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Copper-Mediated Controlled Copolymerization of Methyl Acrylate with 1-Alkenes under Mild Conditions

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The copolymerization of polar vinyl monomers with nonpolar alkenes remains an area of great interest because the combination of the two can greatly enhance the range of currently attainable polymer properties.[1] The polymerization of polar vinyl monomers, such as acrylates, occurs readily by free-radical polymerization to yield high-molecular-weight homopolymers.[2] On the other hand, simple linear 1-alkenes, such as ethene and propene, undergo radical-initiated homo- and copolymerization only under harsh conditions to yield branched materials.[3] To date, the only successful radical-initiated copolymerization of acrylates with 1-alkenes under mild conditions involves the use of strong Lewis acids that complex to the ester functionality of the acrylate.[4] The resultant highly electron-deficient monomer forms a 1:1 alternating copolymer with 1-alkenes in the presence of radical initiators. In the area of metal-catalyzed insertion polymerizations, Brookhart reported the copolymerization of ethene and acrylates with cationic palladium diimine compounds. However, a maximum incorporation of 12% methyl acrylate in the copolymer was achieved.[5] Grubbs has also reported a somewhat related system based on neutral nickel compounds that is able to polymerize functionalized alkenes.[6] However, this system is ineffective for acrylates. Herein, we report the copper-mediated synthesis of random copolymers of methyl acrylate (MA) with 1-alkenes resulting in greater than 20% incorporation of the latter in the copolymer. The system displays many of the characteristics of a living polymerization system, allowing the synthesis of unique block copolymers.

The copper-mediated process used is based on a similar procedure used for the polymerization of methyl acrylate by atom transfer radical polymerization.[7] Our results are summarized in Table 1. The polymerization reactions were carried out at 90 °C, and the resultant copolymers exhibit a range of 1-alkene comonomer incorporations. For comparison, the AIBN-initiated copolymerization of methyl acrylate with 1-alkenes at 60 °C is shown in Table 2. The amount of 1-alkene incorporated is similar or slightly lower. On the other hand, the copolymers have significantly higher molecular weights. In the copolymerization of methyl acrylate with 1-hexene, the yield of the copolymer decreased with decreasing feed ratio of methyl acrylate: 1-hexene (entries 3−6, Table 2).

Table 1. Copper-Mediated Copolymerization of Methyl Acrylate with 1-Alkenes[a]

entry	MA (g)	1-alkene (g)	yield (g)	1-alkene incorp. (mol %)	M_n[b]	M_w/M_n[b]
1[c]	5.0	ethene, 900 psi	1.5	8.6	10,400	1.5
2[d]	5.0	ethene, 900 psi	4.5	14.8	n.d.	n.d.
3	5.0	propene, 17.0 g	3.8	21.7	9,900	1.4
4	5.0	1-butene, 4.2 g	4.5	7.8	9,300 (8,100)[e]	1.3 (1.4)[e]
5	5.0	1-hexene, 3.0 g	4.3	11.8	12,000	1.3
6	3.0	1-hexene, 6.0 g	2.5	21.3	5,800	1.3
7	3.0	1-octene, 7.8 g	3.0	23.6	4,000	1.2

[a] Reaction conditions: CuBr, 0.47 mmol; ethyl 2-bromopropionate (EBP), 0.47 mmol; pentamethyldiethylenetriamine (PMDETA), 0.47 mmol; 90 °C; 16 h. [b] Determined by GPC relative to polystyrene standards using refractive index detector. [c] CuBr, 0.23 mmol; EBP, 0.23 mmol; PMDETA, 0.23 mmol. [d] CuBr, 1.4 mmol; EBP, 1.4 mmol; PMDETA, 1.4 mmol. [e] Using UV detector.

Table 2. AIBN-Initiated Copolymerization of Methyl Acrylate with 1-Alkenes[a]

entry	MA (g)	1-alkene (g)	yield (g)	1-alkene incorp. (mol %)	M_n[b]	M_w/M_n[b]
1	1.9	ethene, 500 psi	1.6	5.7	284,000	9.0
2	1.9	propene, 5.3 g	1.0	21.5	451,000	2.0
3	1.8	1-hexene, 0.2 g	1.7	3.4	320,000 (254,000)[c]	2.9 (3.1)[c]
4	1.0	1-hexene, 1.0 g	0.5	11.6	161,000	1.7
5	0.9	1-hexene, 1.1 g	0.3	13.7	140,000	1.6
6	0.7	1-hexene, 1.3 g	0.2	17.9	154,000	1.5
7	0.9	1-octene, 1.1 g	0.5	12.9	115,000 (90,000)[c]	1.6 (1.6)[c]

[a] Reaction conditions: AIBN, 0.03 mmol; PhCl, 4 mL; 60 °C; 21 h. [b] Determined by GPC relative to polystyrene standards using refractive index detector. [c] Using UV detector.

Table 3. Chemical Shift Assignments for the Backbone Carbons in Triad Sequences of Methyl Acrylate−Propene Copolymer

triad sequence from Figure 2[a]	backbone carbon	calcd shift (ppm)	obsd shift (ppm)
APA	1	35.2	35.3
APA	2	40.8	overlapping
APA	3	39.8	39.9
APA	4	28.6	29.2
AAP	5	39.8	39.9
AAP	6	40.8	overlapping
AAP	7	35.2	35.3
AAP	8	28.6	29.2
AAA	9	35.2	35.3
AAA	10	41.4	41.2

[a] A = acrylate, P = propene

The materials obtained are real copolymers and not simply mixtures of homopolymers as was verified by running gel permeation chromatography (GPC) with both refractive index and UV detectors (the latter is more sensitive to the acrylate groups). As shown in Tables 1 and 2, the molecular weight data obtained by the two methods are in close agreement, implying that the materials are copolymers in which the concentration of the acrylate groups is independent of the molecular weight over the observed unimodal distribution. The formation of real copolymers was also shown by MALDI-MS of copolymers of methyl acrylate with ethene, 1-hexene, and 1-octene (see Supporting Information).

The random nature of the copolymers formed was verified by ^{1}H and ^{13}C NMR spectroscopy (see Supporting Information). The relative simplicity of the ^{1}H and ^{13}C NMR spectra suggests the presence of AAA and AOA sequences but not AOO or OAO sequences (A = acrylate, O = 1-alkene). The ^{13}C NMR spectrum for a methyl acrylate−ethene copolymer showed resonances resulting from runs of acrylate units, 175.5 ($-\underline{C}(O)O$), 51.8 ($-O\underline{C}H_3$), 41.5 ($-\underline{C}H-$), and 35.3 ppm ($-\underline{C}H_2-$), as well as resonances at 176.5, 43.5 ($\underline{C}_2$), 35.3 (br, $\underline{C}_1$), 33.1, 32.4 (br, $\underline{C}_3$)

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(1) (a) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 429. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (c) Boffa, L. S.; Novak, B. M. *Chem. Rev.* **2000**, *100*, 1479.

(2) (a) Odian, G. *Principles of Polymerization*; John Wiley: New York, 1991; p 630. (b) *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Decker: New York; 1992, Chapter 4.

(3) *Handbook of Polymer Synthesis*; Kricheldorf, H. R., Ed.; Marcel Decker: New York; 1992, Chapter 1.

(4) (a) Logothetis, A. L.; McKenna, J. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1978**, *16*, 2797. (b) Logothetis, A. L.; McKenna, J. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15*, 1431. (c) Logothetis, A. L.; McKenna, J. M. *J. Polym. Sci.: Polym. Chem. Ed.* **1977**, *15*, 1441.

(5) (a) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (b) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.

(6) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.

(7) Reviews: (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921. (b) Patten, T. E.; Matyjaszewski, K. *Acc. Chem. Res.* **1999**, *32*, 895. (c) Matyjaszewski, K. In *Controlled Radical Polymerization*; Matyjaszewski, K., Ed.; *ACS Symp. Ser.* **1998**, *685*, 258. (d) Xia, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7697.

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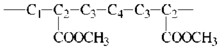
Table 4. Sequential Block Terpolymerization of Methyl Acrylate, Ethene, and Propene[a]

entry	first charge	reaction time (h)	M_n (M_w/M_n)[b,c]	composition MA/E (mol %)	second charge	reaction time (h)	M_n ($M_{w/Mn}$)[b,d]	final yield (g)	final composition MA/E/P (mol %)
1	MA, 18 g E, 700 psi	1	4,500 (1.1)	91.4/8.6	P, 10 g	9	32,000 (1.1)	11.0	89.7/3.1/7.2
2	MA, 16 g E, 500 psi	1	3,000 (1.1)	93.6/6.4	P, 15 g	20	48,000 (1.1)	10.8	86.6/2.2/11.2

[a] Reaction conditions: CuBr, 0.23 mmol; EBP, 0.23 mmol; PMDETA, 0.23 mmol; 90 °C. [b] Determined by GPC relative to polystyrene standards using refractive index detector. [c] After first charge. [d] For final product.



$$-C_1-\underset{COOCH_3}{C_2}-C_3-C_4-C_3-\underset{COOCH_3}{C_2}-$$

Figure 1. Acrylate−ethene−acrylate triad sequence in a methyl acrylate−ethene random copolymer.

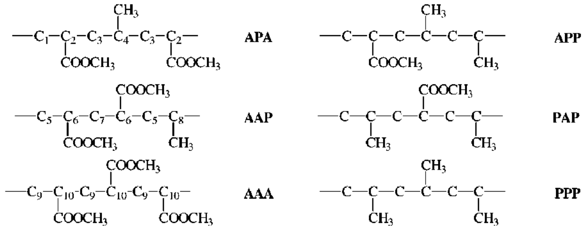


Figure 2. Methyl acrylate−propene copolymer triad sequences (A = MA, P = propene).

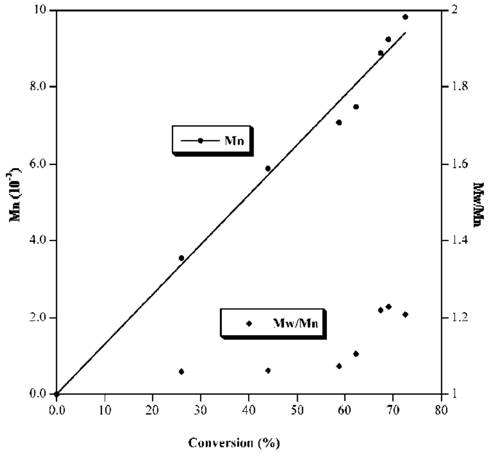


Figure 3. The dependence of molecular weight, M_n, and molecular weight distribution, M_w/M_n, on total monomer conversion for the copolymerization of methyl acrylate with 1-octene at 90 °C in anisole. [CuBr] = [PMDETA] = [EBP] = 0.04 M, [MA] = 5.8 M, [1-octene] = 0.64 M.

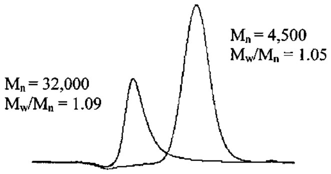


Figure 4. GPC traces of poly(methyl acrylate-*co*-ethene) (right) and poly[(methyl acrylate-*co*-ethene)-*b*-(methyl acrylate-*co*-propene)] (left) formed sequentially.

and 25.1 ppm (br, $\underline{C}_4$), attributable to both the acrylate−ethene−acrylate and acrylate−acrylate−ethene sequences (Figure 1). In particular, the peak at 43.5 ppm suggests a random copolymer since this resonance is absent in the ^{13}C NMR spectrum of the alternating copolymer made by free radical polymerization in the presence of a Lewis acid.[4a]

A ^{13}C DEPT NMR spectrum of the methyl acrylate−propene copolymer was obtained. Chemical shift assignments of the backbone carbons for the triad sequences (see Figure 2) were determined and collected in Table 3. Also included in Table 3 are the corresponding values calculated by the empirical method.[4a] Given the good agreement between the two, it is clear that the observed chemical shifts for the backbone carbons correspond to the APA, AAP, and AAA sequences (A = acrylate, P = propene) and the APP, PAP, and PPP sequences are absent. In addition to the resonances shown in Table 3, the methyl acrylate−propene copolymer made by the copper-mediated procedure showed minor resonances at 173.3 ($-\underline{C}$(O)O), 60.7 ($-O\underline{C}H_2CH_3$), 37.3 ($-\underline{C}HCH_3$), 18.3 ($-CH\underline{C}H_3$) and 14.3 ppm ($-O\underline{CH_2}\underline{C}H_3$) due to the end groups derived from the ethyl bromopropionate initiator. This was further verified by a comparison with the ^{13}C NMR spectrum of a methyl acrylate homopolymer made by the same procedure.

The copper-mediated copolymerization process displays many of the characteristics of a living polymerization system. As shown in Figure 3, the molecular weight of the methyl acrylate−1-octene copolymer was found to increase linearly with monomer conversion. At the same time, the polydispersity remained low ($M_w/M_n \leq 1.1$) for up to 60% monomer conversion, beyond which it increased to approximately 1.2. More significantly, the "living" nature of the system allowed the synthesis of unique block copolymers. This is illustrated by the synthesis of poly[(methyl acrylate-*co*-ethene)-*b*-(methyl acrylate-*co*-propene)] by sequential addition of the latter two monomers. The procedure consisted of two steps. The first step involved the copolymerization of methyl acrylate with ethene. Following this step, the reaction vessel was vented and flushed with purified nitrogen gas, and a polymer sample was taken out for molecular weight measurement. Propene was then charged into the reactor, and a second polymerization cycle was carried out. The molecular weight and composition of the final polymer was determined. Our data is summarized in Table 4. The first entry shows that the molecular weight (M_n) increases from 4500 for the poly(methyl acrylate-*co*-ethene) formed after the first step, to 32 000 for the final poly[(methyl acrylate-*co*-ethene)-*b*-(methyl acrylate-*co*-propene)]. The corresponding polydispersities remained low ($M_w/M_n = 1.1$). Figure 4 shows the GPC traces obtained for the copolymer formed after the first step and the final copolymer.

In conclusion, we have demonstrated the copper-mediated controlled copolymerization of methyl acrylate with nonpolar 1-alkenes ranging from ethene to 1-octene. The polymerizations proceed under mild conditions to afford random copolymers. Because the system displays many of the characteristics of a living polymerization process, the polydispersities of the copolymers obtained are low, and it is possible to synthesize novel block terpolymers of methyl acrylate with 1-alkenes by the sequential addition of the latter monomers.

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Supporting Information Available: ^{13}C NMR spectra, MALDI-MS of copolymers, and kinetics plots of monomer conversion (PDF). This material is available free of charge via the Internet at http://www.pubs.acs.org.

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