.; Okieimen, F. E.; Obazee, E. O.; Bakare, I. O. Utilisation of maleinized rubber seed oil and its alkyd resin as binders in water-borne coatings. *Prog. Org. Coat.* **2003**, *46*, 28–31.

(23) Odian, G. *Principles of Polymerization*; Wiley: New York, 1981.

(24) Kelen, T.; Tudos, F.; Turcsanyi, B. *Polym. Bull.* **1980**, *2*, 71–76.

(25) Chanda, M. *Introduction to Polymer Science and Chemistry: A Problem Solving Approach*; Taylor & Francis, CRC Press: Boca Raton, FL, 2006.

(26) Carraher, C.E. *Introduction to Polymer Chemistry*, 2nd ed.; Taylor & Francis, CRC Press: Boca Raton, FL, 2010.