Lewis Acid-Mediated Copolymerization of Methyl Acrylate and Methyl Methacrylate with 1-Alkenes

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ABSTRACT: The addition of the Lewis acid, $Sc(OTf)_3$, to 2,2′-azobis(2-methylpropionitrile) (AIBN)-initiated copolymerizations of both methyl acrylate (MA) and methyl methacrylate (MMA) with 1-alkenes results in increased reaction rate and increased incorporation of the latter monomer into the polymer backbone. As little as 4 mol % of the Lewis acid is effective in forming a nearly alternating copolymer of MA and ethene at 67% MA conversion. This procedure allows for the control of copolymer composition independent of the starting monomer feed ratio.

Introduction

The synthesis of polymers with precise and reproducible structures allows for the controlled adjustment of macroscopic properties of such materials. With the wide number of monomers available for radical polymerization, the ability to control radically initiated polymerization has been an area of extensive research. For example, the microstructure control in radical polymerization of acrylate-based monomers through the use of Lewis acids has been reported.[1−3] The complexation of Lewis acid to the ester functionality both increases the reactivity of the monomer and affects the tacticity of the resultant polymer.[3] The latter is believed to be due the simultaneous complexation of several monomer units to the Lewis acid, resulting in the formation of meso triads upon polymerization and ultimately an overall increase in isotacticity of the polymer.

An important remaining challenge in polymer synthesis is the copolymerization of polar monomers with simple alkenes. We[4−7] and others[8−10] have reported on the copolymerization of acrylates with ethene and 1-alkenes. The molecular weight and molecular weight distribution of the resultant random copolymers can be regulated using controlled radical polymerization techniques. However, there is little control over polymer tacticity or the amount of 1-alkene incorporated into the polymer backbone. The ability to control the latter properties would result in additional control over bulk properties, such as glass transition temperature (T_g) and material toughness. Herein we report the synthesis of copolymers of methyl methacrylate and methyl acrylate with ethene and 1-alkenes in the presence of the Lewis acid, $Sc(OTf)_3$. We demonstrate that only a catalytic amount of $Sc(OTf)_3$ is sufficient to form nearly alternating copolymers in high yield.

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 were vacuum-distilled from CaH_2 and stored under N_2. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) and scandium(III) trifluoromethanesulfonate ($Sc(OTf)_3$, 97%, Strem Chemicals) were used as received. For reversible addition−fragmentation tranfer polymerization (RAFT), benzyl 1-pyrrolcarbodithioate was synthesized according to the literature.[11] ^1H NMR ($CDCl_3$, ppm): 4.62 (s, 2H, CH_2PH), 6.35 (m, 2H, pyrrole), 7.40 (m, 5H, CH_2-Ph), 7.73 (m, 2H, pyrrole).

Instrumentation. Gas chromatography analysis was obtained on an Agilent 5890 Series II GC using a RTX-5 split capillary column (Restek) connected to an FID detector. With an injector temperature of 250 °C, the sample was heated from 60 to 100 °C at a ramp rate of 5 °C/min. ^1H, ^2H, and ^{13}C NMR spectra were recorded using a Bruker 300-DPX spectrometer at ambient temperature (^1H, 300 MHz; ^2H, 46 MHz; ^{13}C, 75 MHz). Chemical shifts were referenced to $CDCl_3$. 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 bead size: 100−5000, 500−30000, and 2000−4 × 10^6 Da), a Shimadzu RID-10A differential refractometer, and a Shimadzu SPD-10A tunable absorbance detector (254 nm). GPC samples were run in chloroform at a flow rate of 1 mL/min at 35 °C and calibrated against polystyrene standards. Analysis was done using EZSTART 7.2 software.

Synthesis of Homo- and Copolymers. In a typical experiment (Table 1, entry 2) in a N_2-filled dry glovebox, a glass-lined Parr high-pressure reactor was charged with chlorobenzene (5 mL), AIBN (3.9 mg, 0.024 mmol), MMA (0.3 g, 3 mmol), and $Sc(OTf)_3$ (147 mg, 0.3 mmol). The vial was sealed, removed from the glovebox, and filled with ethene to 500 psi. The reaction was stirred in a 60 °C oil bath for 18 h. At the end of this period, the reaction was cooled and vented, and the polymer was precipitated with a large excess of methanol. The polymer was collected by vacuum filtration and dried under high vacuum for 24 h. The reaction produced 0.26 g of copolymer containing 27 mol % ethene (M_w, 245 000; M_w/M_n, 3.0). The polymer composition was determined by ^1H NMR integration of the methoxy protons vs total aliphatic resonances. For those reactions which did not require a Parr reactor, the polymerizations were carried out in a 20 mL scintillation vial.

Synthesis of Methyl Acrylate/1-Hexene Copolymers by RAFT. In a N_2-filled dry glovebox, a 20 mL scintillation vial with a magnetic stir bar was charged with chlorobenzene (4 mL), MA (1.0 g, 11.6 mmol), 1-hexene (1.0 g, 11.9 mmmol), AIBN (0.67 mg, 4.1 μmol), and the appropriate amount of 1-pyrrolcarbodithioate (RAFT agent). The reaction was stirred at 60 °C. After 18 h, the samples were cooled to room temperature and worked up as described above. The RAFT copolymerization results can be found in Table 5.

Kinetic Study of MA/1-Hexene RAFT Copolymerization in the Presence of $Sc(OTf)_3$. In a N_2-filled dry glovebox, a reaction vessel with a magnetic stir bar was charged with chlorobenzene (10 mL), MA (5 g, 58.1 mmol), 1-hexene (5 g, 59.5 mmol), benzyl 1-pyrrolcarbodithiate (42 mg, 0.18 mmol), and AIBN (3 mg, 0.018 mmol). The reaction vessel was then placed in an oil bath at 60 °C. Samples were taken with a

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Table 1. Copolymerization of Methyl Methacrylate (MMA) with 1-Alkenes Using 2,2′-Azobis(2-methylpropionitrile) (AIBN) in the Presence of $Sc(OTf)_3$[a]

entry	$Sc(OTf)_3$:monomer	alkene (psi or g)	yield (g)	$M_w \times 10^{-3}$ [b]	M_w/M_n[b]	alkene incorp (mol %)	MMA conv (%)
1	0	ethene (500)	0.011	152	2.4	22	3.3
2	1:10	ethene (500)	0.26	245	3.0	27	76
3	1:5	ethene (500)	0.26	32.3	1.3	37	76
4	0	1-hexene (3.75)	0.11	49.2	1.3	12	31
5	1:10	1-hexene (3.75)	0.28	111	2.7	19	63

[a] Conditions: AIBN, 4 mg; MMA, 3 mmol; PhCl, 5 mL; 60 °C, 18 h. [b] By GPC relative to polystyrene standards.

syringe and used for GC and GPC analysis to determine monomer conversion, molecular weight, and molecular weight distribution.

Results and Discussion

Copolymerization of Methyl Methacrylate with 1-Alkenes. The effect of the addition of $Sc(OTf)_3$ to AIBN-initiated copolymerization of methyl methacrylate (MMA) with ethene and 1-hexene is summarized in Table 1. In all cases, an increase in 1-alkene incorporation was observed in the presence of $Sc(OTf)_3$. Additionally, this effect becomes greater as the amount of $Sc(OTf)_3$ is increased. For example, comparison of the copolymerization of MMA and ethene in the absence of $Sc(OTf)_3$ to those with the addition of 0.1 and 0.2 equiv of $Sc(OTf)_3$ (versus the MMA) shows the mole percent of ethene incorporated in to the polymer backbone increases from 22 to 27 to 37%, respectively. This then allows for the control of copolymer composition independent of the starting monomer feed ratio. More dramatic is the increase in MMA conversion upon the addition of $Sc(OTf)_3$ to the reaction mixture. In all cases, the MMA conversion more than doubles after the addition of 0.1 equiv of $Sc(OTf)_3$. These observations can be attributed to the interaction of the carbonyl group of MMA with the scandium center. This results in a decrease in electron density around the C=C bond of the acrylate monomer and in a more reactive electrophilic radical. The higher electrophilicity also promotes addition to the electron rich C=C bond of the nonpolar alkene.[12]

The addition of $Sc(OTf)_3$ during the homopolymerization of MMA results in an increased number of isotactic triads as a consequence of more than one monomer simultaneously coordinating to the scandium center at the growing chain end.[3] The obvious question that arose was whether the enhancement of isotactic triads was maintained in the copolymerization reaction. However, for the copolymers with 1-alkenes, the triad information calculated from integration of the α-methyl resonances in the ^1H NMR spectrum between 0.7 and 1.3 ppm could not be obtained due to overlapping signals from the 1-alkene comonomer now incorporated into the polymer backbone. Therefore, a copolymer was prepared from MMA and C_2D_4. The incorporation of the latter monomer was confirmed by ^2H NMR spectroscopy. From the integration of the α-methyl peaks in the ^1H NMR spectrum, it was clear that the tacticity of the MMA triads in the copolymer was no different than that in PMMA prepared in the absence of $Sc(OTf)_3$ (Table 2). Presumably, the presence of the 1-alkene units in the copolymer backbone interferes with the simultaneous coordination of several MMA units to the scandium center, a condition necessary for the enhanced formation of isotactic triads.

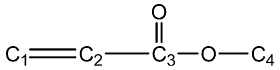
Copolymerization of Methyl Acrylate and α-Olefins. Unlike MMA, the addition of $Sc(OTf)_3$ during the radical-initiated homopolymerization of methyl acrylate (MA) did not result in polymer microstructure different from the usual atactic structure obtained in the absence of the Lewis acid. Therefore, ^{13}C NMR spectroscopy was employed to examine the interaction between MA and $Sc(OTf)_3$. As shown in Table 3, there are small but distinct shifts of the resonances in the presence of $Sc(OTf)_3$. The biggest shift is for the carbon of the carbonyl group: the expected binding site for scandium. These results are similar to those observed for MMA[3] and once again suggest an interaction between the ester group of the MA and scandium center of $Sc(OTf)_3$.

Table 2. Tacticity of Poly(methyl methacrylate) (PMMA) Segments after Homo- and Copolymerization in the Presence of $Sc(OTf)_3$[a]

			tacticity[b]		
entry	$Sc(OTf)_3$:monomer	comonomer	% mm	% mr	% rr
1	0	none	7	36	67
2	1:10	none	18	42	40
3	1:10	C_2D_4[c]	7	37	68

[a] Conditions: AIBN, 4 mg; MMA, 3 mmol; PhCl, 5 mL; 60 °C, 18 h. [b] Determined by ^1H NMR integration of the methyl resonances in accordance with literature report.[13] [c] C_2D_4, 300 psi.

Table 3. Changes in the ^{13}C NMR Chemical Shifts of Methyl Acrylate (MA) upon the Addition of $Sc(OTf)_3$


$C_1{=}C_2{-}C_3(=O){-}O{-}C_4$

carbon	MA (ppm)	added $Sc(OTf)_3$ (ppm)[a]	Δδ (ppm)
1	129.86	131.19	1.34
2	128.65	128.29	−0.36
3	165.66	167.11	1.45
4	51.17	51.72	0.55

[a] MA:$Sc(OTf)_3$ = 10 (molar ratio).

Although tacticity change was not observed in the MA homopolymer obtained in the presence of $Sc(OTf)_3$, the above NMR results suggested that the interaction between the MA and $Sc(OTf)_3$ may still be strong enough to promote the copolymerization of MA with nonpolar 1-alkenes. Our results in this area are summarized in Table 4. In every case the addition of $Sc(OTf)_3$ resulted in significant increase of the amount of alkene incorporation. For example, the copolymerization of MA and ethene in the presence of 0.1 mole ratio of $Sc(OTf)_3$ vs MA produced a copolymer containing 47 mol % of the latter. The ^{13}C NMR spectrum of this polymer contained five dominant resonances at 176.4 (−C(O)−), 51.8 ($-OCH_3$), 45.7 (−CH−), 32.7 ($-CH_2-$), and 25.8 ppm ($-CH_2-$). These represent the five signals from a perfectly alternating MA−ethene copolymer sequence.[14] Two less intense resonances at 43.6 and 34.8 ppm were also present and are due to consecutive MA units, suggesting some nonperfect alternation. Alternating MA/ethene copolymers have been previously reported, but the synthesis requires a stoichiometric amount of a strong Lewis acid such as $AlCl_3$ or BF_3.[15,16] $Sc(OTf)_3$ is

Scheme 1

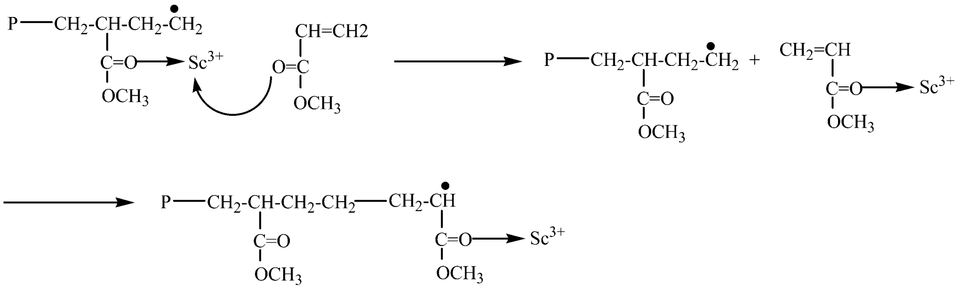


Table 4. Copolymerization of Methyl Acrylate (MA) with 1-Alkenes Using 2,2′-Azobis(2-methylpropionitrile) (AIBN) in the Presence of $Sc(OTf)_3$[a]

entry	MA (g)	$Sc(OTf)_3$:monomer	comonomer (psi or g)	yield (g)	$M_w \times 10^{-3}$ [b]	M_w/M_n[b]	olefin incorp (mol %)	MA conv (%)
1	0.31	0	ethene (500)	0.069	99	1.7	30	20
2	0.31	1:10	ethene (500)	0.298	132	2.9	47	74
3	0.30	0	propene (6.5)	0.010	49	1.6	41	1.3
4	0.26	1:10	propene (6.5)	0.081	238	2.2	46	22
5	0.30	0	1-hexene (1)	0.010	25	1.6	26	1.2
6	0.31	1:10	1-hexene (1)	0.064	86	2.1	41	12
7	0.31	0	1-decene (3.3)	0.18	37	1.4	25	19
8	0.33	1:10	1-decene (3.3)	0.279	58	2.3	40	41
9	0.33	0	norbornene (2.9)	0.19	47	1.6	22	22
10	0.32	1:10	norbornene (2.9)	0.304	36	2.3	33	62

[a] Conditions: AIBN, 4 mg; MA, 3.5 mmol; PhCl, 5 mL; 60 °C, 18 h. [b] By GPC relative to polystyrene standards.

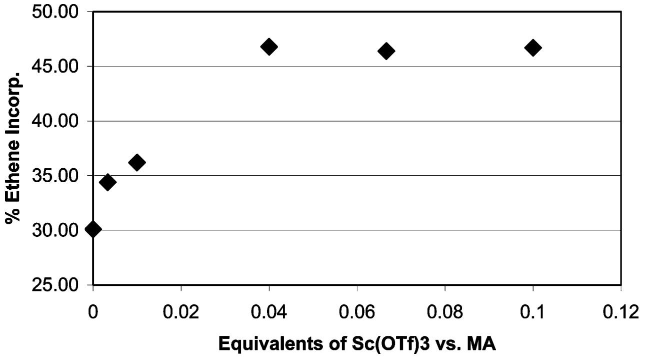


Figure 1. Ethene (mol %) in the copolymer as a function of the amount of $Sc(OTf)_3$ present in methyl acrylate (MA)/ethene copolymerization. MA, 0.70 M; ethene, 500 psi; AIBN, 4.9 mM; chlorobenzene, 60 °C, 18 h.

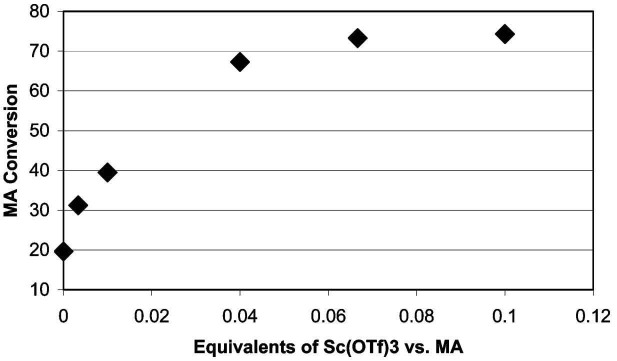


Figure 2. Methyl acrylate (MA) conversion as a function of the amount of $Sc(OTf)_3$ present in MA/ethene copolymerization. MA, 0.70 M; ethene, 500 psi; AIBN, 4.9 mM; chlorobenzene, 60 °C, 18 h.

a relatively air stable compound that offers much the same result in significantly lower concentrations.

The effect of varying the amount of $Sc(OTf)_3$ was also examined for the copolymerization of MA with ethene. In all cases, the result is increased ethene incorporation into the copolymer, but the level of increase is directly dependent on the amount of $Sc(OTf)_3$ present (Figure 1). Clearly, the results point to the ability to "dial-in" a copolymer composition by simply adjusting the amount of $Sc(OTf)_3$ added to the radically initiated copolymerization.

As with the MMA copolymerization, the presence of the $Sc(OTf)_3$ also affects the yield of the MA/alkene copolymers obtained. The amount of product from the reaction increases as the amount of $Sc(OTf)_3$ in the system increases (Figure 2). As seen from Figures 1 and 2, it is possible to synthesize a polymer that is nearly alternating in MA and ethene at 67% MA conversion with only 4 mol % of $Sc(OTf)_3$ per MA. The fact that an alternating copolymer can be prepared using such a low $Sc(OTf)_3$:MA ratio suggests facile Sc^{3+} exchange between MA units in the polymer and monomeric MA as shown in Scheme 1.

In all cases it was confirmed by gel permeation chromatography (GPC) that these were in fact true copolymers and not a mixture of two homopolymers. The GPC chromatogram showed only one peak for both the refractive index (RI) and UV detectors (see Supporting Information). The latter is of course more sensitive to acrylate groups. This indicates a true copolymer over the entire molecular weight distribution range.

Controlled Polymerization of MA and 1-Hexene in the Presence of $Sc(OTf)_3$. In the conventional free-radical copolymerization of acrylates with 1-alkenes, there is little control over molecular weight or molecular weight distribution. We[16] and others[17] have reported on controlled copolymerization using the reversible addition−fragmentation transfer (RAFT) technique. RAFT polymerization was also found to control the alternating copolymerization of MA and ethene in the presence of the Lewis acid, $AlCl_3$.[16]

We have examined the effect of RAFT agent on the AIBN-initiated copolymerization of MA with 1-hexene in the presence of $Sc(OTf)_3$. The RAFT agent, benzyl 1-pyrrolcarbodithioate, was chosen since it has been shown to be effective for copolymerizations in the presence of $AlCl_3$. As shown in Figure 3, the copolym-

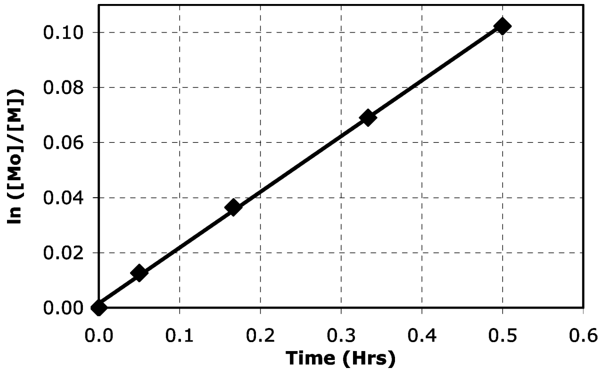


Figure 3. First-order kinetic plot for the copolymerization of methyl acrylate (MA) with 1-hexene. MA, 2.6 M; 1-hexene, 2.7 M; RAFT, 8.3 mM; AIBN, 0.83 mM; chlorobenzene, 60 °C.

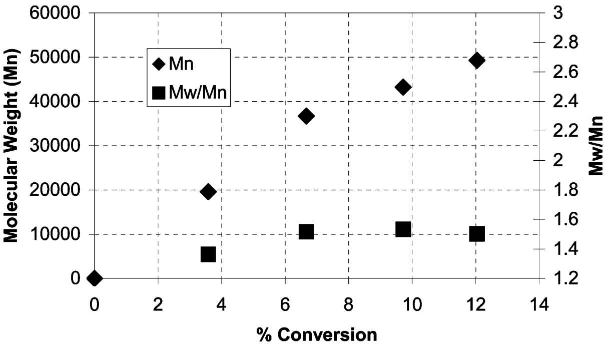


Figure 4. Dependence of molecular weight (M_n) and molecular weight distribution (M_w/M_n) on overall conversion in the copolymerization of methyl acrylate (MA) with 1-hexene. MA, 2.6 M; 1-hexene, 2.7 M; RAFT, 8.3 mM; AIBN, 0.83 mM; chlorobenzene, 60 °C.

Table 5. RAFT Copolymerization of Methyl Acrylate (MA) and 1-Hexene with Sc(OTf)$_3$/2,2′-Azobis(2-methylpropionitrile) (AIBN)[a]

entry	RAFT/AIBN (molar ratio)	$M_w \times 10^{-3}$ [b]	M_w/M_n [b]	1-alkene (mol %)	MA conv (%)
1	0	209	2.8	30	71
2	5	140	2.2	27	37
3	10	70	1.7	25	6.0

[a] Conditions: MA, 2.6 M; 1-hexene, 2.7 M; AIBN, 0.83 mM; chlorobenzene, MA:Sc(OTf)$_3$ = 10, 60 °C, 18 h. [b] By GPC relative to polystyrene standards.

erization displays first-order kinetics. Additionally, there is initially a linear increase in molecular weight with conversion (Figure 4). However, the line curves at higher conversions, and there is a simultaneous increase in polydispersity of the copolymer obtained. This suggests that the reaction does not meet the criteria for "living" polymerizations.

The results from increasing the amount of RAFT agent present during the copolymerization of MA with 1-hexene are summarized in Table 5. Both the molecular weight and molecular weight distribution decrease with increasing concentration of the RAFT agent. For example, as the RAFT/AIBN molar ratio increases from 0 to 5 to 10, the M_w decreases from 209 000 to 140 000 to 70 000, and the polydispersity index decreases from 2.7 to 2.2 to 1.7. Thus, although the molecular weight drops and the polydispersity appears to narrow, the copolymerizations are not as well behaved as that observed without Sc(OTf)$_3$. One can speculate that Sc(OTf)$_3$ interferes with the functioning of the RAFT agent. The observation that the amount of 1-hexene incorporated into the copolymer decreases with increasing concentration of the RAFT agent provides indirect support for this hypothesis. Nevertheless, the amount of 1-alkene incorporated is significantly greater with the introduction of Sc(OTf)$_3$ into the system. A maximum of 12 mol % 1-hexene incorporation was reported for controlled copolymerization with a RAFT/AIBN ratio of 10 without Sc(OTf)$_3$.[15] With Sc(OTf)$_3$, and a RAFT/AIBN ratio of 10, the mol % of 1-hexene is 25.

Conclusion

The addition of the Lewis acid, Sc(OTf)$_3$, to AIBN-initiated copolymerizations of both MA and MMA with 1-alkenes results in increased reaction rate and increased incorporation of the latter monomer into the polymer backbone. As little as 4 mol % of the Lewis acid is effective in forming a nearly alternating copolymer of MA and ethene at 67% MA conversion. This procedure allows for the control of copolymer composition independent of the starting monomer feed ratio.

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Supporting Information Available: NMR data and GPC traces. This material is available free of charge via the Internet at http://pubs.acs.org.

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