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Nitroxide-Mediated Copolymerization of Methyl Acrylate with 1-Alkenes and Norbornenes

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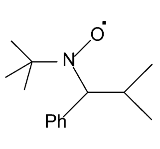
1. Introduction. The copolymerization of polar vinyl monomers with nonpolar alkenes remains an area of great interest because the combination of the two can greatly enhance the range of currently attainable polymer properties.[1−3] The inherent difficulty in the copolymerization of the two kinds of monomers arises from the very different mechanisms through which they normally undergo polymerization. The former, such as acrylates, are readily polymerized through a free-radical mechanism. In contrast, 1-alkenes such as ethene and propene undergo free-radical polymerization only under harsh conditions to yield branched materials; more commonly, they undergo transition-metal-catalyzed insertion polymerization. Prior to our initial report that polar and nonpolar olefins can be copolymerized by copper-mediated atom transfer radical polymerization (ATRP),[4] the only successful radical-initiated copolymerization of acrylates with 1-alkenes under mild conditions involved the use of strong Lewis acids that complex to the ester functionality of the acrylate. The resultant highly electron-deficient monomer forms a 1:1 alternating copolymer with 1-alkenes in the presence of radical initiators.[5] In the area of metal-catalyzed copolymerization of polar and nonpolar olefins, Brookhart reported the copolymerization of ethene and acrylates with cationic palladium(II) diimine compounds.[6] The copolymers are branched and have a maximum incorporation of 12% methyl acrylate. Drent used a palladium(II) complex of di(2-methoxyphenyl)phosphinobenzene-2-sulfonic acid and obtained a copolymer of ethene and acrylates with acrylates units “built in” the chain.[7] The acrylate incorporation was again low (<17%). Finally, the Exxon group has reported a copper bis(benzimidazole) catalyst that can copolymerize ethene and acrylates.[8] While copolymers have a high acrylate content, the polymerization is not controlled and the mechanism remains uncertain.

We have described the living copper-mediated atom transfer radical polymerization (ATRP) of acrylates with simple linear 1-alkenes and norbornene derivatives.[4,9] More recently, Klumperman reported the copolymerization of methyl methacrylate and 1-octene by ATRP.[10] One of the major disadvantages of using metal-based ATRP is that the resultant polymer contains traces of metal impurities and are often colored. This limits their potential applications. Thus, there is a need for a nonmetal-based system for controlled copolymerization of polar vinyl monomers with simple alkenes. Hawker, Tondo, and others have pioneered the nitroxide-mediated controlled polymerization of polar monomers.[11−17] We now report that a similar system can be employed for controlled random copolymerization of polar vinyl monomers and simple alkenes. Our system involves the use of 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (compound **2**) as the initiator and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (compound **1**) as the control agent. The resultant polymers are white and free of metal impurities. Our procedure significantly broadens the scope of nitroxide-mediated polymerizations.



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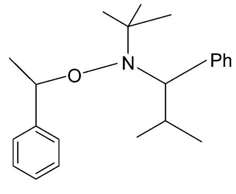

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2. Experimental Section. a. General. All polymerizations were performed in a nitrogen atmosphere glovebox. The monomers were degassed by three freeze−pump−thaw cycles before being brought into the glovebox. ^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker PX-300 (^{1}H, 300 MHz), a Bruker CX-300 (^{1}H, 300 MHz), or a Bruker RX-400 (^{1}H, 400 MHz) spectrometer using chloroform-*d* as the solvent. Chemical shifts are reported in δ ppm downfield from TMS. Molecular weights and polydispersities were measured on a Shimadzu size exclusion chromatograph (SEC) using a flow rate of 1 mL/min and a three-column bed (Styragel HR 7.8 × 300 mm columns with 5 μm bead size: 100−10 000, 500−30 000, and 5000−6 000 000 Da), a Shimadzu RID 10A differential refractometer, and SPD-10A UV−vis detector (at 254 nm). SEC samples were run in $CHCl_3$ at ambient temperature and calibrated to polystyrene standards.

b. Materials. Methyl acrylate (MA, 99%), 1-hexene (99+%), and 1-octene (98%) were purchased from Aldrich and vacuum-transferred from calcium hydride and stored in Schlenk flasks Norbornene derivatives were donated by Promerus LLC. All other chemicals were purchased from Aldrich and used as received.

The initiator, 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (compound **2**), and the control agent, 2,2,5-trimethyl-4-phenyl-3-azahexane-3-nitroxide (compound **1**), were synthesized and purified following the established procedure.[12]

c. Copolymerization of Methyl Acrylate with 1-Alkenes and Norbornene Derivatives. For copolymerization of methyl acrylate with ethene and propene: a glass-lined 300 mL stainless steel autoclave was used in which the nitroxide initiator (0.2 mmol), the control agent (0.01 mmol), and MA (0.04 mol) were added using a glovebox. The autoclave was then charged with ethene or propene and heated in a 120 °C oil bath. After the reaction, the gas was vented and methanol (50 mL) was added to the reaction mixture. Volatiles were then evacuated. For other polymerizations: in a typical reaction, the nitroxide initiator (0.2 mmol), the control agent (0.01 mmol), MA (0.04 mol), and 1-alkene (0.02 mol) were added to a flask using a glovebox. The reaction was then heated in a 120 °C oil bath and worked up as described above. ^{1}H NMR (ppm) of methyl

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

monomer	1-alkene incorp (mol %)	M_n [b]	M_w/M_n [b]	yield (g)
ethene (700 psi)	13.6	9000	1.19	1.5
propene (100 psi)	15.5	4200	1.22	1.2
1-hexene (0.02 mol, 1.68 g)	6.8	6000	1.08	1.6
1-hexene (0.02 mol, 1.68 g)[c]	5.5	11200	1.13	2.3
1-hexene (0.03 mol, 2.52 g)	9.7	5000	1.10	0.7
1-octene (0.005 mol, 0.56 g)	4.9	6800	1.16	1.6
1-octene (0.02 mol, 2.24 g)	8.0	4900	1.13	1.2

[a] Reaction conditions: nitroxide initiator, 0.2 mmol; control agent, 0.01 mmol; MA, 0.04 mol (3.44 g); 120 °C, 15 h. [b] M_n: number-average molecular weight; M_w: weight-average molecular weight. Both determined by SEC relative to polystyrene standards using refractive index detector. [c] Reaction time, 30 h.

acrylate/propene copolymer: 3.60 (OCH_3), 2.24 (CH), 1.88, 1.61, 1.43 (CH_2 from MA), 1.15 (CH_2 from propene), 0.87 (CH_3). ^1H NMR (ppm) of methyl acrylate/norbornene copolymer: 3.61 (OCH_3), 0.8−2.3 (broad).

d. Kinetic Studies of Methyl Acrylate/1-Octene Copolymerization. The nitroxide initiator (0.2 mmol), the control agent (0.01 mmol), MA (0.04 mol), and 1-octene (0.01 mol) were added to a flask, together with 0.00394 mol of DMSO as the internal standard. Samples were taken at different time intervals using a syringe and analyzed by ^1H NMR spectroscopy. The conversions of methyl acrylate and 1-octene were calculated from the integration of the vinyl CH peak of methyl acrylate at 6.3 ppm and terminal vinyl CH_2 resonance for 1-octene at 4.9 ppm, with respect to DMSO internal standard. The sample mixtures were quenched in methanol. After volatiles were removed, the molecular weight of the copolymer was measured by size exclusion chromatography.

e. Synthesis of Methyl Acrylate/Norbornene-*b*-Methyl Acrylate/1-Hexene Copolymer. Methyl acrylate/norbornene copolymer (0.4 g, $M_n = 7000$, PDI = 1.17, 18 mol % norbornene), methyl acrylate (1.5 g), and 1-hexene (0.5 g) were added to a round-bottom flask to form a homogeneous solution. The reaction mixture was heated to 120 °C for 18 h. Polymer was precipitated by addition of methanol and analyzed.

3. Results and Discussion. a. Copolymerization of Methyl Acrylate with 1-Alkenes. Table 1 shows results of nitroxide-mediated copolymerization of methyl acrylate with 1-alkenes. The 1-alkene content was calculated from the ratio of CH resonance of the methyl acrylate units at 2.24 ppm to CH_3 resonance of the 1-alkene units at 0.87 ppm. For methyl acrylate/ethene copolymer, the CH_2 peak at 1.15 ppm from the ethene units in the copolymer was used. The reaction is clearly quite general. The molecular weight and the yield increase with longer reaction time. In addition, the copolymer polydispersities are low, suggesting a controlled polymerization process. Size exclusion chromatography (SEC) of the copolymers all give unimodal distributions, and the polymer curves from the refractive index and UV−vis detectors are superimposable, indicating the formation of copolymers rather than a mixture of homopolymers.

The ^1H NMR and ^{13}C NMR spectra of the copolymers closely match those for analogous random polymers prepared by ATRP.[4] For example, in the ^{13}C NMR spectrum of the copolymer of methyl acrylate with propene, in addition to resonances at 175.3 (C(O)O), 52.1 (OCH_3), 41.5 (CH), and 35.3 ppm (CH_3) from the methyl acrylate units, broad resonances at 35.9−35.3 ppm and a peak at 28.4 ppm (CH) from propene units were observed.

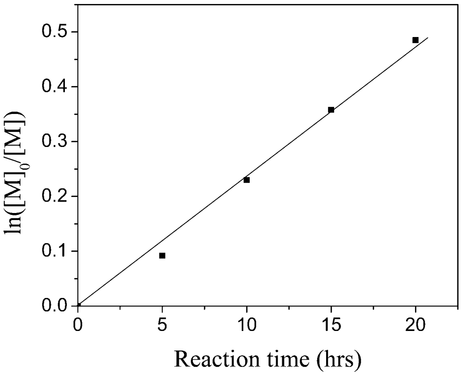


Figure 1. Polymerization kinetics of methyl acrylate with 1-octene. Reaction conditions: initiator, 0.2 mmol; control agent, 0.01 mmol; MA, 0.04 mol; 1-octene, 0.01 mol; 120 °C.

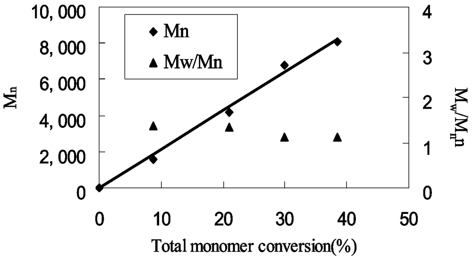


Figure 2. Dependence of molecular weight and polydispersity of methyl acrylate/1-octene copolymer on total monomer conversion. Reaction conditions: initiator, 0.2 mmol; control agent, 0.01 mmol; MA, 0.04 mol; 1-octene, 0.01 mol; 120 °C.

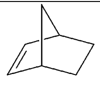
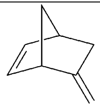
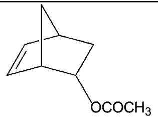
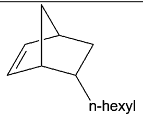
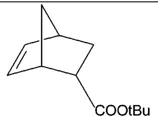
Table 1 shows that increasing the ratio of 1-alkene in the feed increases its incorporation into the copolymer; however, the molecular weight and the yield are decreased. Similar results have been reported previously.[4,10] Presumably, this is due to the higher concentration of the less stable secondary alkyl radical in the polymerization system. Such radicals are more prone to undergo termination.

b. Copolymerization Kinetics. The first-order kinetic plot for the copolymerization of methyl acrylate with 1-octene is shown in Figure 1. The conversions of methyl acrylate and 1-octene were calculated from the integration of the vinyl CH peak of methyl acrylate at 6.3 ppm and terminal vinyl CH_2 resonance for 1-octene at 4.9 ppm, with respect to DMSO internal standard. The linearity of the plot of total monomer conversion vs time indicates that the copolymerization follows first-order kinetics. Similar linear plots were also obtained when the conversion of the individual monomers were plotted vs time.

The relationship between molecular weight, polydispersity, and total monomer conversion is shown in Figure 2. The molecular weight increases linearly with total monomer conversion while polydispersity remains low. These results confirm the “living” character of the copolymerization system.

c. Copolymerization of Methyl Acrylate with Norbornene Derivatives. Copolymers of acrylates with norbornene derivatives are of interest as materials for deep UV photolithography. Polyacrylates show good adhesion and have been used extensively as photoresist materials but suffer from poor dry etch resistance. On the other hand, polynorbornenes exhibit superior etch resistance and thermal stability, and copolymers of the

Table 2. Nitroxide-Mediated Copolymerization of Methyl Acrylate with Norbornene Derivatives[a]

Monomer	Norbornene incorp. (mol %)	M_n[b]	M_w/M_n[b]	Yield (g)
 (0.04 mol, 3.77 g)	18.0	7,000	1.17	1.9
 (0.04 mol, 4.32 g)	16.1	7,300	1.51	2.1
 (0.04 mol, 6.08 g)	25.5	4,800	1.43	2.3
 (0.04 mol, 6.10 g)	24.9	6,900	1.26	2.2
 (0.04 mol, 7.76 g)	28.1	7,500	1.33	3.0

[a] Reaction conditions: nitroxide initiator, 0.4 mmol; control agent, 0.02 mmol; MA, 0.04 mol (3.44 g); 120 °C, 15 h. [b] M_n: number-average molecular weight; M_w: weight-average molecular weight. Both determined by SEC relative to polystyrene standards using refractive index detector.

two may provide the optimum properties.[18-20] Although we have described the controlled copolymerization of these monomers by copper-based ATRP, the presence of metal traces in the copolymer precludes its widespread use in the electronic sector. The nitroxide-mediated polymerization provides an alternative methodology for the synthesis of metal-free materials.

Our results are shown in Table 2. The copolymer compositions were calculated from the ^{1}H NMR integration of the methoxy group from methyl acrylate units vs the total aliphatic region containing resonances from both acrylate and norbornene units. The procedure can be applied to a variety of norbornene derivatives although the yields are somewhat low. The copolymers have relatively low polydispersity (although higher than that for methyl acrylate/1-alkene copolymers), suggesting that the polymerization proceeds in a "controlled" manner. Again, unimodal distributions and superimposable polymer chromatograms using RI and UV−vis detectors were observed by SEC, indicating the formation of copolymers. The ^{1}H NMR and ^{13}C NMR spectra of the copolymers closely match those for analogous random methyl acrylate/norbornene copolymers prepared by ATRP.[9]

Finally, the living nature of the polymerization system was verified by the synthesis of the block terpolymer: methyl acrylate/norbornene-*b*-methyl acrylate/1-hexene terpolymer. Copolymerization of methyl acrylate and 1-hexene was initiated starting with a methyl acrylate/norbornene copolymer ($M_n = 7000$, PDI = 1.17, 18 mol % norbornene) as macroinitiator. Following polymerization, M_n increased to 8800 with a PDI of 1.60. SEC of the final product shows unimodal polymer chromatograms using both RI and UV−vis detectors, which are superimposable. The ^{1}H NMR spectrum of the final product showed a triplet from the methyl group of hexene units at 0.87 ppm. The ^{13}C NMR spectrum resembled a similar block terpolymer made by ATRP.[9] The molar ratio of methyl acrylate, norbornene, and 1-hexene in the block copolymer was 1:0.24:0.13. The relatively high polydispersity of the final terpolymer suggests that not all methyl acrylate/norbornene copolymer chains initiate polymerization in the second step.

4. Conclusions. We have demonstrated nitroxide-mediated controlled copolymerization of methyl acrylate with 1-alkenes and norbornene derivatives. Because of the "living" nature of the copolymerization, synthesis of materials with controlled molecular weight, low polydispersity, and predictable composition becomes possible. The procedure broadens the scope of nitroxide-mediated polymerization in the synthesis of metal-free materials with novel properties.

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