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Recyclable, Heterogeneous, Lewis Acid-Mediated Copolymerization of Acrylate with Nonpolar Alkenes

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The physical and chemical properties of polymers are significantly influenced by their microstructures. In this context, the synthesis of copolymers of acrylates with simple alkenes with predictable compositions and structures is of great current interest because the combination of the two classes of monomers can greatly enhance the range of currently attainable polymer properties.[1−3] We[4−9] and others[10−12] have reported the free radical copolymerization of acrylates with ethene and 1-alkenes. Random acrylate-rich copolymers in relatively low yield were obtained. More recently, we have shown that the presence of a catalytic amount of the Lewis acid, $Sc(OTf)_3$, leads to increased reaction rate and increased incorporation of the nonpolar alkene.[9] Thus, essentially alternating copolymers in good yield can be obtained. The Lewis acid coordinates to the ester carbonyl group of the acrylate monomer and reduces the electron density in the conjugated C═C bond, thereby (a) increasing the reactivity of the radical generated there from and (b) making the radical more susceptible to attack by the relatively electron-rich nonpolar alkene.[13]

Although the presence of a Lewis acid serves to increase the copolymer yield and the incorporation of the nonpolar alkene, most Lewis acids employed thus far are relatively expensive materials that are soluble in the reaction medium and, therefore, not easily recycled.[9,13−18] From the standpoint of practical "green chemistry", the ideal Lewis acid should be insoluble that can be separated by filtration and reused.[19] At first glance, this appears to be a difficult problem because the radical polymerization would be expected to occur in the liquid monomer phase and the insoluble Lewis acid would be expected to have a minimal influence on the polymerization. However, as discussed above, the bonding of the acrylate monomer to the Lewis acid significantly increases its reactivity. Thus, under ideal conditions, the acrylate monomer units that participate in the polymerization would be predominantly those that are bound to the heterogeneous Lewis acid.

Herein, we report the copolymerization of methyl acrylate (MA) and with nonpolar ethene and 1-alkenes in the presence of solid acidic alumina (Al_2O_3) as Lewis acid. The copolymerization proceeds with increased 1-alkene incorporation and increased acrylate conversion. Most importantly, acidic alumina can be recycled repeatedly with no loss of activity. This led to the design of an Al_2O_3-filled column reactor system for the copolymerization reactions.

The addition of acidic alumina (Aldrich, acidic, Brockmann I, standard grade, ∼150 mesh, pH = 4.5 ± 0.5 in aqueous solution) to the AIBN-initiated homopolymerization of methyl acrylate led to a significant increase in polymerization rate and conversion; however, the tacticity of the resultant polymer was unaffected (Table 1). Clearly, even a Lewis acid that is insoluble in the reaction medium can still increase the reactivity of the propagating radical by coordination through the ester carbonyl group. The effect is particularly dramatic since only a small fraction of the Lewis acid sites that are present on the alumina surface can actually interact with the acrylate.

Table 1. Homopolymerization of Methyl Acrylate (MA) in the Presence and Absence of Acidic Al_2O_3[a]

entry	$[Al_2O_3]$/[MA]	yield (%)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]	tacticity[c] mm	mr	rr
1	0	42	1.7	2.23	29	44	25
2	1:5	58	1.6	2.37	28	42	30
3	1:2	83	1.9	2.22	30	42	28

[a] Conditions: MA, 0.3 g; AIBN, 0.005 g; PhCl, 5 mL; 75 °C, 18 h. [b] By GPC using polystyrene standards. [c] From ^{1}H NMR spectra.

Table 2. Copolymerization of Methyl Acrylate (MA) with Ethene in the Presence and Absence of Acidic Al_2O_3 at Different Temperatures[a]

entry	temp (°C)	$[Al_2O_3]$/[MA]	yield (g)	ethene incorp (mol %)	MA conv (%)	M_n[b] ($\times 10^{-4}$)	M_w/M_n[b]
1	60	0	0.084	35	23	12.6	1.57
2	60	1:5	0.189	35	54	10.7	1.49
3	60	1:2	0.223	43	60	4.6	1.87
4	75	0	0.140	40	39	9.4	1.57
5	75	1:5	0.212	45	56	3.5	1.86
6	75	1:2	0.232	45	61	3.4	1.75
7	90	0	0.186	44	50	5.4	1.60
8	90	1:5	0.292	46	76	2.5	1.85
9	90	1:2	0.304	48	78	2.3	1.71

[a] Conditions: MA, 0.3 g; ethene, 500 psi; AIBN, 0.005 g; PhCl, 5 mL; 18 h. [b] By GPC using polystyrene standards.

The effect of added acidic alumina to the AIBN-initiated copolymerization of methyl acrylate (MA) with ethene at three different temperatures was examined (Table 2). The copolymer compositions were determined from ^{1}H NMR integration of the methoxy protons vs aliphatic resonances. Irrespective of the reaction temperature, the ethene incorporation and, especially, the copolymer yield increased significantly upon the addition of alumina. 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. The latter is of course more sensitive to acrylate groups. This indicates a true copolymer over the entire molecular weight distribution range. The copolymer microstructure was examined by ^{1}H and ^{13}C NMR spectroscopy. At high ethene incorporation, the structure was nearly alternating. The ^{13}C NMR spectrum showed five major resonance at 175.9 (−C(O)−), 51.8 ($-OCH_3$), 45.6 (−CH−), 32.5 ($-CH_2-$), and 25.5 ppm ($-CH_2-$) from alternating MA−ethene copolymer sequence. Less intense peaks were observed at 43.6 and 35.0 ppm attributable to consecutive MA units and even lower intensity peaks at 29.8 and 27.7 ppm attributable to consecutive ethene units, suggesting a small degree of nonalternation. A similar microstructure was previously observed for $Sc(OTf)_3$-mediated radical copolymerization of MA with ethene.[9] Table 3 summarizes the results for the copolymerization of ethene, 1-hexene, and 1-decene with MA in the presence and absence of acidic alumina at 75 °C. Again, a dramatic increase (approximately 2−3 times higher) in monomer conversion was observed in the presence of the Lewis acid, irrespective of the alkene employed (also see kinetic data in the Supporting

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Table 3. Copolymerization of Methyl Acrylate (MA) with 1-Alkenes in the Presence and Absence of Acidic Al_2O_3[a]

entry	alkene (psi or g)	$[Al_2O_3]$/[MA]	yield (g)	alkene incorp (mol %)	MA conv (%)	M_n[d] $(\times 10^{-4})$	M_w/M_n[d]	Al_2O_3 recovered (%)
1	ethene (500)	0	0.140	40	39	9.4	1.57	
2	ethene (500)	1:5	0.212	45	56	3.5	1.86	93.8
3	ethene (500)	1:2	0.232	45	61	3.4	1.75	90.6
4[b]	ethene (500)	1:2	0.223	47	58	9.6	1.43	95.1
5[c]	1-hexene (1.0)	0	0.061	31	14	2.0	1.75	
6	1-hexene (1.0)	0	0.050	29	11	3.0	1.78	
7[c]	1-hexene (1.0)	1:5	0.146	31	34	2.8	1.54	89.0
8	1-hexene (1.0)	1:5	0.138	32	32	1.3	2.24	83.2
9[c]	1-hexene (1.0)	1:2	0.179	33	40	2.5	1.71	98.1
10	1-hexene (1.0)	1:2	0.176	35	38	1.6	2.37	90.2
11[b]	1-hexene (1.0)	1:2	0.152	35	33	1.1	1.97	94.4
12	1-decene (1.5)	0	0.071	27	15	1.2	2.24	
13	1-decene (1.5)	1:5	0.131	32	25	1.0	2.19	94.4
14	1-decene (1.5)	1:2	0.176	32	33	1.2	2.34	89.8

[a] Conditions: MA, 0.3 g; AIBN, 0.005 g; PhCl, 5 mL; 75 °C, 18 h. [b] Using recycled Al_2O_3. [c] Run for 4 h. [d] By GPC using polystyrene standards.

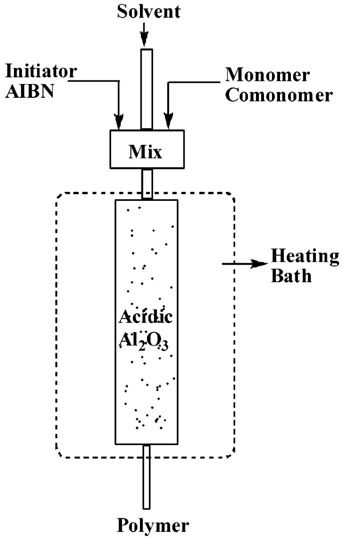

Figure 1. Alumina-filled column reactor.

Information). Furthermore, the alumina could be recovered by simple filtration and reused with no attenuation of activity (entries 4 and 11, Table 3). Note that while the polymerizations were routinely allowed to proceed for 18 h, entries 5, 7, and 9 in Table 3 suggest that the reactions are completed in the first 4 h.

Our observation that relatively inexpensive, air-stable, alumina can be used to significantly increase the yield of MA/alkene copolymers prompted us to explore the possibility of employing an alumina-filled column as a reactor system (Figure 1). The concept was to carry out the copolymerization inside the column, wash out the copolymer formed subsequently, and reuse the column for another copolymerization (see Supporting Information for details). A total of 12 cycles were carried out. While there are some variations in polymer yields, especially in the beginning, after several cycles copolymer with 30 mol % incorporation of 1-hexene was obtained with an approximately steady 25−30% acrylate conversion. The conversion was lower than that observed in batch reactors; nevertheless it was 2 times higher than that observed in the absence of alumina (entries 5 and 6, Table 3).

The variation in yield observed during recycling may be ascribed to incomplete removal of the polymer formed on the alumina surface. However, if the alumina surface was indeed covered with polymer, its ability to activate the acrylate monomer through coordination to the ester group would be quenched. The clear trend of increased polymer yield in the column reactor through many cycles when compared to the yield in the absence of alumina would appear to rule out such a scenario.

In summary, the addition of the insoluble Lewis acid, acidic alumina, to the AIBN-initiated homo- and copolymerizations of acrylate with nonpolar 1-alkenes resulted in increased monomer conversion and increased incorporation of the latter monomer into the polymer backbone. The effect is particularly dramatic since only a small fraction of the Lewis acid sites that are present on the alumina surface can actually interact with the acrylate. Preliminary NMR studies on the coordination of soluble Lewis acids to the ester carbonyl of acrylate monomers and polymers suggest that the interaction with the monomer is significantly stronger than that with the polymer,[14] thus explaining why only a catalytic amount of Lewis acid is required for polymerization rate enhancement. Alumina can be recovered by filtration and reused repeatedly with no loss of activity. This led to the design of an Al_2O_3-filled column reactor system for the copolymerization reactions. In principle, the latter can be modified into a flow reactor where the polymerization occurs in the column and the polymer solution flows out and is continuously replaced by fresh solution containing the monomers and initiator.

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Supporting Information Available: Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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