Free-radical terpolymerization of *n*-butyl acrylate/butyl methacrylate/D-limonene

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ABSTRACT: D-Limonene (Lim) is a renewable monoterpene derived from citrus fruit peels. We investigated it for use as part of a more sustainable polymer formulation. The bulk free-radical terpolymerization of *n*-butyl acrylate (BA)/butyl methacrylate (BMA)/Lim was carried out at 80°C with benzoyl peroxide as the initiator. The terpolymerization was studied at various initial BA/BMA/Lim molar ratios, and the products were characterized for conversion, terpolymer composition, molecular weight, and glass-transition temperature. Lim was observed to undergo a significant degradative chain-transfer reaction, which greatly influenced the polymerization kinetics. The rate of polymerization, final conversion, and polymer molecular weight were all significantly reduced because of the presence of Lim. Nonetheless, polymers with relatively high weight-average molecular weights (20,000–120,000 Da) were produced. The terpolymer composition was well predicted with the reactivity ratios estimated for each of the three copolymer subsystems. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42821.

INTRODUCTION

Multicomponent polymerization is a common strategy used for tuning the properties of various polymer products, especially for coatings and adhesives. Through the manipulation of the monomer feed composition, the addition of other components (e.g., chain-transfer agent, crosslinker), and the control of the reaction conditions, specific physical and mechanical properties were achieved.

Driven by the need to reduce our dependence on fossil fuels and to mitigate environmental effects, increased effort is being directed toward the use of renewable materials to replace fossil-based monomers in polymerization. Various natural raw materials, such as cellulose, lignin, starch, vegetable oils, lactic acid, itaconic acid, terpenes, and rosins, have shown great potential in the development of renewable polymers.[1–7] Depending on the microstructural and final application requirements, different approaches, such as physical blending, chemical modification, and *in situ* polymerization, have been used to achieve the integration of the renewable feedstock into polymers.[8–10]

D-Limonene (Lim) is a naturally occurring monoterpene that is mainly extracted from orange peels as a byproduct of the juicing industry. Compared to the extraction and refinement of fossil-based feedstocks, the production of Lim (e.g., mechanical

separation and distillation) releases many fewer greenhouse gases and toxic pollutants to the environment. The current annual worldwide production of Lim is over 70 million kg.[11] Because it is essentially nontoxic (on the basis of both *in vitro* and *in vivo* toxicological studies)[12,13] and provides an intense citrus fruit odor, Lim has been widely used in food, fragrances, and medicine and as a safe alternative to many toxic solvents.[14–16] Lim is a cyclic olefin that contains two unconjugated C=C double bonds: an endocyclic double bond and an exocyclic double bond. As a monomer, Lim presents great potential for replacing nonpolar monomers (e.g., styrene) because it is renewable and nontoxic. The rigid structure of the limonene molecule results in a polymer glass-transition temperature (T_g) of about 116°C.[17] The use of limonene in multicomponent polymer formulations, therefore, could improve the hardness and stiffness and increase the application temperature range of the resulting polymer.

Many studies have shown that limonene has a high propensity toward chain-transfer reactions, as the allylic hydrogens next to the double bonds are very reactive and tend to be easily captured by living radicals.[18–22] During polymerization, molecular weight development is greatly influenced by this chain-transfer reaction mechanism. Thus, limonene could be used to modify the molecular weight in multicomponent systems where lower molecular weights may be required.

In this article, we present a study of the *n*-butyl acrylate (BA)/ butyl methacrylate (BMA)/Lim bulk terpolymerization. A primary goal was to demonstrate the use of the copolymer reactivity ratios for each of the three copolymer subsystems (i.e., BA/ BMA, BA/Lim, and BMA/Lim) to predict the terpolymer composition. Other data, such as the conversion, molecular weight, and T_g, were collected to provide further kinetic information.

EXPERIMENTAL

Materials

Lim was obtained from Fisher Scientific (96% purity) and was distilled *in vacuo* before use. BA ($\geq$99% purity), BMA ($\geq$99% purity), and benzoyl peroxide (BPO) were purchased from Sigma Aldrich. BA and BMA were purified from the monomethyl ether hydroquinone inhibitor with an inhibitor removal column (Sigma Aldrich). BPO was recrystallized twice with acetone and deionized water, dried *in vacuo* at room temperature, and then stored in a refrigerator at 4°C before use. All of the other solvents used for sample workup and characterization were used as received.

Polymerization

Bulk free-radical polymerizations of BA/BMA/Lim were carried out in glass ampules (10 mm in diameter and 200 mm in length; 15.7 mL). About 5 g of monomer plus initiator (1.0 wt % BPO) was pipetted into each ampule. Initial molar ratios of BA/BMA/ Lim of 80 : 10 : 10, 40 : 50 : 10, 70 : 10 : 20, 40 : 40 : 20, 60 : 10 : 30, 50 : 20 : 30, and 50 : 10 : 40 were used. Each ampule was degassed with a pump–freeze–thaw procedure (typically, three cycles), flame-sealed, and subsequently immersed in a constant temperature oil bath at 80°C. For each of the seven reaction conditions, a total of five to seven ampules were prepared and removed from the oil bath at predetermined times to achieve a range of monomer conversions. The polymeric products were precipitated in a 10-fold excess of methanol and refrigerated at 4°C for 4 h. The excess liquid was decanted, and the polymer samples were dried in a vacuum oven at 25°C until a constant weight was achieved. With ^{1}H-NMR spectroscopy, the decanted liquid was verified for the presence of oligomeric materials, and only insignificant amounts were detected.

Characterization

The overall monomer conversion was determined by gravimetry on the basis of the mass of dried polymer. The terpolymer composition [molar fractions of *n*-butyl acrylate, butyl methacrylate, and D-limonene (F_{BA}, F_{BMA}, and F_{Lim}, respectively)] was measured with an ^{1}H-NMR spectrometer (Bruker, 400 MHz) with CDCl$_3$ as the solvent at room temperature. The molecular weights were obtained with a gel permeation chromatography system (Agilent technology) with two columns in series (MZ-Gel SD plus 10^5 Å, 300 $\times$ 8.00 mm, particle size = 5 μm) and tetrahydrofuran as an eluent. The detection system consisted of a multi-angle laser light scattering detector (Wyatt Dawn Heleos II, λ = 633 nm), a differential refractive-index detector (Wyatt Optilab T-rEX), and a differential viscometer (Wyatt ViscoStar II). Samples diluted in tetrahydrofuran were filtered through a 0.45-μm syringe filter before injection into the gel permeation chromatograph. Data analysis was performed with Wyatt Astra software. The refractive-index increment (*dn/dc*) used to
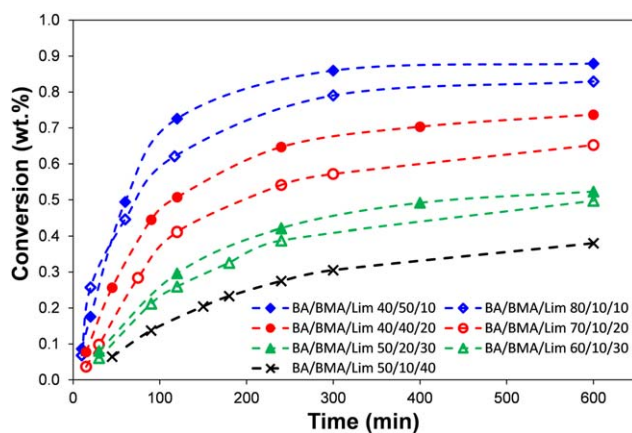

Figure 1. Monomer conversion versus the time for various BA/BMA/Lim compositions at 80°C and 1 wt % BPO. The dashed lines are not model predictions but are used for clarity. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

calculate the molecular weight was estimated based on the *dn/ dc* values for the homopolymers weighted by each terpolymer composition. For poly(*n*-butyl acrylate) and poly(butyl methacrylate), the *dn/dc* (tetrahydrofuran, 25°C) values were taken to be 0.064 and 0.076 mL/g, respectively;[23] for poly(D-limonene) [poly(Lim)], a *dn/dc* value of 0.133 mL/g for poly(Lim) resin (donated by Pinova, Inc.) was measured and used. The use of the weighted average of the *dn/dc* values was verified experimentally for two separate terpolymer compositions, and the approach was found to be consistent and accurate. Because of the use of a multi-angle light scattering technique, the molecular weights measured were considered absolute values. The T_g values of the terpolymers were determined with differential scanning calorimetry (TA Instruments, model Q1000). The polymer samples were put into a closed sample pan and underwent the following heating procedure in air: heating from -95 to 150°C at 10°C/min, isothermal for 3 min at 150°C, cooling from 150 to -95°C, isothermal treatment for 3 min at -95°C, and then reheating from -95 to 150°C to eliminate the thermal history of the sample. T_g was determined as the inflection point on the heat flow curve with the second heating cycle.

RESULTS AND DISCUSSION

Conversion–Time Results

The monomer conversions plotted versus the time for the seven feed compositions are shown in Figure 1. Within the group of seven monomer feeds, there were four acrylic (i.e., BA + BMA)/ Lim feed ratios and seven separate BA/BMA ratios. In a comparison of the runs at four different acrylic/Lim levels, we observed how the polymerization rate and final conversion levels related to both the Lim level and the BA/BMA ratio. When the Lim level was increased from 10 to 40 mol %, the polymerization rate decreased, and the final (limiting) conversion was lowered. For example, the polymerization presented final conversions of 85, 65, and 50 wt % for BA/BMA/Lim feed compositions of 80 : 10 : 10, 70 : 10 : 20, and 60 : 10 : 30, respectively. This was related to the fact that limonene's allylic structure led
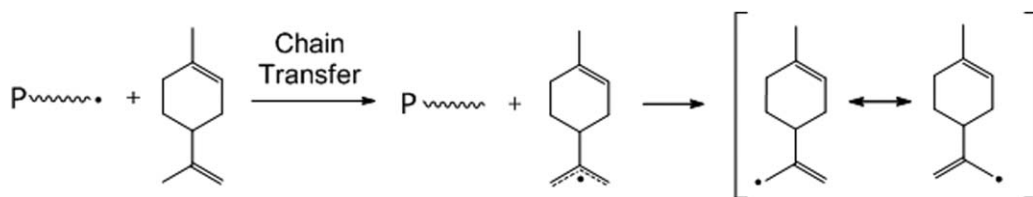
Figure 2. Schematic representation of the degradative chain transfer of Lim.

to significant degradative chain-transfer reactions. According to the degradative chain-transfer mechanism, free radicals reacting with the allylic hydrogen of limonene resulted in highly stable radicals that did not react further but tended to react with macroradicals and terminate the polymer chains; this slowed the polymerization rate (Figure 2). The limiting conversions supported the inability of limonene to homopolymerize via free-radical mechanisms. It was evident that limonene could only be incorporated into the polymer chain, although there was acrylic (BA and/or BMA) monomer remaining in the system. The composition results shown later supported this as well. Similar behavior was previously observed in the BA/Lim system.[24]

Composition–Conversion Results
The prediction of the terpolymer composition has been accomplished successfully for other systems with the Mayo–Lewis equation and the corresponding copolymerization reactivity ratios up to high conversion levels for bulk, solution, and emulsion polymerizations.[25,26] In previous studies, we investigated the copolymerization of BMA/Lim and BA/Lim.[24,27] For these systems, the reactivity ratios were estimated from low-conversion polymerizations and were then validated with full-

conversion runs. Reliable experimental values of the reactivity ratios for BA/BMA were not available in the literature, and therefore, with similar techniques as reported for the BA/Lim and BMA/Lim systems, estimates of the reactivity ratios of butyl methacrylate and *n*-butyl acrylate were found to be $r_{BMA} = 2.008$ and $r_{BA} = 0.460$, respectively.

The molar fraction of each monomer bound in the terpolymer chains was determined with ^{1}H-NMR spectroscopy. A typical NMR spectrum along with the peak assignment for the BA/BMA/Lim terpolymer is shown in Figure 3. Similar to the BA/Lim copolymer NMR results,[24] two types of Lim units (Lim and Lim′) were detected from the terpolymer NMR spectra: the Lim unit (containing only an internal C=C double bond), which was incorporated through an addition reaction on the external C=C double bond, and the Lim′ unit (containing both the internal and external C=C double bonds), which was integrated into the polymer chain as an end group through the degradative chain-transfer mechanism. The terpolymer composition–conversion results and model predictions for each feed composition are plotted in Figure 4. Note that the model predictions were obtained by the integration of the Mayo–Lewis
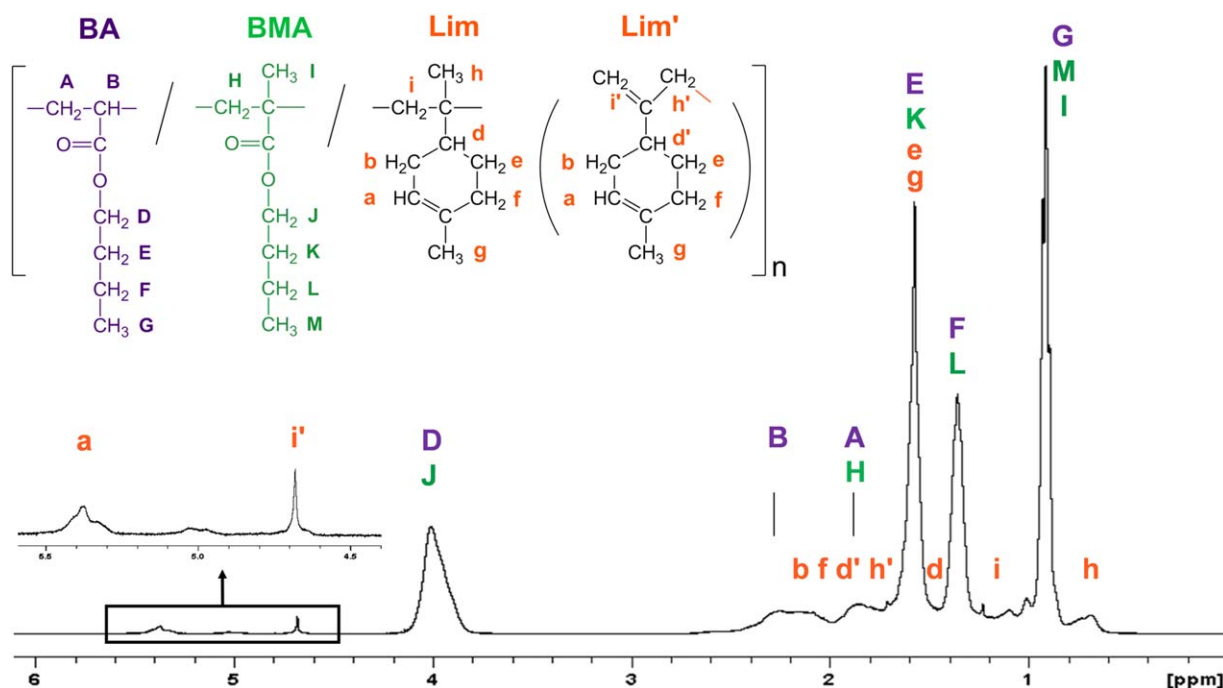

Figure 3. ^{1}H-NMR spectrum for the BA/BMA/Lim terpolymer (BA/BMA/Lim sample feed composition = 50 : 10 : 40, BA/BMA/Lim polymer composition = 65 : 25 : 10, conversion = 38 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
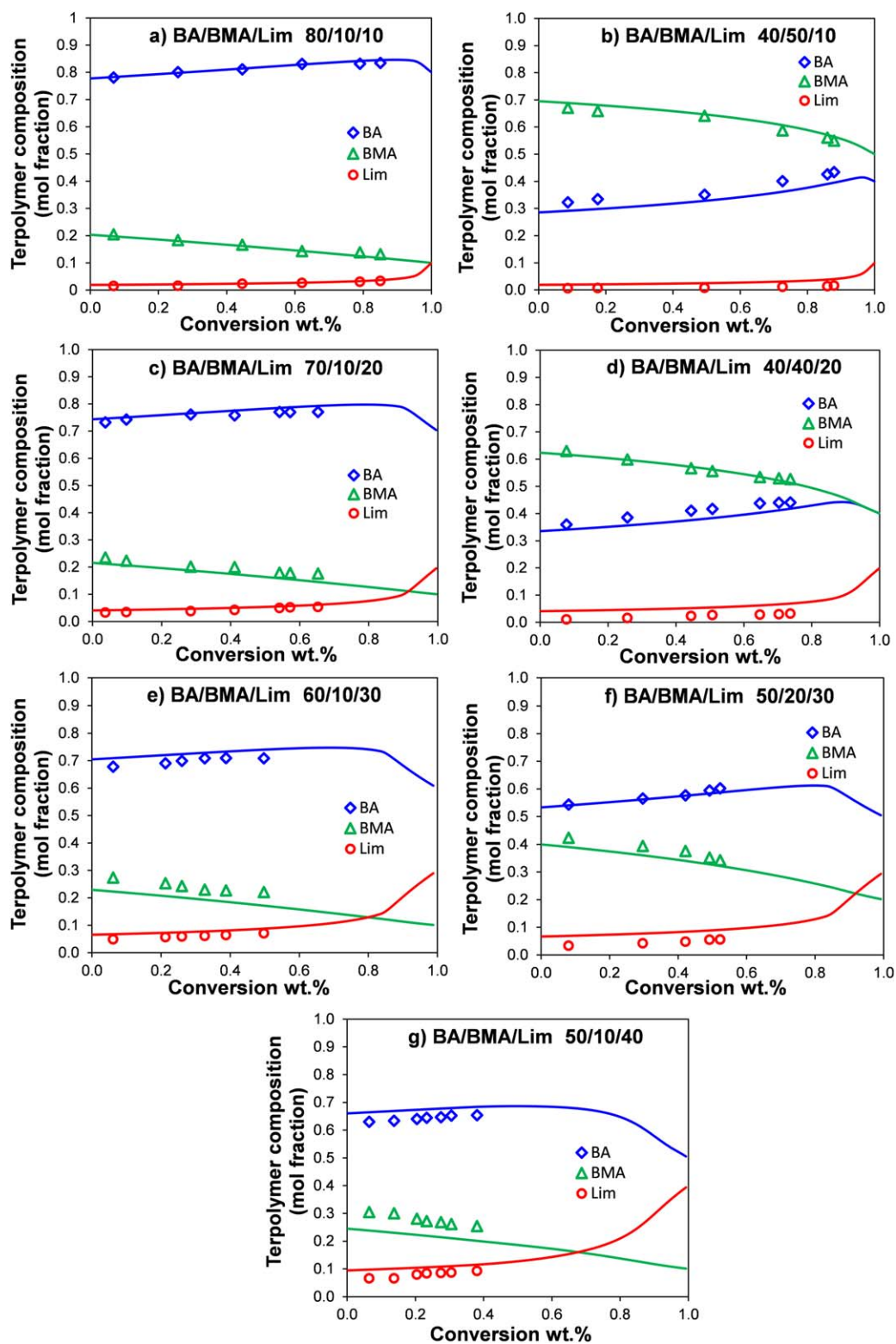
Figure 4. Terpolymer composition versus the conversion for various BA/BMA/Lim monomer feed ratios at 80°C and 1 wt % BPO. The solid lines represented integrated Mayo–Lewis model predictions with the three reactivity ratios shown in Table I. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

equation with the three pairs of reactivity ratios estimated from the low-conversion bulk copolymerization experiments at 80°C (Table I). The composition data for each feed are fitted well by the integrated Mayo–Lewis model, which further validated the reactivity ratio estimated from previous work.[24,27] In all of the composition–conversion plots, a fairly constant composition

Table I. BMA/BA, BMA/Lim, and BA/Lim Reactivity Ratios at 80°C

Monomers	r_1	r_2
BMA/BA[a]	2.008	0.460
BMA/Lim[27]	6.096	0.046
BA/Lim[24]	6.008	0.007

r_1 is reactivity ratio for monomer 1; r_2 is reactivity ratio for monomer 2.
[a] The reactivity ratios for the BMA/BA copolymerization were estimated with a series of low-conversion experiments in work to be published elsewhere.

(low composition drift) was observed. This was related to the widely differing reactivity ratios for the BA/Lim and BMA/Lim systems, whereas r_{BA} and r_{BMA} were each above 6, and the reactivity ratio values of Lim values were close to zero. The behavior of this terpolymer system was remarkably similar in this respect to that of BA/methyl methacrylate/vinyl acetate.[25] Therein, the copolymer reactivity ratios of the acrylic comonomers were high (>5), whereas the corresponding reactivity ratios of the vinyl acetate was well below 0.1 in both cases.[28,29] In our case, the polymerization was dominated by BA and BMA, and the polymer composition exhibited very little drift initially. As the polymerization proceeded, more significant changes in composition were only observed when BA and BMA were nearly depleted. The Mayo–Lewis model predictions indicated significant composition drift beyond the experimental data points. It should be noted, however, that once the acrylic monomers were depleted, no further polymerization could occur because of the fact that Lim could not undergo homopolymerization. As shown in Figure 4, all of the polymerizations stopped before the predicted composition drift could occur. As a result, narrow composition distributions were achieved for all of the BA/BMA/Lim terpolymers.

The effect of the initial feed composition on the terpolymer composition was also evident. With a higher BA content in the feed, the initial terpolymer composition was higher in BA [Figure 4(a,c,e,g)] compared to the case with a lower BA feed content [Figure 4(b,d)]. The Lim content in the terpolymer was relatively insensitive to the change in the BA/BMA ratio because of the similar reactivity ratios of the BA/Lim and BMA/Lim systems.

Molecular Weight–Conversion Results
The absolute molecular weights of the BA/BMA/Lim terpolymers are reported in Figure 5 for BA/BMA/Lim monomer feed ratios of 80 : 10 : 10, 70 : 10 : 20, and 50 : 10 : 40. Figure 6 shows the SEC traces of selected terpolymer samples at different feed compositions and different polymerization times. In the copolymerization of BA/Lim, we observed that the molecular weight development was dominated by the degradative chain-transfer reaction of Lim.[24] Not surprisingly, this effect was observed in the terpolymerization. The highest molecular weight [weight-average molecular weight (M_w) = 125.8 kDa, number-average molecular weight (M_n) = 42.0 kDa] was observed in the runs carried out at the lowest Lim level (80 : 10 : 10 BA/BMA/Lim). For the same feed, we observed that the polydispersity index (PDI) increased from an initial value of 1.5–3.0 at a con-

version of 83 wt % [see Figure 6(a)]. This was related to the branching reactions because of the high BA concentrations along with the diffusion-controlled behavior, which occurred at high conversions when the reaction medium became viscous. With an increasing Lim fraction in the monomer feed, the terpolymers exhibited lower molecular weights and relatively narrower molecular weight distributions [cf. Figure 6(a–c) to Figure 6(b–d)]; this implied that more frequent chain-transfer events occurred. For example, at BA/BMA/Lim feeds of 70 : 10 : 20 and 50 : 10 : 40, the final M_n and PDI values were 25.7 kDa and 2.0 and 13.9 kDa and 1.6, respectively. The relative small PDI was also related to the fact that Lim could not undergo homopolymerization; thus the remaining Lim, which acted more like a solvent, diluted the reaction medium, maintained a low viscosity, and prevented any gel effect during the final stages of polymerization.

The terpolymer average chain length and the average number of Lim units per chain for the highest conversion sample of each feed composition were calculated on the basis of the composition and absolute molecular weight data (see Table II). Generally, the average number of Lim units in each BA/BMA/Lim terpolymer chain ranged from 5 to 11. The presence of more than one Lim unit per chain indicated that Lim was not only incorporated through the degradative chain-transfer mechanism as an end group of a polymer chain but also by means of chain propagation through the addition reaction at the external C≡C double bond. This conclusion further supported the observations from our NMR spectra discussed previously.

The effect of varying the BA/BMA monomer feed ratio on the molecular weight at a fixed Lim level was also examined. Only slight differences were observed in the M_n values when the BA/BMA ratio was changed, whereas the polydispersity development of the terpolymer was quite different. It is known that polydispersity is directly related to the termination mechanism. At a high BA feed of 80 : 10 : 10 [see Figure 6(a)], the initial PDI of 1.5 indicated that termination by a combination
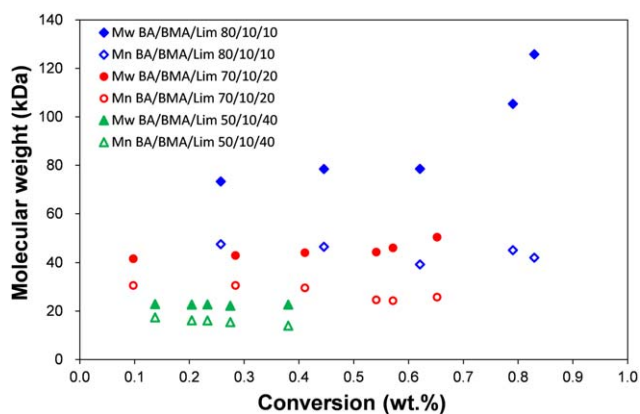

Figure 5. Terpolymer molecular weight versus the conversion at various BA/BMA/Lim monomer feed ratios, 80°C, and 1 wt % BPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
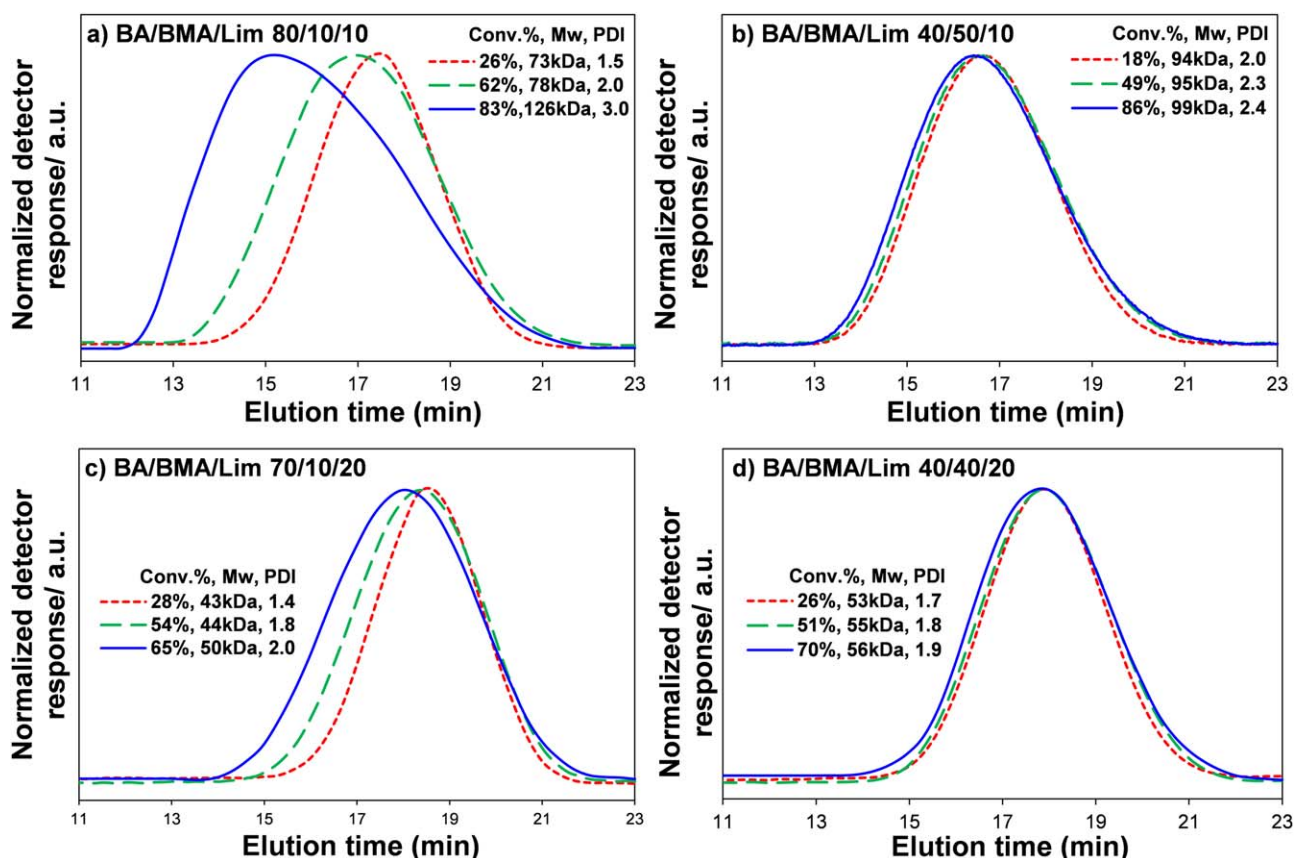
Figure 6. Gel permeation chromatograms of the selected samples at various feed compositions, 80°C, and 1 wt % BPO. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

mechanism was favored, as was the case for BA homopolymerization.[30] In contrast, at the high BMA monomer feed ratio of 40 : 50 : 10 [see Figure 6(b)], the initial PDI of 2.0 was a consequence of greater termination by disproportionation, which is favored by methacrylate monomers;[31,32] the PDI then increased to 2.4 at 86% conversion. Similar molecular weight and PDI trends were observed in the feeds of 70 : 10 : 20 and 40 : 40 : 20 [see Figure 6(c,d)]. These findings have important implications for future efforts in the modeling of this terpolymer system.

T_g versus the Composition and Molecular Weight

The T_g results for the BA/BMA/Lim terpolymer samples of each feed composition are shown in Table II. The observed T_g trends were primarily related to the terpolymer composition. The rigid molecular structure of Lim endowed it with a relatively high T_g; a T_g of 116°C was reported for poly(Lim).[17] A low-molecular-weight poly(Lim) resin (donated by Pinova, Inc.) was tested, and a T_g of 78°C was measured. In general, the terpolymer T_g increased with decreasing proportion of BA and increasing proportions of BMA and Lim. Normally, for polymers with M_n

Table II. Characterization Results for the BA/BMA/Lim Terpolymers with Various Feed Compositions at 80°C and 1.0 wt % BPO

BA/BMA/Lim feed composition	Conversion (wt %)	F_{BA} (mol %)	F_{BMA} (mol %)	F_{Lim} (mol %)	M_n (kDa)	X_n	Average number of Lim units per chain	T_g (°C)
80 : 10 : 10	85.1	0.835	0.132	0.034	42.0	323	11	−39.6
40 : 50 : 10	87.9	0.434	0.550	0.016	45.5	335	5	−16.6
70 : 10 : 20	65.2	0.770	0.176	0.053	25.7	196	10	−35.9
40 : 40 : 20	73.7	0.441	0.527	0.032	30.9	227	7	−16.1
60 : 10 : 30	49.7	0.708	0.221	0.071	18.4	139	10	−31.8
50 : 20 : 30	52.3	0.602	0.342	0.056	18.4	138	8	−30.9
50 : 10 : 40	38.0	0.653	0.254	0.092	13.9	105	10	−30.2

X_n, terpolymer average chain length.

values above 20,000 Da, the molecular weight did not affect T_g. However, for the relatively low-molecular-weight sample (BA/BMA/Lim feed ratio of 50 : 10 : 40), T_g was lower than expected on the basis of the polymer composition effects. This reflected the effect of the lower molecular weight, which provided greater polymer chain mobility and led to a lower T_g. Thus, for the low-molecular-weight samples, the terpolymer composition was only one factor modifying the terpolymer T_g. For instance, the 50 : 20 : 30 sample ($F_{BA} = 0.602$, $F_{BMA} = 0.342$, and $F_{Lim} = 0.056$) showed a T_g of $-30.9°C$ with an M_n of 18.4 kDa, whereas a slightly higher T_g of $-30.2°C$ was detected for the 50 : 10 : 40 sample ($F_{BA} = 0.654$, $F_{BMA} = 0.254$, and $F_{Lim} = 0.093$) at a fairly low M_n of 13.9 kDa. By comparing the compositions of these two samples, one would expect significantly different T_g values. However, the effect of the molecular weight (notably at in the molecular weight range below 20 kDa) compensated for the composition effect.

CONCLUSIONS

Lim is an ideal green material because it is renewable and essentially nontoxic and has very low global warming potential. Our investigation of the use of Lim in a polymer formulation was part of a greater movement toward more sustainable polymer production. In this study, the bulk free-radical terpolymerization of BA/BMA/Lim was examined at 80°C. We found that Lim had a dominant influence on the molecular weight development, polymerization rate, and terpolymer composition. The allylic structure of Lim resulted in a significant chain transfer; this competed remarkably with chain propagation. With increasing amounts of Lim, polymers with shorter average chain lengths were produced, whereas the allylic radicals resulted in a reduced rate of polymerization. In terms of terpolymer composition, because of the large difference in the copolymer reactivity ratios, the terpolymer exhibited a fairly constant composition (i.e., very little drift) with conversion for every monomer feed studied.

These findings have led to a better understanding of the kinetic mechanism of the multicomponent polymerization with Lim as a comonomer. This has provided us with insight into ways to incorporate greater amounts of this renewable component into a polymer matrix. For example, the use of a lower reaction temperature may help reduce the rate of degradative chain transfer due to Lim relative to the propagation reaction. Another option would include the addition of crosslinkers to compensate for the mechanical property losses resulting from reduced molecular weights. Semibatch feed policies could also be implemented to encourage the incorporation of the less reactive monomer and eliminate composition drift. With the comonomers used in this study (i.e., BA and BMA), we envision their potential applications in adhesives and coatings.

ACKNOWLEDGMENTS

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