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Effect of Lewis Acids on Reactivity Ratios for (Meth)acrylate/Nonpolar Alkene Copolymerizations

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ABSTRACT: The effect of Lewis acids ($AlCl_3$ and $Sc(OTf)_3$) on the reactivity ratios for (meth)acrylate/1-hexene and methacrylate/norbornene radical copolymerizations was investigated. The reactivity ratio r_1 for both methyl acrylate and methyl methacrylate decreases in the presence of Lewis acids; 1-alkene reactivity ratio r_2 is close to zero. The substantial decrease in r_1 values and an increased polymerization rate demonstrate that Lewis acids promote (meth)acrylate cross-propagation significantly more than self-propagation, especially for methyl acrylate. The alkenes do not undergo self-propagation under our conditions. Furthermore, due to (a) enhanced binding of the Lewis acid to the carbonyl group on the monomer compared to those on the polymer and (b) the facile exchange of the Lewis acid between the monomer and the polymer, only a catalytic amount to Lewis acid is required to strongly influence alkene uptake and copolymerization rate.

Introduction

The copolymers of polar vinyl monomers, such as methacrylates and acrylates, with simple 1-alkenes with predictable compositions and architectures are of great interest because the combination of these two classes of monomers can significantly enhance the currently attainable polymer properties. However, because of the wide disparity between the respective reactivity ratios, random (meth)acrylate-rich copolymers in relatively low yields are typically obtained by free radical copolymerization of the two. We have recently reported the free radical copolymerization of acrylates with simple 1-alkenes in the presence of either Lewis or Brønsted acids can lead to both a significant increase in the polymerization rate and nonpolar alkene incorporation.[1−4] The qualitative explanation is that Lewis acids can coordinate with the carbonyl group of the (meth)acrylate monomer and reduce the electron density of the conjugated double bond, thereby (a) increasing the reactivity of the (meth)acrylate radical and (b) making the now electrophilic radical more susceptible to attack by the relatively electron rich nonpolar alkene. Conversely, the propagating radical derived from 1-alkene is relatively nucleophilic and has a higher propensity toward addition to the more electrophilic Lewis acid-coordinated (meth)acrylate monomer. In the extreme, as discussed below, an alternating copolymer is formed.

For radical copolymerizations, the copolymer composition is governed by the reactivity ratios of the two monomers. The monomer reactivity ratios, r_1 and r_2, are the ratios of the rate constants for the different propagation reactions, as shown below (in this paper, M_1 = (meth)acrylate; M_2 = 1-alkene).

$$\begin{aligned}
&\sim M_1^\bullet + M_1 \rightarrow M_1M_1^\bullet && k_{11} \\
&\sim M_1^\bullet + M_2 \rightarrow M_1M_2^\bullet && k_{12} && r_1 = k_{11}/k_{12} \\
&\sim M_2^\bullet + M_2 \rightarrow M_2M_2^\bullet && k_{22} && r_2 = k_{22}/k_{21} \\
&\sim M_2^\bullet + M_1 \rightarrow M_2M_1^\bullet && k_{21}
\end{aligned}$$

Since the copolymer composition is different depending on the absence and presence of Lewis acids, it is clear that the latter have a significant influence on the reactivity ratios. To date, many Lewis acids have been used in radical copolymerizations;[1−13] however, quantitative data on their effect on monomer reactivity ratios is lacking. Herein, we describe the influence of Lewis acids on the monomer reactivity ratios for (meth) acrylates/nonpolar alkene copolymerizations. The r_1 and r_2 values have been calculated in accordance with the Kelen−Tudos[14] equation and nonlinear least-squares[15,16] (NLLS) method. We have also examined the kinetics of the copolymerization reactions. The results indicate that Lewis acids significantly increase the cross-propagation rate (k_{12}) compared to self-propagation (k_{11}), resulting in a large decrease in the reactivity ratio (r_1) for (meth)acrylates.

In order to understand why only a catalytic amount of Lewis acid is sufficient to strongly influence the copolymerization reactions,[1−4,17−19] we also closely examined the interaction of Lewis acids with both the methacrylate monomer and the polymer and found that the Lewis acid interaction with the carbonyl group of the monomer is significantly stronger than that with the polymer. Furthermore, there is a fast exchange of the Lewis acid between the carbonyl groups of the polymer and that in the monomer.

Results and Discussion

1. Effect of Lewis Acid on Monomer Reactivity Ratios in Methyl Methacrylate/Nonpolar Alkene Copolymerization. The effect of adding increasing amounts of the Lewis acid, $AlCl_3$, on methyl methacrylate (MMA)/1-hexene copolymerization for different monomer feed ratios is graphically illustrated in Figure 1. Some of the data is also summarized in Table 1. There is a clear trend toward increasing incorporation of 1-hexene (as determined by ^{1}H NMR spectroscopy) with increasing amount of Lewis acid present, especially at low MMA/1-hexene feed ratios. For example, without $AlCl_3$, when the MMA mol fraction in the feed is 0.1, 1-hexene incorporation in copolymer is less than 15 mol %. Simply by adding 0.1 equiv. of $AlCl_3$ relative to MMA,

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1-hexene incorporation increased to over 30 mol %. For the experiments with only 10 mol % MMA in the monomer feed, Et_3N (20 mg) was added to inhibit cationic polymerization initiated by $AlCl_3$. In the absence of the base, low molecular weight poly(1-hexene) ($M_n \sim 1500$) was formed and GPC traces showed bimodal distributions. To maintain the monomer feed ratio over the course of the polymerization, all of the reactions were terminated before MMA conversion reached 8%. The copolymer compositions were determined from ^1H NMR integration of the methoxy protons (at 3.6 ppm) versus all the aliphatic resonances (0.5–2.2 ppm). The polymers obtained were random copolymers. There are MMA–MMA dyads and MMA–hexene dyads in the polymer chain, but no hexene–hexene dyads.[20] The detailed elucidation of polymer microstructure is discussed in subsection 5.

Using the data from Figure 1, the monomer reactivity ratios for MMA and 1-hexene were calculated by the Kelen–Tudos equation and NLLS method and shown in Table 2. The r_1 value clearly decreases with increasing amount of added Lewis acid. Since both k_{11} and k_{12} are enhanced in the presence of $AlCl_3$, the increase in k_{12} must be significantly larger than in k_{11}; i.e. the Lewis acid is more effective in promoting cross-propagations (see subsection 2). The calculated r_2 values are negative using the Kelen–Tudos equation. These values do not have a physical meaning, only suggesting that the real value of r_2 is near zero. This is consistent with the observed absence of sequential alkene units in the copolymer backbone.

Figure 2 presents the data on free radical copolymerization of MMA with norbornene at different comonomer and Lewis acid feed ratios. Again, the copolymerizations were

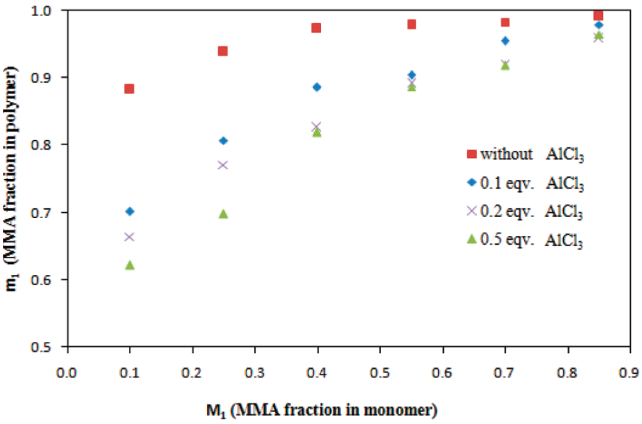


Figure 1. Copolymer composition versus monomer feed ratio in methyl methacrylate (MMA)/1-hexene copolymerization. Conditions: MMA, 0.3 g; 2,2′-azobis(isobutyronitrile), 0.005 g; toluene, 5 mL; $AlCl_3$, 0.04 g (0.1 equiv. to MMA), 0.08 g (0.2 equiv. to MMA), 0.2 g (0.5 equiv. to MMA), 60 °C. For the experiments when $M_1 = 0.1$ in the presence of $AlCl_3$, Et_3N (20 mg) was added to inhibit cationic polymerization.

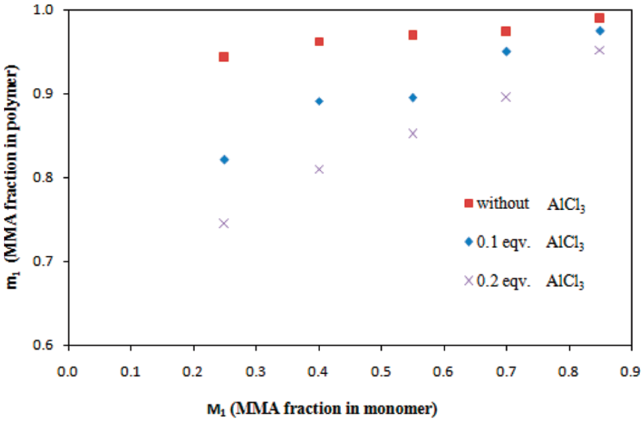


Figure 2. Copolymer composition versus monomer feed ratio in methyl methacrylate (MMA)/norbornene copolymerization. Conditions: MMA, 0.3 g; 2,2′-azobis(isobutyronitrile), 0.005 g; toluene, 5 mL; $AlCl_3$, 0.04 g (0.1 equiv. to MMA), 0.08 g (0.2 equiv. to MMA); 60 °C.

Table 1. Selected Data of Methyl Methacrylate (MMA)/1-Hexene Copolymerization[a]

entry	$AlCl_3$/MMA molar ratio	M_1 (MMA mol fraction in monomer)	m_1 (MMA mol fraction in polymer)	MMA (% convn)	M_n[b] ($\times 10^{-4}$)	PDI[b] (M_w/M_n)
1	0.1	0.10	0.70	3.45	3.2	1.3
2	0.1	0.25	0.81	3.39	4.1	1.3
3	0.1	0.40	0.89	6.32	4.6	1.4
4	0.1	0.55	0.90	3.43	4.4	1.4
5	0.1	0.70	0.96	2.50	4.2	1.3
6	0.1	0.85	0.98	1.41	3.9	1.3
7	0.2	0.10	0.66	4.56	3.7	1.4
8	0.2	0.25	0.77	4.72	4.9	1.4
9	0.2	0.40	0.83	2.75	4.5	1.3
10	0.2	0.55	0.89	3.84	5.2	1.4
11	0.2	0.70	0.92	1.34	4.6	1.3
12	0.2	0.85	0.96	1.67	4.3	1.3

[a] Conditions: MMA, 0.3 g; 2,2′-azobis(isobutyronitrile), 0.005 g; toluene, 5 mL; $AlCl_3$, 0.04 g (0.1 equiv. to MMA), 0.08 g (0.2 equiv. to MMA), 60 °C. For the experiments when $M_1 = 0.1$ in the presence of $AlCl_3$, Et_3N (20 mg) was added to inhibit cationic polymerization. [b] By GPC relative to polystyrene standards. M_n is number-average molecular weight, M_w is weight-average molecular weight and PDI (polydispersity index) = M_w/M_n.

Table 2. Reactivity Ratios (r_1, and r_2) for Methyl Methacrylate (MMA)/1-Hexene Copolymerization with and without $AlCl_3$[a]

		Kelen–Tudos[b]		nonlinear least-squares (NLLS)[b]	
entry	$AlCl_3$/MMA molar ratio	r_1(MMA)	r_2(1-hexene)	r_1 (MMA)	r_2(1-hexene)
1	0	88.5 ± 2.9	−0.1 ± 0.1	54.04 ± 0.01	0.00 ± 0.00
2	0.1	11.2 ± 1.8	−0.2 ± 0.2	10.37 ± 0.01	0.00 ± 0.01
3	0.2	3.1 ± 1.7	−0.2 ± 0.2	6.41 ± 0.02	0.02 ± 0.01

[a] Conditions: MMA, 0.3 g; 2,2′-azobis(isobutyronitrile), 0.005 g; toluene, 5 mL; $AlCl_3$, 0.04 g (0.1 equiv. to MMA), 0.08 g (0.2 equiv. to MMA), 60 °C. [b] Confidence level 95%.

Table 3. Reactivity Ratios (r_1, and r_2) of Methyl Methacrylate (MMA)/Norbornene Copolymerization with and without $AlCl_3$[a]

		Kelen−Tudos[b]		nonlinear least-squares (NLLS)[b]	
entry	$AlCl_3$/MMA molar ratio	r_1(MMA)	r_2(norbornene)	r_1(MMA)	r_2(norbornene)
1	0	35.1 ± 3.4	−0.1 ± 0.1	39.83 ± 0.02	0.00 ± 0.01
2	0.1	5.4 ± 1.4	−0.3 ± 0.3	9.72 ± 0.05	0.00 ± 0.02
3	0.2	2.0 ± 0.7	−0.4 ± 0.4	4.77 ± 0.07	0.00 ± 0.02

[a] Conditions: MMA, 0.3 g; 2,2′-azobis(isobutyronitrile), 0.005 g; toluene, 5 mL; $AlCl_3$, 0.04 g (0.1 equiv. to MMA), 0.08 g (0.2 equiv. to MMA); 60 °C. [b] Confidence level 95%.

Table 4. Apparent (Co)Polymerization Rates for Methyl Methacrylate (MMA) in the Absence and Presence of $AlCl_3$[a]

entry	$AlCl_3$/MMA molar ratio	alkene	k_p(MMA) (min^{-1})
1	0	none	0.00117
2	0.1	none	0.00127
3	0.2	none	0.00140
4	0.5	none	0.00184
5	0	1-hexene	0.00110
6	0.1	1-hexene	0.00186
7	0.2	1-hexene	0.00278
8	0.5	1-hexene	0.00356
9	0	norbornene	0.00252
10	0.1	norbornene	0.00322
11	0.2	norbornene	0.00339

[a] Conditions: MMA, 0.3 g; 1-hexene, 0.44 g; norbornene, 0.28 g; 2,2′-azobis(isobutyronitrile), 0.005 g; toluene, 5 mL; tetrachloroethane, 0.05 g (internal standard); $AlCl_3$, 0.04 g (0.1 equiv. to MMA), 0.08 g (0.2 equiv. to MMA), 0.2 g (0.5 equiv. to MMA); 60 °C; 4 h (copolymerization), 2 h (homopolymerization).

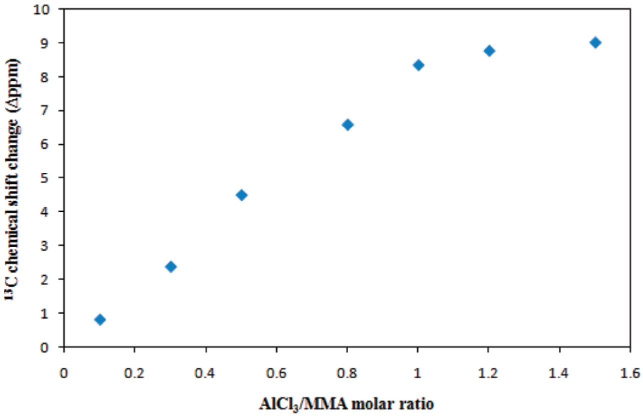


Figure 3. Change in ^{13}C NMR chemical shift ($CDCl_3$, 50 °C) of the carbonyl carbon of methyl methacrylate (MMA) versus $AlCl_3$/MMA molar ratio. ^{13}C NMR chemical shift in the absence of $AlCl_3$, 167.3 ppm.

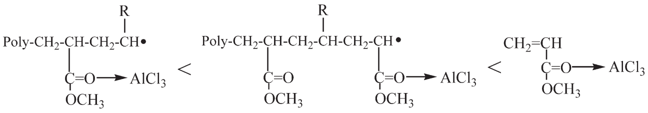
stopped before MMA conversion reaches 8%. The trend observed is very similar to that for MMA/1-hexene copolymerizations. The corresponding reactivity ratios are given in Table 3 and are again consistent with that observed for MMA/1-hexene copolymerizations.

2. Methyl Methacrylate Homopolymerization and MMA/Alkene Copolymerization Kinetics. Table 4 summarizes the apparent polymerization rates (k_p) for a series of MMA homo and copolymerizations. The values of k_p were obtained from linear plots of $\ln([MMA]_0/[MMA])$ versus time. In all cases, k_p increases with increasing amount of added Lewis acid. Further, the enhancement in k_p is larger in the copolymerization reactions. This observation, together with the decrease in r_1 in the presence of a Lewis acid (Tables 2 and 3) clearly indicates that Lewis acid promotes cross-propagation (k_{12}) more than MMA self-propagation (k_{11}).

3. NMR Study of the Interaction of Methacrylate Monomer and Polymer with Lewis Acids. In order to understand why a substoichiometric (i.e., catalytic) amount of Lewis acid is sufficient to strongly influence the copolymerization reactions, we examined the interaction of Lewis acids with both MMA and the corresponding polymer PMMA. As shown in Figure 3, the addition of $AlCl_3$ to a solution of MMA resulted in a gradual downfield shift in the carbonyl group in the ^{13}C NMR spectrum until $AlCl_3$/MMA ratio reaches 1. At that point, all the MMA carbonyl groups are expected to be bonded to $AlCl_3$. Cooling a solution in which the $AlCl_3$/MMA ratio is ~0.5 to −90 °C did not result in the observation of separate resonances for free and $AlCl_3$-bound carbonyl groups suggesting an extremely fast exchange rate between the two.

We also observed a pronounced preference for Lewis acids to coordinate to the carbonyl group of the monomer MMA over those in a polymer (see Table 5). Thus, we hypothesize a facile Lewis acid exchange between MMA units in the polymer and monomeric MMA as shown below (Scheme 1), consistent with the large effect of Lewis acids even when added in catalytic amounts.

As proposed above, the enhancement of k_{12} is due to increased electrophilicity of the Lewis acid-coordinated (meth)acrylate radical which then becomes more susceptible to attack by the relatively electron rich nonpolar alkene. This requires the Lewis acid to remain bound to the (meth)acrylate radical during the next monomer addition. While the relative binding of $AlCl_3$ to the (meth)acrylate radical of the growing polymer chain could not be determined experimentally, it is likely that the strength of the interaction of the Lewis acid with the ester carbonyl group will *increase* in the following order, although NMR experiments suggest that all three species are likely to be in rapid equilibrium with each other:



$$\text{Poly-CH}_2\text{-}\overset{\text{R}}{\underset{\substack{|\\ \text{C=O}\rightarrow\text{AlCl}_3\\ \text{OCH}_3}}{\text{C}}}\text{H-CH}_2\text{-CH}\bullet < \text{Poly-CH}_2\text{-}\overset{\text{R}}{\underset{\substack{|\\ \text{C=O}\\ \text{OCH}_3}}{\text{C}}}\text{H-CH}_2\text{-CH-CH}_2\text{-}\underset{\substack{|\\ \text{C=O}\rightarrow\text{AlCl}_3\\ \text{OCH}_3}}{\text{C}}\text{H}\bullet < \text{CH}_2\text{=}\underset{\substack{|\\ \text{C=O}\rightarrow\text{AlCl}_3\\ \text{OCH}_3}}{\text{C}}\text{H}$$

The coordination of the Lewis acid to the carbonyl group results in an incipient positive charge on the corresponding sp^2-hybridized carbon, which is stabilized by the π-electron(s) on the neighboring sp^2-hybridized carbon atoms; the stabilization is somewhat less in the acrylate radical compared to that in the monomer because the former has 1 π-electron instead of 2.[21,22]

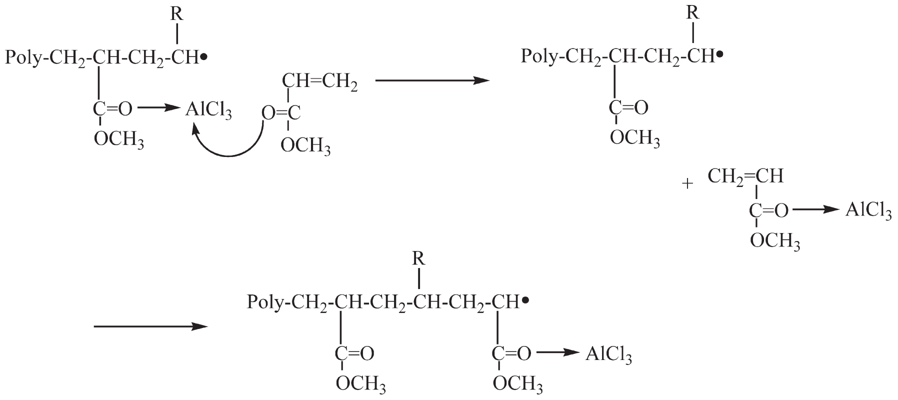
4. Effect of Lewis Acid on Monomer Reactivity Ratios in Methyl Acrylate (MA)/Alkene Copolymerization. As with copolymerizations involving MMA, we observed enhanced polymerization rate[1] and enhanced alkene incorporation in the copolymerization of MA with 1-hexene in the presence of

Table 5. Shift in ^{13}C-NMR Carbonyl Resonances of Poly(methyl methacrylate) (PMMA) and Methyl Methacrylate (MMA) in the Presence of Lewis Acids[a]

	PMMA/MMA/$TiCl_4$ molar ratio = 1/1/0.5		PMMA/MMA/$AlCl_3$ molar ratio = 1/1/0.5	
	PMMA	MMA	PMMA	MMA
shift in ^{13}C NMR carbonyl resonance (Δ ppm)	1.09	3.80	0.60	3.12

[a] Conditions: MMA, 0.05 g; PMMA, 0.05 g; $TiCl_4$, 0.047 g; $AlCl_3$, 0.033 g; 25 °C; $CDCl_3$. ^{13}C NMR chemical shift in the absence of Lewis acid: 167.3 ppm (MMA), 177.8 ppm (PMMA).

Scheme 1



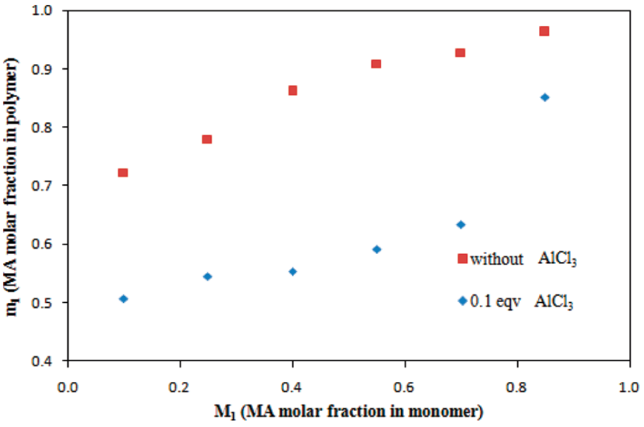


Figure 4. Copolymer composition versus monomer feed ratio in methyl acrylate (MA)/1-hexene copolymerization. Conditions: MA, 0.3 g; 2,2′-azobis(isobutyronitrile), 0.005 g; toluene, 5 mL; $AlCl_3$, 0.04 g (0.1 equiv. to MA); 60 °C.

Lewis acids (Figure 4 and Table 6). Two Lewis acids, $AlCl_3$ and $Sc(OTf)_3$, were employed. For the latter, due to poor solubility in toluene, 1,2-dichlorobenzene was used as solvent. The copolymer compositions were determined from ^{1}H NMR integration of the methoxy protons versus all the aliphatic resonances. The copolymer microstructures were determined by NMR spectroscopy (see subsection 5). The copolymers synthesized with $AlCl_3$ are nearly alternating when $M_1 < 0.70$; with the predominant presence of MA–hexene dyads.[23] The nearly alternating nature of the copolymer obtained is also consistent with both r_1 and r_2 values being near-zero (see Table 6). For both Lewis acids, the MA cross-propagation (k_{12}) is clearly promoted much more so than MA self-propagation (k_{11}).

5. Elucidation of Copolymer Microstructures. Figure 5 shows typical GPC traces for MMA/1-hexene copolymers. The complete overlap of the traces using the refractive index (RI) and ultraviolet (UV, 254 nm) detectors suggests that the materials obtained are true copolymers rather than a mixtures of homopolymers. Note that the UV detector is specifically sensitive to the carbonyl groups present in the copolymers. A similar overlap between the GPC traces obtained using RI and UV detectors was observed for the MA/1-hexene copolymers synthesized.

The MMA/1-hexene copolymer structures were studied by ^{1}H, ^{13}C and ^{13}C DEPT135 NMR spectroscopy (Figure 6). Three polymer samples from Figure 1 and a pure homopolymer PMMA sample were compared: (a) M_1 (MMA mole fraction in monomer feed) = 0.1, m_1 (MMA mole fraction in polymer) = 0.62, $AlCl_3$ = 0.5 equiv. to MMA; (b) M_1 = 0.1, m_1 = 0.70, $AlCl_3$ = 0.1 equiv. to MMA; (c) M_1 = 0.1, m_1 = 0.89, $AlCl_3$ = 0; (d) pure PMMA. Samples a, b, and c were synthesized with the same MMA/hexene feed ratio but different amounts of $AlCl_3$. By increasing the Lewis acid amount from zero (sample c), 0.1 equiv. relative to MMA (sample b) to 0.5 equiv. relative to MMA (sample a), 1-hexene incorporation increased from 11%, 30% to 38% (determined from ^{1}H NMR spectra). ^{13}C NMR spectra support copolymer formation. The C^{a*} resonance at 55 ppm is attributable to MMA–MMA dyads and is prominent in samples c and d. On the other hand, resonance at 43 ppm due to hexene–hexene dyads (observed in poly(1-hexene)[20]) is absent from the spectra of all the samples. The presence of MMA–hexene dyads results in a broad resonance at 47 ppm, and its intensity increase with increasing hexene content in the copolymer. Thus, the copolymers contain MMA–MMA and MMA–hexene dyads but not the hexene–hexene dyad.

The structures of MA/1-hexene copolymers were also analyzed by NMR spectroscopy. Figure 7 shows the ^{1}H, ^{13}C and ^{13}C DETP135 NMR spectra of two copolymers from Figure 4, as well as the homopolymer PMA. Sample a has a MA molar fraction of 51% and is essentially an alternating copolymer.[23] Resonances for neither MA–MA dyads at 35 ppm nor hexene–hexene dyads at 43 ppm are observed. On the other hand, the presence of MA–hexene dyads is signaled by the resonance at 37.5 ppm. In sample b, with MA molar fraction of 85%, the presence of MA–MA dyads results in C^{a*} appearing at 35 ppm. At the same time, the resonance at 37.5 ppm due to MA–hexene dyads

Table 6. Reactivity Ratios for Methyl Acrylate (MA)/1-Hexene Copolymerization in the Presence of Lewis Acids[a]

			Kelen−Tudos[d]		nonlinear least-squares (NLLS)[d]	
entry	Lewis acid	LA/MA molar ratio	r_1(MA)	r_2(1-hexene)	r_1(MA)	r_2(1-hexene)
1[b]	none	0	3.9 ± 1.3	−0.3 ± 0.2	9.56 ± 0.06	0.00 ± 0.02
2[b]	$AlCl_3$	0.1	0.2 ± 0.6	0.0 ± 0.3	0.35 ± 0.02	0.00 ± 0.01
3[c]	none	0	4.7 ± 0.7	−0.3 ± 0.2	7.60 ± 0.01	0.00 ± 0.00
4[c]	$Sc(OTf)_3$	0.1	1.5 ± 0.6	−0.2 ± 0.2	2.73 ± 0.02	0.00 ± 0.01

[a] Conditions: MA, 0.3 g; 2,2′-azobis(isobutyronitrile), 0.005 g; 60 °C. [b] Toluene, 5 mL. [c] 1,2-Dichlorobenzene, 5 mL. [d] Confidence level 95%.

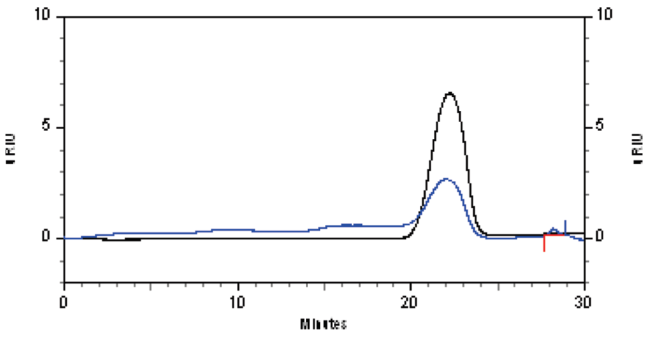


Figure 5. GPC traces for methyl methacrylate (MMA)/1-hexene copolymer using RI (black) and UV (blue) detectors (λ = 254 nm). Sample is from entry 7, Table 1.

becomes less intense. Again, the resonance from hexene−hexene dyads at 43 ppm is not observed Thus sample b contains MA−MA and MA−hexene dyads but not the hexene−hexene dyad.

Conclusions

The effect of Lewis acids on the reactivity ratios for (meth)acrylate/nonpolar alkene radical copolymerizations was investigated. The reactivity ratio r_1 for both MA and MMA decreases in the presence of Lewis acids; 1-alkene reactivity ratio r_2 is close to zero. The substantial decrease in r_1 values and an increased polymerization rate demonstrate that Lewis acids promote (meth)acrylate cross-propagation (k_{12}) significantly more than self-propagation (k_{11}), especially for MA. The alkenes do not undergo self-propagation under our conditions. Furthermore, due to (a) enhanced binding of the Lewis acid to the carbonyl group on the monomer compared to those on the polymer and (b) the facile exchange of the Lewis acid between the monomer and the polymer, only a catalytic amount to Lewis acid is required to strongly influence alkene uptake and copolymerization rate.

Consistent with an r_2 value of zero, hexene and norbornene do not undergo self-propagation under our conditions. This limits the highest incorporation of these and related nonpolar alkenes in the copolymers with (meth)acrylates to 50 mol %. At the other extreme, Brookhart, Drent, and others have shown that metal-catalyzed insertion polymerization of alkenes with acrylates (but not methacrylates) can lead to copolymers with alkene content of 100−85 mol %.[24−28] This leaves a “35 mol % gap” in the compositions that are not readily accessible through the copolymerization of acrylates with alkenes.[29] The composition gap is even higher for methacrylates since they do not participate in metal-catalyzed insertion polymerizations due to rapid β-hydrogen elimination following insertion.[30−32]

Experimental Section

Materials. All chemicals and reagents were obtained from Aldrich unless otherwise stated. Methyl acrylate (MA, 99%), methyl methacrylate (MMA, 99%) and 1-hexene (97%) were passed through basic alumina column to remove the inhibitor and impurities, then degassed and stored under N_2. Tetrachloroethane, norbornene (99%) and triethylamine (Et_3N, 99.5%) were degassed and stored under N_2. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%), titanium chloride ($TiCl_4$, 99.9%), aluminum chloride ($AlCl_3$, anhydrous, 99.99%, Strem Chemicals), and scandium(III) trifluoromethanesulfonate ($Sc(OTf)_3$, Alfa Aesar, 98%) were used as received.

Instrumentation. NMR spectra were recorded using a Bruker 300-DPX spectrometer at ambient temperature (^1H NMR, 300 MHz; ^{13}C NMR, 75 MHz). Chemical shifts are referenced to $CDCl_3$. Gas chromatography analysis was performed on an Agilent 5890 Series II GC using a RTX-5 split capillary column (Restek) connected to an FID detector. The samples were heated from 40 to 100 °C at a ramp rate of 5 °C/min. Molecular weights and molecular weight distributions were determined on a Shimadzu gel permeation chromatography (GPC) chromatograph containing a three-column bed (Styragel HR 7.8 × 300 mm columns with 5 μm beads size; 100−5000, 500−30000, and 2000 to 4×10^6 Da), a Shimadzu RDI-10A differential refractometer, and a Shimadzu SPD-10A tunable absorbance detector (254 nm). GPC samples were run in tetrahydrofuran at a flow rate of 1 mL/min at 35 °C and calibrated against polystyrene standards. Analysis was done using EZSTART 7.2 software.

Copolymerization of (Meth)Acrylate with Nonpolar Alkene. In a typical experiment, in a N_2-filled glovebox, AIBN (0.005 g, 0.03 mmol), MMA (0.3 g, 3 mmol), $AlCl_3$ (0.04 g, 0.3 mmol), 1-hexene (2.27 g, 27 mmol) and toluene (5 mL) were added into a 20 mL scintillation vial. The vial was sealed, removed from glovebox. Then the reaction mixture was allowed to stir in a 60 °C oil bath for a certain amount of time until it reaches desired monomer conversion ($<$8%). The resulting polymer was precipitated in 200 mL of methanol and collected by centrifugation, then dissolved in dichloromethane and precipitated again in methanol to remove impurities. The product was finally dried under high vacuum overnight. The copolymer composition was determined from ^1H NMR integration of the methoxy protons versus all the aliphatic resonances. Other copolymerization reactions were conducted similarly by varying the feed of 1-hexene or norbornene, while keeping MMA feed constant.

Kinetic Study of Methacrylate Homopolymerization in the Presence of Lewis Acids. In a N_2-filled glovebox, MMA (0.3 g, 3 mmol), AIBN (0.005 g, 0.03 mmol), $AlCl_3$ (0.04 g, 0.3 mmol), toluene (5 mL), and tetrachloroethane (0.05 g, 0.3 mmol) as internal standard were added into a reaction vessel equipped with a magnetic stirring bar. The reaction was stirred in 60 °C oil bath for 2 h. GC samples were taken every $^1/_2$ h to determine MMA conversion.

Kinetic study of Methacrylate/Alkene Copolymerization in the Presence of Lewis Acids. In a N_2-filled glovebox, a reaction vessel equipped with a stirring bar was charged with MMA (0.3 g, 3 mmol), 1-hexene (0.44 g, 5 mmol), AIBN (0.005 g, 0.03 mmol), $AlCl_3$ (0.04 g, 0.3 mmol), toluene (5 mL), and tetrachloroethane (0.05 g, 0.3 mmol). The reaction vessel was sealed and stirred in 60 °C oil bath for 4 h. GC samples were taken at a regular interval to determine MMA and hexene conversions.

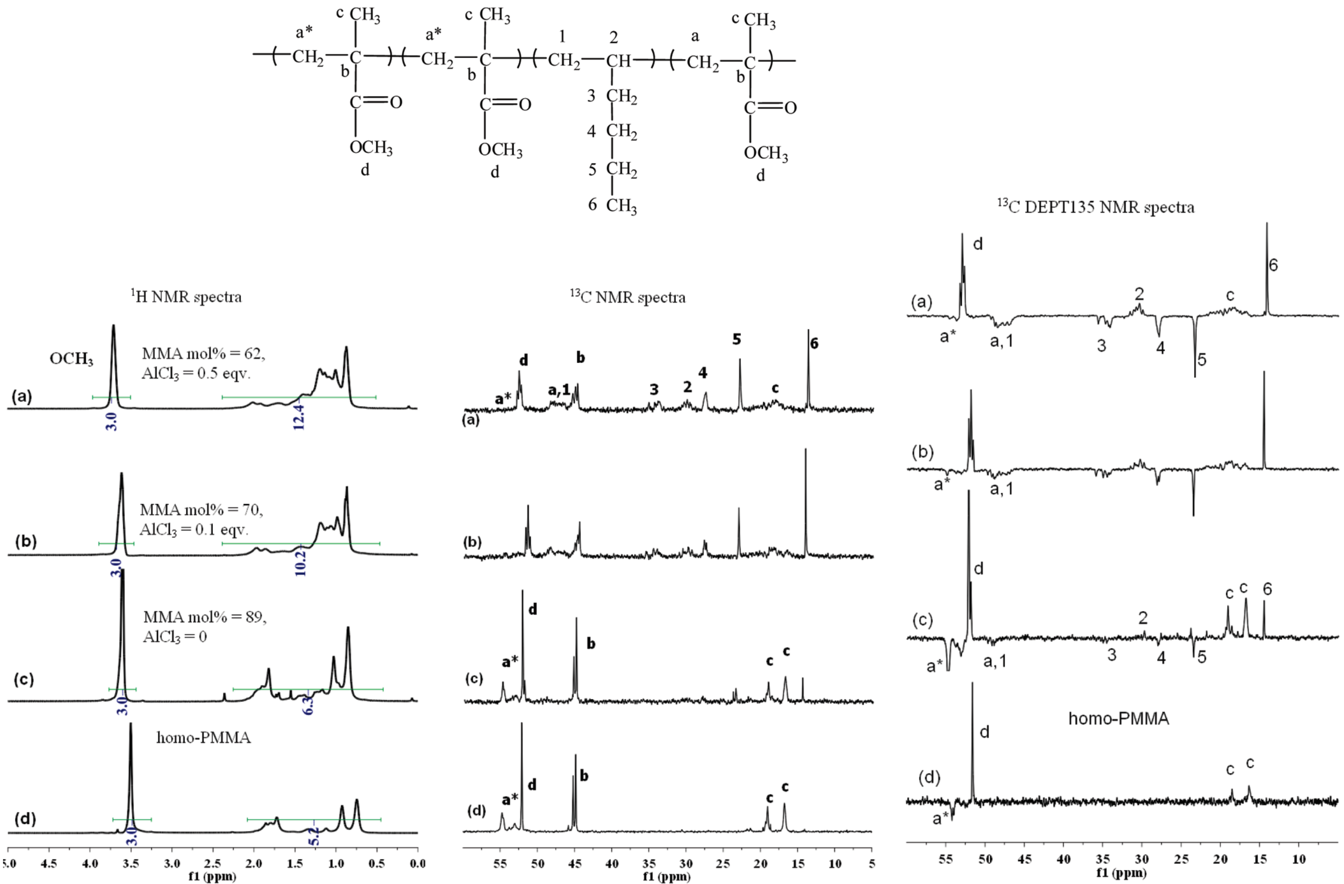


Figure 6. ^{1}H, ^{13}C, and ^{13}C DEPT135 NMR spectra of poly(methyl methacrylate) (PMMA) and methyl methacrylate (MMA)/1-hexene copolymers in CDCl$_3$. Key: (a) $M_1 = 0.1$, $m_1 = 0.62$, AlCl$_3$ = 0.5 equiv. relative to MMA; (b) $M_1 = 0.1$, $m_1 = 0.70$, AlCl$_3$ = 0.1 equiv. relative to MMA; (c) $M_1 = 0.1$, $m_1 = 0.89$, AlCl$_3$ = 0; (d) commercial PMMA.

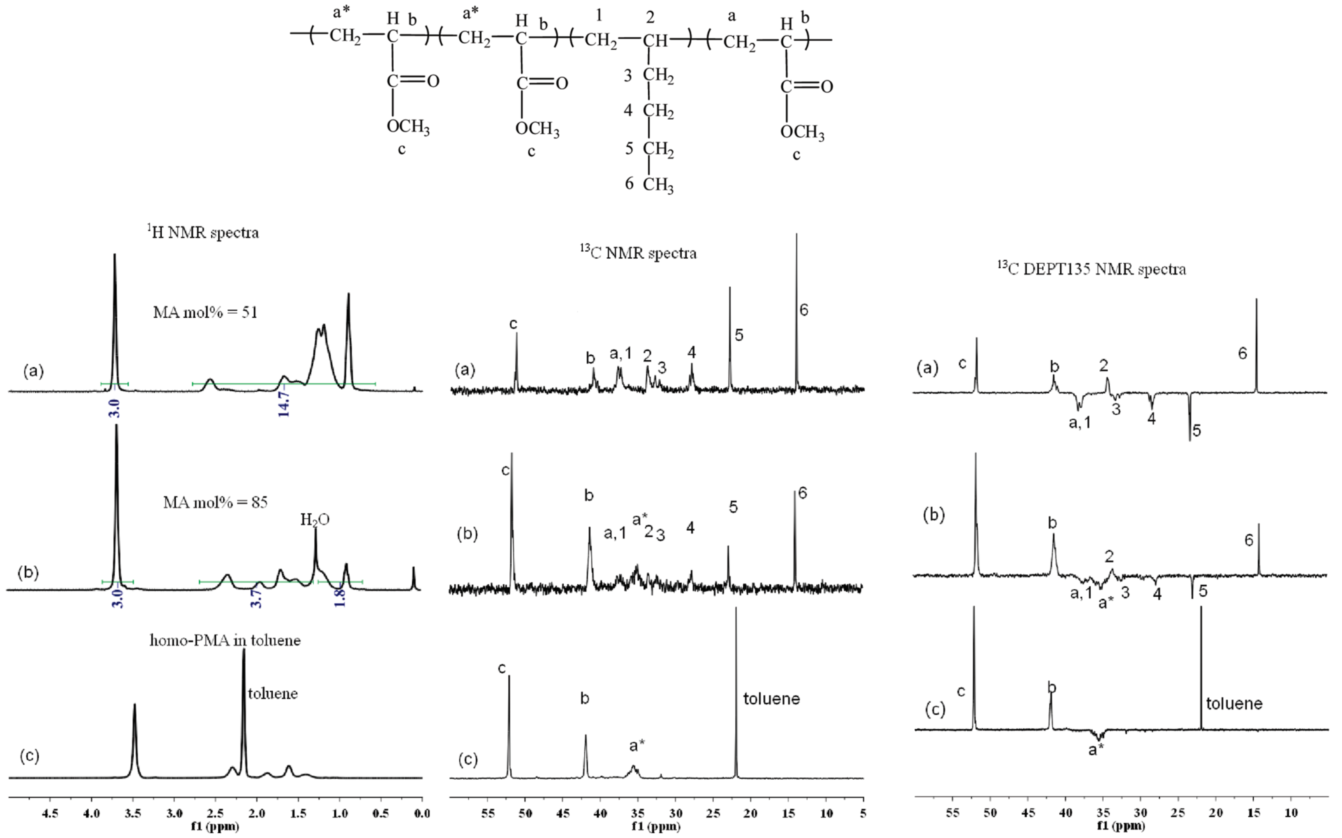


Figure 7. ^{1}H, ^{13}C, and ^{13}C DEPT135 NMR spectra of poly(methyl acrylate) (PMA) and methyl acrylate (MA)/1-hexene copolymers in CDCl$_3$. Samples were taken from Figure 4. Key: (a) $M_1 = 0.1$, $m_1 = 0.51$, AlCl$_3$ = 0.1 equiv. relative to MA; (b) $M_1 = 0.85$, $m_1 = 0.85$, AlCl$_3$ = 0.1 equiv. relative to MA; (c) commercial PMA, 40 wt % in toluene.

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References and Notes

(1) Luo, R.; Sen, A. *Macromolecules* **2007**, *40*, 154–156.
(2) Nagel, M.; Poli, D.; Sen, A. *Macromolecules* **2005**, *38*, 7262–7265.
(3) Liu, S.; Sen, A. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 6175–6192.
(4) Luo, R.; Chen, Y.; Sen, A. *J. Polym. Sci Part A: Polym. Chem.* **2008**, *46*, 5499–5505.
(5) Lee, H.-Y.; Herman, M. S.; Padias, A. B.; Hall, H. K.; Tack, J. R. D. *Acta Polym.* **1994**, *45*, 413–418.
(6) Braun, D.; Manger, E. *Angew. Makromol. Chem.* **1986**, *145*, 101–124.
(7) Lutz, J. F.; Kirci, B.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 3136–3145.
(8) Lutz, J.-F.; Neugebauer, D.; Matyjaszewski, K. *J. Am. Chem. Soc.* **2003**, *125*, 6986–6993.
(9) Ray, B.; Isobe, Y.; Matsumoto, K.; Habaue, S.; Okamoto, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2004**, *37*, 1702–1710.
(10) Yutaka Isobe, T. N. Y. O. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1463–1471.
(11) Logothetis, A. L.; Mckenna, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1978**, *16*, 2797–2807.
(12) Logothetis, A. L.; Mckenna, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 1431–1439.
(13) Logothetis, A. L.; Mckenna, J. M. *J. Polym. Sci., Part A: Polym. Chem.* **1977**, *15*, 1441–1445.
(14) Tüdős, F.; Kelen, T.; Földes-Berezhnykh, T.; Turcsányi, B. *React. Kinet. Catal. Lett.* **1975**, *2*, 439–447.
(15) van Herk, A. M.; Dröge, T. *Macromol. Theory Simul.* **1997**, *6*, 1263–1276.
(16) Behnken, D. W. *J. Polym. Sci, Part A: Polym. Chem.* **1964**, *2*, 645–668.
(17) Hirai, H.; Komiyama, M. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2701–2719.
(18) Yuan, Y.; Song, H.; Xu, G. *Polym. Int.* **1993**, *31*, 397–402.
(19) Rodriguez-Delgado, A.; Chen, E. Y.-X. *J. Am. Chem. Soc.* **2005**, *127*, 961–974.
(20) Subramanyam, U.; Rajamohanan, P. R.; Sivaram, S. *Polymer* **2004**, *45*, 4063–4076.
(21) Zipse, H. *Top. Curr. Chem.* **2006**, *263*, 163–189.
(22) Crich, D.; Brebion, F.; Suk, D.-H. *Top. Curr. Chem.* **2006**, *263*, 1–38.
(23) Liu, S.; Gu, B.; Rowlands, H.; Sen, A. *Macromolecules* **2004**, *37*, 7924–7929.
(24) Johnson, L. K; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *125*, 267–268.
(25) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283–316.
(26) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169–1204.
(27) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888–899.
(28) Drent, E.; van Dijk, R.; van Ginkel, R.; van Oort, B.; Pugh, R. I. *Chem. Commun.* **2002**, 744–745.
(29) Sen, A.; Borkar, S. *J. Organomet. Chem.* **2007**, *692*, 3291–3299.
(30) Elia, C.; Elyashiv-Barad, S.; Sen, A.; Lopez-Fernandez, R.; Albeniz, A. C.; Espinet, P. *Organometallics* **2002**, *21*, 4249–4256.
(31) Gibson, V. C.; Tomov, A. *Chem. Commun.* **2001**, 1964–1965.
(32) Borkar, S.; Yennawar, H.; Sen, A. *Organometallics* **2007**, *26*, 4711–4714.