

Chain Transfer of Vegetable Oil Macromonomers in Acrylic Solution Copolymerization

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ABSTRACT: The use of vegetable oil macromonomers (VOMMs) as comonomers in emulsion polymerization enables good film coalescence without the use of solvents that constitute volatile organic compounds (VOCs). VOMMs are derived from renewable resources and offer the potential of post-application crosslinking via auto-oxidation. However, chain transfer reactions of VOMMs with initiator and/or polymer radicals during emulsion polymerization reduce the amount of allylic hydrogen atoms available for primary auto-oxidation during drying. Vegetable oils and derivatives were reacted with butyl acrylate and methyl methacrylate via solution polymerization, and

the polymerization was monitored using *in situ* infrared spectroscopy to determine the extent of chain transfer. ¹H NMR spectroscopy was used to determine the loci of chain transfer and the molecular weight characteristics of the polymers were characterized by SEC. Solution polymerization was utilized because this limited temperature fluctuations and insolubility of the polymer. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 1390–1396, 2011

Key words: macromonomers; copolymerization; renewable resources

INTRODUCTION

Vegetable oils have a long standing history in the coating industry, particularly in unsaturated polyesters (alkyds).¹ Use of vegetable oil-based coatings waned a few decades ago due to the advent of synthetic alternatives, such as, polyurethanes, epoxies, and acrylics, but concerns over petroleum sustainability has renewed interest in vegetable oils. Vegetable oils are triglyceride esters of fatty acids and their general structure is shown in Figure 1. They vary in molecular weight, unsaturation, and conjugation. Table I provides a list of oils along with their major fatty acid components and percentages. The fatty acid composition of any oil can be altered by varying environmental conditions, such as, soil type and growing location, and climactic changes, such as, humidity and temperature.²

Vegetable oils can be modified in a variety of ways which include, but is not limited to transesterification, amidation, maleinization, metathesis, epoxida-

tion, and acrylation.³ Vegetable oil macromonomers (VOMMs) have been synthesized and studied in our labs as viable comonomers, in particular, for emulsion polymers. The design basis is for a VOMM to plasticize conventionally hard/high T_g latex particles, temporarily softened to reduce or eliminate the need for coalescing solvents in waterborne coatings that constitute volatile organic compounds (VOCs). The unique design brings together the advantages of latex polymer and auto-oxidizable natural products. Moreover, when allylic unsaturation is retained through the polymerization and storage process, VOMMs auto-oxidize to increase the polymer T_g , chemical resistance, and many thin film performance properties. The monomers are derived from renewable resources and further complement zero-VOC latex polymer development and utilization without performance sacrifices.^{4–6} Figure 2 shows two examples of VOMMs produced in our labs.

Auto-oxidative drying mechanisms are characterized by two stages, primary and secondary oxidation. After an induction period where oxygen reacts with the oil's antioxidants, primary oxidation begins via oxygen uptake through allylic and bisallylic hydrogen abstraction reactions followed by hydroperoxide formation. Primary oxidation increases double bond conjugation and forms hydroperoxides that dissociate to initiate secondary oxidation. In this step, loss of unsaturation leads to the formation of C–C and

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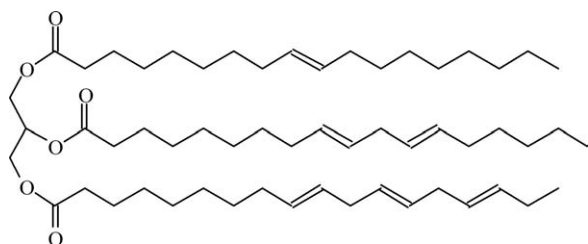


Figure 1 Generic vegetable oil structure.

C—O—C bonds that generates cyclic and acyclic products (alcohols, carboxylic acids, ketones, and aldehydes)^{7,8} and crosslinked polymer.^{9,10} Metal salts (known commonly as driers) accelerate auto-oxidation by decomposing hydroperoxides through a redox mechanism.¹¹ Cobalt and manganese salts function as primary driers in curing the coating surface, whereas zirconium and calcium salts serve as secondary driers to promote drying throughout the film.¹²

During free-radical emulsion polymerization, varying degrees of chain transfer reactions occur between VOMMs and the initiator and/or polymer radicals. Chain transfer is common with many emulsion polymerization monomers, however, a primary goal for optimal VOMM utility is allylic unsaturation retention. Besides reducing the latex molecular weight,¹³ chain transfer reactions also reduce the allylic hydrogen atom content available for auto-oxidation, both of which lower the potential for optimal coalescence and flow during film formation and hinder ultimate performance properties limited by chain transfer induced pre-crosslinking reactions. Chain transfer reactions are also observed in bulk and solution polymerizations. As a starting point for understanding VOMM interactions during free-radical polymerization, the research below was characterized with solution polymerization conditions to limit thermal fluctuations and maintain full solubility of all materials throughout the course of the reaction, unlike the results common for high molecular weight emulsion polymerization particles. The goal of this research was to determine the extent and location of chain transfer that occurs when acrylic monomers are copolymerized in the presence of vegeta-

ble oils and vegetable oil derivatives in solution. Methyl methacrylate and butyl acrylate were selected as the monomers of choice from our experience with emulsion polymerization and the blends copolymerized in benzene. The acrylate conversion was measured using *in situ* infrared spectroscopy.

EXPERIMENTAL

Materials

Methyl methacrylate and butyl acrylate were purchased from Fisher Scientific. Oleic acid, stearic acid, and their ethoxylated derivatives, EO-5 and ES-5, and polyethylene glycol (PEG1000) were purchased from Sigma-Aldrich, whereas soybean oil, linseed oil, and tung oil were purchased from Alnor Oil. These raw materials were used without further purification. 2,2'-Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich and was purified before each experiment by dissolving in chloroform and recrystallizing in petroleum ether.

Infrared spectroscopy

A ReactIR 4000[®] (Mettler-Toledo) equipped with a diamond composite (DiComp) ATR probe was used to monitor acrylate polymerization. ATR-FTIR is an established technique for monitoring acrylate and methacrylate monomer conversion in real time.^{14,15} The ReactIR 4000[®] uses mid-infrared radiation to measure functional group concentration and is fitted with a MCT detector, allowing for rapid data acquisition. Data was collected every 2 min for 5 h under isothermal conditions for each reaction.

Solution copolymerization

The control polymer was synthesized without vegetable oils, polyethylene oxide chains, or VOMMs. A 20.81 g of butyl acrylate (0.162 mol), 15.82 g of methyl methacrylate (0.158 mol), and 160 mL of benzene were added to a 250 mL, three neck, round-bottom flask. The flask was equipped with a

TABLE I
Oils and Fatty Acid Contents²

Oil	Saturated ^a	Oleic	Linoleic	Linolenic	α -Eleostearic
Soybean	15	22	55	8	—
Sunflower	12	15	73	—	—
Linseed	9	17	14	60	—
Tung	5	11	15	—	69
Safflower	6	16	78	—	—

^a Also contains unsaturated fatty acids that represent very small fractions of the total composition.

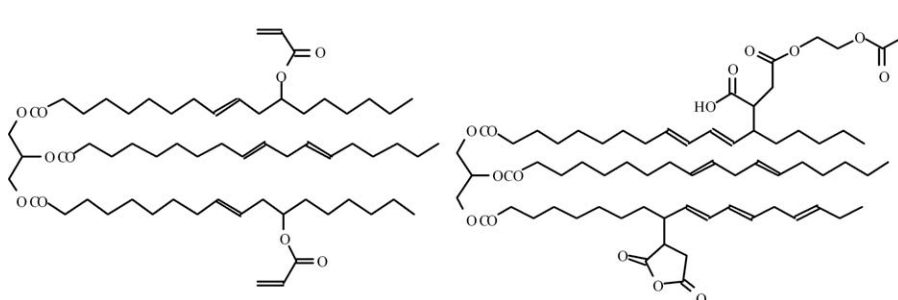


Figure 2 Castor acrylate monomer (CAM) and acrylated maleinized soybean oil (SAM), respectively.

magnetic stir bar, reflux column, thermocouple, temperature probe, and a DiComp ATR probe. The monomer solution was heated to 75°C using a J-KEM® Gemini temperature control unit. A 0.6 g of recrystallized AIBN (3.6 mmol) was added to the reaction flask and data collection was initiated once the temperature reached 75°C. Other copolymerizations were conducted by incorporating 9–33 wt % (based on total monomer weight) of the vegetable oil and vegetable oil derivatives to the control formulation.

Size exclusion chromatography

Size exclusion chromatography (SEC) was performed using a Waters Alliance 2695 Separations Module equipped with three Polymer Labs PLgel 5 μm mixed-C columns (300 mm \times 7.5 mm) in series, a Waters Model 2414 Refractive Index detector, a Waters Model 2996 Photodiode Array detector, a Wyatt Technology miniDAWN multi-angle light scattering (MALS) detector, and a Wyatt Technology ViscoStar viscometer. Absolute molecular weights (viz. M_w) were determined using measured dn/dc

values. In addition, molecular weights and molecular weight distributions were determined by conventional calibration against poly(methyl methacrylate) standards as well as universal calibration using polystyrene, poly(methyl methacrylate), and poly(*t*-butyl acrylate) standards.

A Wyatt Technology Optilab rEX refractive index detector was used in conjunction with a Harvard Apparatus PHD 2000 Infusion syringe pump to determine dn/dc values. Solutions of various concentrations ranging from nominally 1.0 to 10.0 mg/mL were prepared and allowed to equilibrate for several days before measurement. The dn/dc values were calculated using Astra V software.

RESULTS AND DISCUSSION

Chain transfer reactions were characterized via *in situ* FTIR. The (meth)acrylate peak at 810 cm^{-1} ($=\text{CH}_2$ twist)¹⁵ was monitored over time and monomer conversion was determined by calculating the area under the curve between 790 cm^{-1} and 840 cm^{-1} . Copolymerizations involving vegetable oils and their derivatives exhibited increased retardation in the polymerization rate versus higher material concentrations. Figure 3 is a single infrared spectrum, whereas Figure 4 summarizes the entire

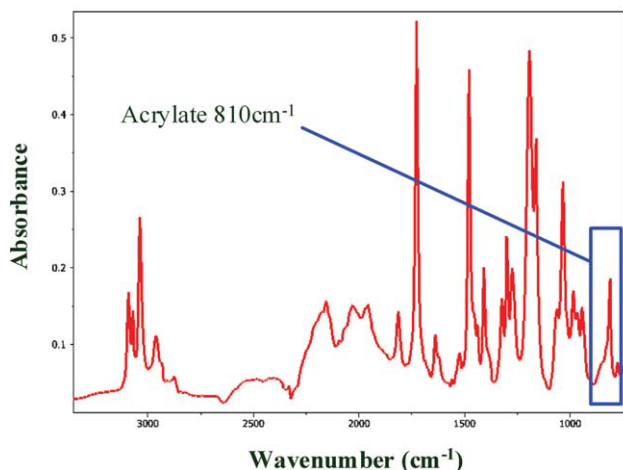


Figure 3 Infrared spectrum of control highlighting acrylate peak. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

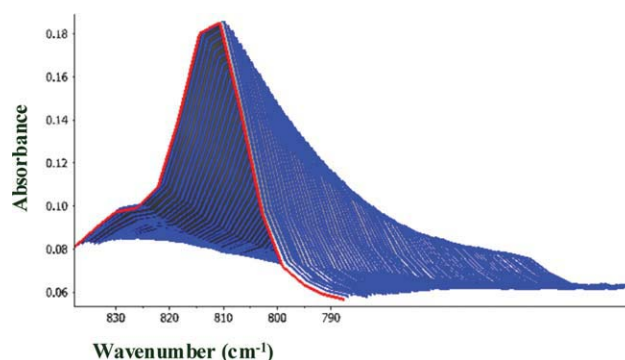


Figure 4 3D waterfall plot of acrylate peak (810 cm^{-1}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

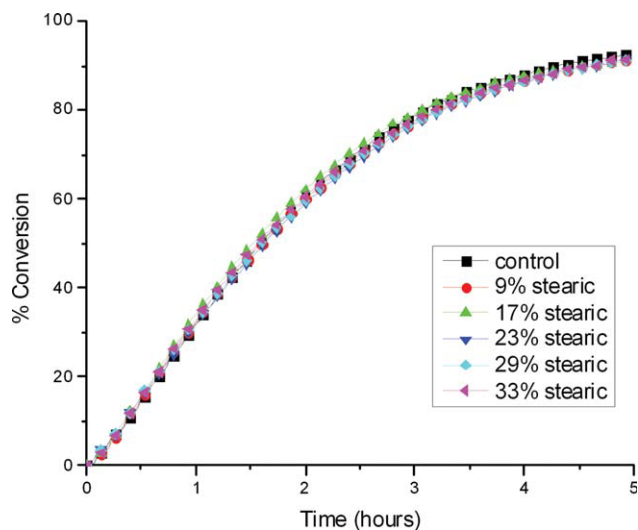


Figure 5 Acrylate profiles for stearic acid copolymerizations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

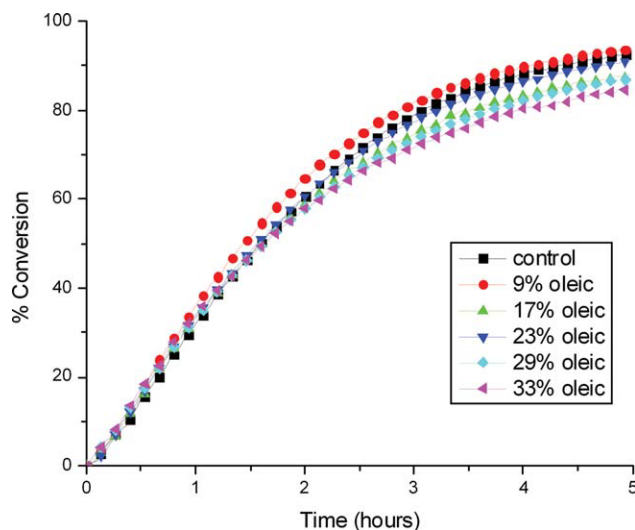


Figure 6 Acrylate profiles for oleic acid copolymerizations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

timeline as a waterfall plot acquired during the control polymerization and focused on the 810 cm^{-1} acrylate peak area.

Copolymerizations in the presence of stearic acid were used as an internal control. The experiment confirmed methodology and clarified whether any natural products were present, for example, potentially common antioxidants, that would also modify conversion or kinetics. Figure 5 shows the acrylate profiles for polymerizations blended with varying amounts of stearic acid (9–33 wt %). In the absence of allylic unsaturation, there is very little difference between the six profiles confirming the absence of chain transfer reactions during polymerization in the presence of stearic acid.

Copolymer synthesis in combination with oleic acid, however, exhibited decreasing monomer conversion and lower polymerization rates with increasing oleic acid content at the end of 5 h. Oleic acid

contains one double bond that is positioned at the ninth carbon from the glycerol ester. Chain transfer is thought to occur by reaction of a growing polymer chain or initiator fragment with the allylic hydrogen atoms of the double bond.¹⁶ The resulting radical is stabilized by resonance and can further react with another polymer chain or initiator fragment through bimolecular coupling. Figure 6 plots the profiles of copolymerizations with different levels of oleic acid.

Chemonic[®] O-5 and Brij[®] 72 are ethoxylated derivatives of oleic acid and stearic acid (hereafter referred to as EO-5 and ES-5) with an average of five ethoxy groups per molecule. Polymerizations with EO-5 resembled the polymerizations with oleic acid as monomer conversion decreased with increasing EO-5 content. However, at the same level of incorporation, monomer conversion was less for every EO-5 copolymerization than with oleic acid. Figure 7(a) plots the profiles of copolymerizations

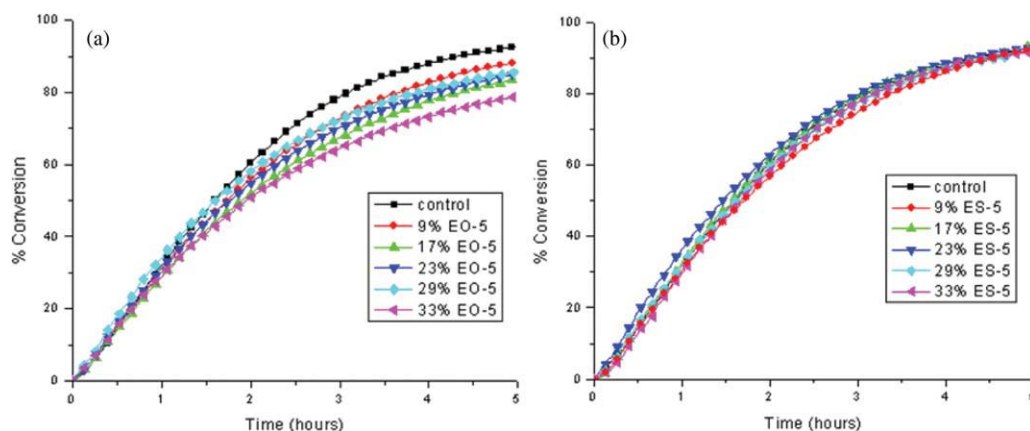


Figure 7 Acrylate profiles for (a) EO-5 copolymerizations and (b) ES-5 copolymerizations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

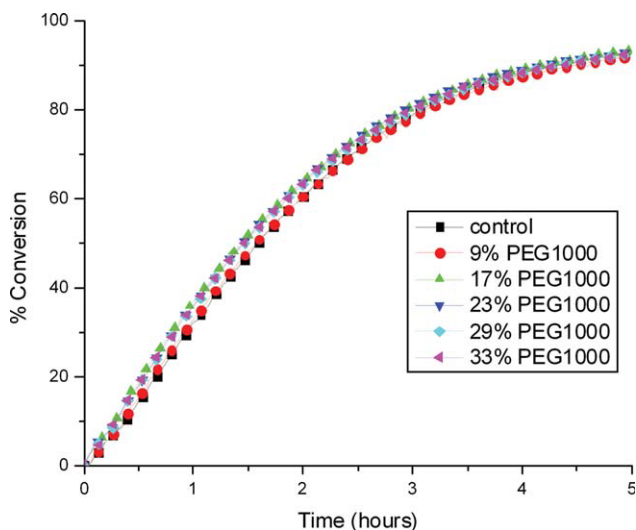


Figure 8 Acrylate profiles for PEG1000 copolymerizations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

with different levels of EO-5. The lower conversions observed with EO-5 copolymerizations are possibly due to chain transfer to hydroperoxides or hydrogen atoms of the ethoxylate repeat units. Ethers are known to be susceptible to hydroperoxide formation,¹⁷ which can participate in chain transfer reactions. Figure 7(b) plots the profiles of copolymerizations with different levels of ES-5. In like manner to the stearic acid profiles, very little change in polymerization rate is noted for ES-5.

Polymerizations conducted in the presence of polyethylene glycol (PEG) (molecular weight ~ 1000 g/mol) exhibited very little chain transfer or differences in overall conversion (Fig. 8). Under these reaction conditions, the hydrogen atoms alpha to oxygen in PEG are not typically labile and, therefore, do not retard polymerization rate.

Figure 9 provides a compilation of all the 33 wt % samples along with 33 wt % soybean oil, linseed oil, and tung oil, for comparison. Higher levels of unsaturation and conjugated unsaturation, in particular, produce greater quantities of abstractable hydrogen atoms. Additionally, the higher degrees of unsaturation support greater electron delocalization and increase the resonance stability of the radicals, thereby promoting chain transfer reactions. Hydroperoxides are more easily formed in linoleic and linolenic fatty acids than in oleic acid because of the active methylene group situated between the double bonds that lead to enhanced allylic radical stability and rearrangement to conjugated unsaturation. The energy of activation is very low when conjugated double bonds are present.¹⁸

Chain transfer greatly retarded the polymerization rate in reactions conducted in the presence of vegetable oils with the effect increasing in order of soy-

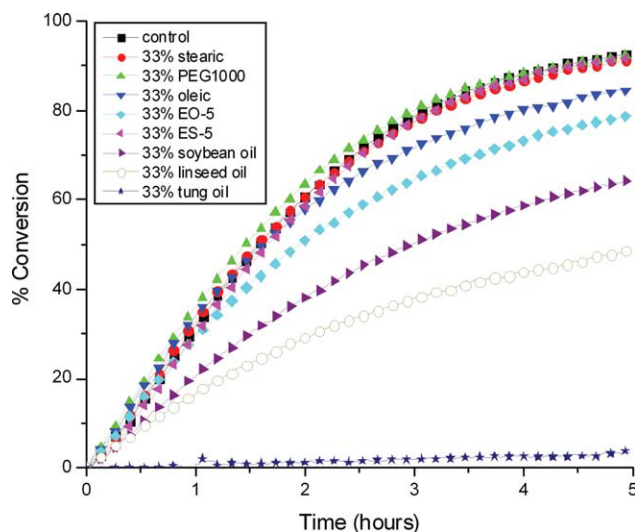


Figure 9 Acrylate profiles for polymerizations in the presence of 33 wt % additives. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bean oil, linseed oil, and tung oil. Polymerization was almost completely inhibited when conducted in the presence of 33% tung oil. Tung oil contains $\sim 70\%$ α -eleostearic acid, a fatty acid with three conjugated double bonds. Linseed oil contains $\sim 60\%$ linolenic acid and 14% linoleic acid with three and two double bonds, respectively (unconjugated in the natural state). Soybean oil contains 8% linolenic acid and 55% linoleic acid. Higher conjugation (greater electron delocalization) increases the resonance stability and lifetime of the radical, and promotes additional chain transfer reactions. The activation energy for hydroperoxide formation is lower in linolenic and linoleic fatty acids than in oleic acid due to the active methylene group between the double bonds.

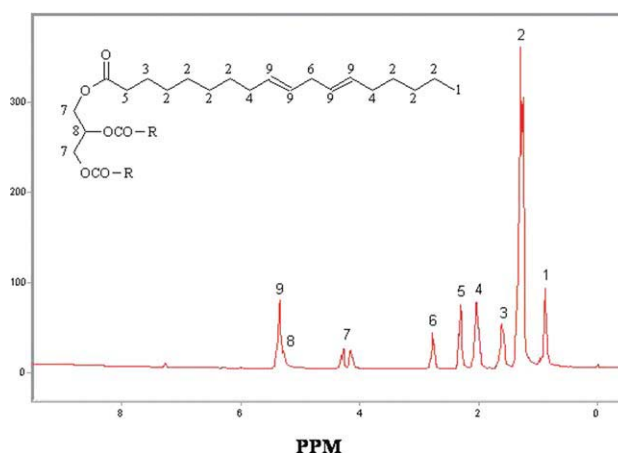


Figure 10 $^1\text{H-NMR}$ spectrum of soybean oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

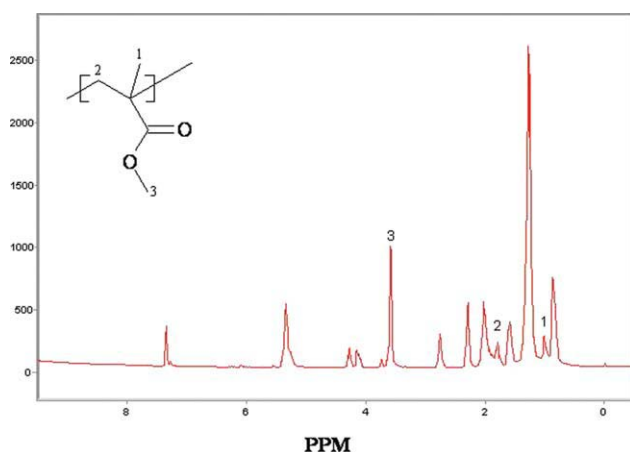


Figure 11 $^1\text{H-NMR}$ spectrum of PMMA after solution polymerization in the presence of 33% soybean oil. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The copolymerization reactions were analyzed further to validate the ratio of allylic double bonds before and after acrylate copolymerization. The effect of free-radical polymerization on vegetable oil unsaturation was evaluated via solution polymerization of methyl methacrylate in benzene with and without soybean oil under the same reaction conditions as noted earlier in the Experimental section. The soybean oil unsaturation (5.3 ppm) peak was integrated and compared with the glycidyl methylene protons (4.2 ppm) before and after polymerization (Figs. 10 and 11). Soybean oil had ~ 8.4 vinylic protons before the reaction and ~ 7.6 protons after polymerization. Because a 10% margin of error is associated with this technique, it was inferred that most, if not all, double bonds were retained after polymerization.

SEC analysis was performed on methacrylic polymers formed in the presence of 33 wt % vegetable oil to characterize the molecular weight versus concentration. While desired, specific data on branching could not be determined as the threshold of molecular weights for these polymers did not exceed the

minimum for accurate branching analysis. M_n , M_w , and polydispersity index (PDI) were determined from multiple methods. The molecular weight data is shown in Table II. The polymers were precipitated (Ppt) several times from methanol (MeOH) and hexanes to remove unbound vegetable oil.

Molecular weight data from Table II validate that the number of chain transfer events increases in proportion with iodine value, that is, in order of soybean, linseed, and tung oil. In all cases and regardless of measurement process/method, the molecular weight and PDI decreased with an increase in unsaturation, especially if the unsaturation was conjugated as in the case of tung oil.

CONCLUSIONS

VOMMs are beneficial for use in emulsion polymerization as they facilitate particle coalescence during film formation and have the potential to elevate the final T_g via auto-oxidation. Copolymerizing VOMMs with conventional acrylic monomers is complicated by the occurrence of chain transfer reactions and difficult to interpret during emulsion polymerization processes. *In situ* infrared spectroscopy studies confirmed that chain transfer increased with increasing concentrations of vegetable oils and vegetable oil derivatives. The quantity of chain transfer event increased when the reactions were blended with unsaturated oils, especially if the unsaturation was conjugated. The ethoxylated surfactant, EO-5, also facilitated chain transfer reactions. EO-5 retarded acrylate polymerization primarily through chain transfer with allylic hydrogen atoms but may also included reaction of hydroperoxides. PEG1000 and ES-5 did not contain hydroperoxides and they did not result in any appreciable chain transfer. SEC data was correlated with infrared data and showed increased chain transfer with increased amounts of unsaturation when methyl methacrylate was polymerized with soybean, linseed, and tung oil. This work is useful in determining a suitable pathway for the incorporation of VOMMs in acrylic polymers

TABLE II
Size Exclusion Chromatography Data

Treatment	PMMA Ppt MeOH	33% Soy oil Ppt MeOH 1 \times , hexanes 1 \times	33% Linseed Ppt MeOH 1 \times , hexanes 1 \times	33% Tung Ppt 3 \times hexanes
dn/dc (mL/g)	0.0802	0.0807	0.0838	0.0924
M_w ,MALLS (g/mol)	37,900	28,800	21,300	11,900
PDI ,MALLS	1.33	1.26	1.22	1.16
M_n ,conventional (g/mol)	25,800	21,100	16,900	9,180
PDI ,conventional	1.47	1.40	1.33	1.26
M_n ,universal (g/mol)	25,300	21,100	16,100	8,270
PDI ,universal	1.69	1.56	1.50	1.43

produced by emulsion polymerization. Adding VOMMs as comonomers in emulsion polymerizations will lead to chain transfer upon initiation with a redox or thermal radical initiator to varying degrees. The reactions will reduce the molecular weight of the resulting acrylic copolymer, whereas simultaneously reducing the amount of auto-oxidative functionality available to self-crosslinking polymers. The solutions studies summarized above clarify that VOMM incorporation would be more ideally accomplished by using a nonradical process, however, the total loss of unsaturation is minimal during copolymerization in the presence of soybean oil as measured by NMR. Further models are being synthesized to refine the understanding of an ideal network, that is, no chain transfer or loss of unsaturation before coating application. Post-polymerization attachment has been achieved by reacting functionalized fatty acids onto the backbone at varying degrees of incorporation for study. Further characterization method development to quantify the percentage of retention of allylic unsaturation during emulsion polymerization versus solution processes is critical.

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