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Copolymerization of Methyl Acrylate with Norbornene Derivatives by Atom Transfer Radical Polymerization

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Introduction

The copolymerization of polar vinyl monomers with nonpolar alkenes remains an area of great interest in synthetic polymer chemistry,[1] because the addition of functionalities to a polymer that is otherwise nonpolar can greatly enhance the range of attainable properties. One particular area of interest has been the copolymerization of acrylates with norbornene derivatives to form materials suitable for photolithography at 193 and 157 nm. 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 two may provide the optimum properties.[2] There are very few reports of the copolymerization of acrylates with norbornene monomers. Starmer patented the radical-initiated synthesis of acrylate/norbornene copolymers.[3] The maximum incorporation of norbornene in the copolymers was 5%. More recently, we reported the copolymerization of acrylates and norbornene in the presence of palladium complexes.[4] Herein, we report a copper-mediated atom transfer radical polymerization procedure for the controlled synthesis of acrylate/norbornene copolymers.

Results and Discussion

Copolymerization of Methyl Acrylate (MA) with Norbornene Derivatives. Atom transfer radical polymerization (ATRP) has gained increased attention due to the controlled/living nature of the polymerization process.[5] In this approach, a rapid equilibrium between the active radicals and the dormant halide chain ends ensues. To date, numerous reports documenting the atom transfer radical polymerization of various monomers, including acrylates, have appeared in the literature. However, to our knowledge, the copolymerization of acrylates with norbornene derivatives using this procedure has not been reported.

The copper-mediated polymerizations described herein are based on the reported copper-mediated ATRP of acrylates.[5,6] Table 1 shows selected results for the polymerization of methyl acrylate with norbornene at 90 °C. The polymer composition was determined from ^{1}H NMR integration of the methoxy group of the acrylate vs the total aliphatic region containing resonances from both the acrylate and norbornene units. The synthesis of higher molecular weight copolymers of methyl acrylate and norbornene was achieved using a higher monomer-to-initiator ratio (Table 1, entry 4). At higher methyl acrylate to norbornene feed ratios, essentially pure poly(methyl acrylate) was formed. On the other hand, the relative amount of norbornene incorporated into the copolymer increased with increasing norbornene feed ratios. However, only trace polymer was obtained when pure norbornene was used.

Norbornene derivatives such as 5-*n*-butyl-2-norbornene, 5-methylene-2-norbornene, and 5-ethyl ester-2-norbornene were also successfully copolymerized in the presence of methyl acrylate (Table 2). Again, higher molecular weight copolymers were obtained using a higher monomer-to-initiator ratio. With the exception of 5-methylene-2-norbornene, the polymer composition for a given monomer feed ratio did not vary significantly with the norbornene derivatives. This contrasts sharply with metal-catalyzed insertion polymerizations where the functionalized norbornene polymers, such as 5-ethyl ester-2-norbornene, are much less reactive due to coordination of the functionality to the metal center.[7]

The incorporation of 5-methylene-2-norbornene in the copolymer was significantly higher than those of the other norbornene derivatives employed. The ^{1}H NMR spectrum of the methyl acrylate/5-methylene-2-norbornene copolymer showed that both the cyclic and exocyclic C═C double bonds of the latter have disappeared. The polymer structure is discussed below.

Table 3 summarizes results from the copolymerization of acrylates with norbornene derivatives at 60 °C using 2,2-azobis(isobutyronitrile) (AIBN) as the initiator. The resulting copolymers have similar polymer compositions as those obtained through ATRP; however, both the molecular weight and molecular weight distributions are higher, as expected for an uncontrolled polymerization system. The AIBN-initiated copolymerization of methyl acrylate with 5-methylene-2-norbornene resulted in an insoluble, cross-linked material.

The copolymers were characterized by size exclusion chromatography (SEC), NMR spectroscopy, and mass spectrometry. SEC showed unimodal distributions, implying that the polymers are copolymers rather than a mixture of homopolymers. The MALDI-MS spectra of methyl acrylate/norbornene (Figure 1) and methyl acrylate/ethyl ester norbornene copolymers show that the molecular masses of individual polymer chains differ by either an acrylate or norbornene unit, suggesting the formation of copolymers rather than mixtures of homopolymers.

^{1}H and ^{13}C NMR spectroscopies were used to establish the random nature of the copolymers formed. The ^{13}C NMR spectrum of the copolymer of methyl acrylate and norbornene showed resonances at 175.0 ($-\mathbf{C}$(O)O), 51.8 ($-\mathrm{O}\mathbf{C}\mathrm{H}_3$), 41.4 ($-\mathbf{C}\mathrm{H}-$), and 35.0 ppm ($-\mathbf{C}\mathrm{H}_2-$) attributable to consecutive acrylate units. A minor resonance was also observed at 173.75 ppm ($-\mathbf{C}$(O)O) due to the end group derived from the methyl bromopropionate initiator. Additional resonances attributable to the acrylate−norbornene sequence and the initiator were observed; however, it is difficult to make specific assignments due to the presence of overlapping norbornene resonances.

The ^{13}C NMR spectrum of poly(methyl acrylate-*co*-5-*n*-butyl-2-norbornene) provided additional information about the copolymer due to the increased solubility

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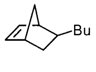
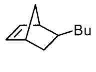
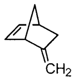
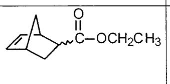
Table 1. Copolymerization of Methyl Acrylate (MA) and Norbornene (NB) by ATRP[a]

MA (mmol)	NB (mmol)	MA:NB	yield (%)	polymer composition[b] MA:NB	M_n[c]	M_w/M_n[c]
21.0	2.2	10:1	75	PMA	5900	1.2
19.0	3.8	5:1	60	PMA	n.d.	n.d.
11.2	11.2	1:1	45	1:0.28	2400	1.2
41.8[d]	41.4	1:1	35	1:0.24	9200	1.6
7.6	14.9	0.5:1	35	1:0.46	1700	1.2
22.2			95	PMA	4800	1.1
	21.2		5	PNB		

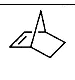
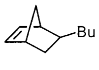
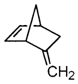
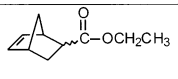
[a] Reaction conditions: CuBr, 0.38 mmol; EBP, 0.38 mmol; PMDETA, 0.38 mmol; total monomer (MA + NB), 2.0 g; 90 °C, 15 h. [b] Determined by ^{1}H NMR integration. [c] Determined by SEC in $CHCl_3$ relative to poly(styrene). [d] Total monomer, 7.5 g.

Table 2. Copolymerization of Methyl Acrylate (MA) and Norbornene Derivatives by ATRP[a]

MA (mmol)	Comonomer (mmol)	Yield (%)	Polymer composition[b] (MA: comonomer)	M_n[c]	M_w/M_n[c]
17.4	 17.3	54	1:0.27	2,400	1.4
41.9[d]	 42.0	32	1:0.23	16,100	1.7
20.9	 21.7	39	1:0.63	2,200	1.6
16.3	 16.3	25	1:0.22	1,300	1.3

[a] Reaction conditions: CuBr, 0.38 mmol; MBP, 0.38 mmol; PMDETA, 0.38 mmol; 90–95 °C, 21 h. [b] Determined by ^{1}H NMR integration. [c] Determined by SEC in $CHCl_3$ relative to poly(styrene). [d] CuBr, 0.21 mmol; MBP, 0.21 mmol; PMDETA, 0.21 mmol.

Table 3. AIBN-Initiated Copolymerization of Methyl Acrylate (MA) and Norbornene Derivatives[a]

MA (mmol)	Comonomer (mmol)	Yield (%)	Polymer composition[b] (MA:comonomer)	M_n[c]	M_w/M_n[c]
11.6	 10.6	50	1:0.32	45,800	2.0
8.1	 8.7	40	1:0.29	45,900	1.9
10.5	 10.4	65	insoluble	n.d.	n.d.
7.0	 7.8	26	1:0.24	47,600	1.6

[a] Reaction conditions: AIBN, 0.03 mmol; PhCl, 4 mL; 60 °C, 21 h. [b] Determined by ^{1}H NMR integration. [c] Determined by SEC in $CHCl_3$ relative to poly(styrene).

brought on by the presence of butyl branches. As in the case of poly(methyl acrylate-*co*-norbornene), ^{13}C NMR resonances were observed at 175.1, 51.9, 41.5, and 34.5 ppm corresponding to runs of acrylate units. Additional resonances at 175.4–175.0, 52.0–51.5, 41.8–41.3, 40.5–32.7, 31.2, 23.1, and 14.4 ppm were observed for the methyl acrylate–butyl norbornene sequence. The ^{1}H NMR spectrum of the copolymer showed a broad singlet at 3.67 ppm for the methoxy groups in the acrylate units, as well as broad resonances between 2.66 and 0.33 ppm.

The methyl acrylate/5-ethyl ester-2-norbornene copolymer showed similar resonances in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum showed resonances at 3.61 and 2.90–0.79 ppm, as well as an additional resonance at ~4.0 ppm, attributable to the ester group of the norbornene monomer.

The ^{1}H NMR spectrum of the methyl acrylate/5-methylene-2-norbornene copolymer showed the disappearance of both the cyclic (6.11 and 6.10 ppm) and exocyclic C=C double bonds (4.98 and 4.71 ppm). The vinylic resonances were also absent in the ^{13}C NMR spectrum of the copolymer. On the other hand, relatively upfield resonances at 22.98 and 14.71 ppm were observed in the latter spectrum. These resonances are similar to those reported for quadricyclane (22.99 and 14.71 ppm, respectively), suggesting that the polymerization of 5-methylene-2-norbornene proceeds according to Scheme 1. The structure of the repeat unit is similar to that observed for the radical polymerization of norbornadiene.[8] Thus, the polymerization of 5-methylene-2-norbornene proceeds differently from that of the other norbornene monomers examined, and its higher incorporation into the copolymer may be a reflection of this (Table 2).

Choice of Ligand and Initiator. The effects of different initiators and ligands on the atom transfer radical copolymerization of methyl acrylate and norbornene were examined. Similar polymer yields and compositions, molecular weights, and molecular weight distributions were obtained for reactions initiated with methyl 2-bromopropionate (MBP), ethyl 2-bromopropionate (EBP), and ethyl 2-bromoisobutyrate (EBiB). As expected, higher molecular weight copolymers were obtained using a higher monomer-to-initiator ratio (Table 4).

The copolymerization of methyl acrylate and norbornene was also carried out in the presence of two different added ligands, *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) and 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA). Varying the

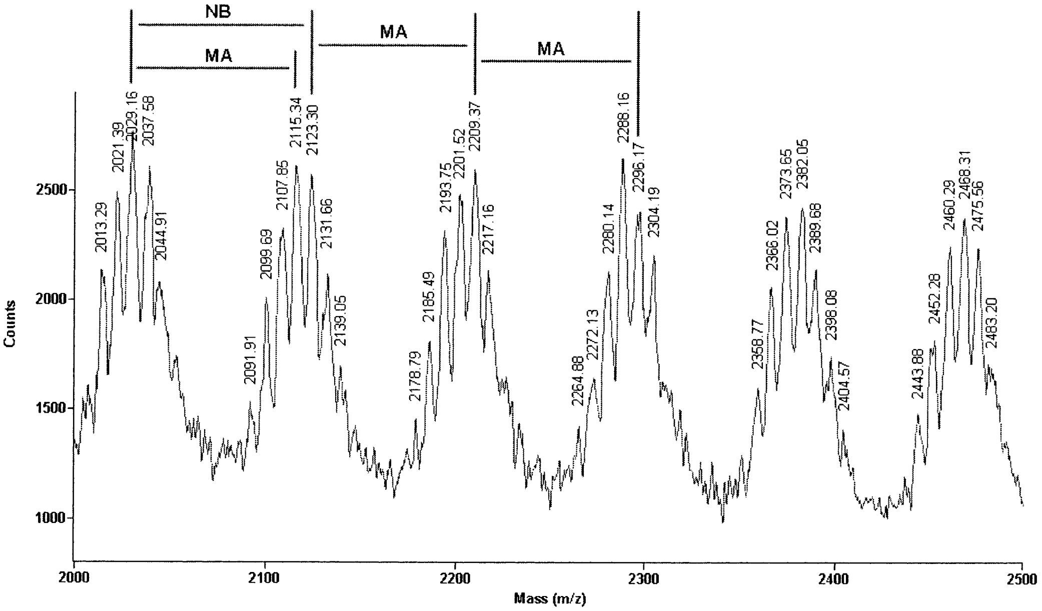


Figure 1. MALDI-MS spectrum of a low molecular weight copolymer of methyl acrylate and norbornene synthesized using a 1:1 monomer feed ratio.

Scheme 1

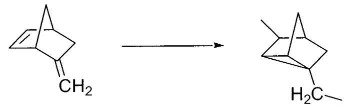


Table 4. Effect of Monomer: Initiator Ratio on the Molecular Weight of Poly(methyl acrylate-*co*-norbornene)[a]

MA (mmol)	NB (mmol)	monomer: initiator	yield (%)	polymer composition[b] (MA:NB)	M_n[c]	M_w/M_n[c]
19.8	19.1	95:1	37	1:0.26	2600	1.4
38.4	38.2	200:1	43	1:0.25	7500	1.7
76.7	76.4	394:1	23	1:0.21	11700	1.7

[a] Reaction conditions: CuBr, 0.38 mmol; MBP, 0.38 mmol; PMDETA, 0.38 mmol; 92 °C; 21 h. [b] Determined by ^{1}H NMR integration. [c] Determined by SEC in $CHCl_3$ relative to poly(styrene).

Table 5. Effect of Ligand:Cu Ratio on the Copolymerization of Methyl Acrylate and Norbornene[a]

MA (mmol)	NB (mmol)	PMDETA: CuBr	yield (%)	polymer composition[b] (MA:NB)	M_n[c]	M_w/M_n[c]
24.4	22.3	1:1	40	1:0.25	2700	1.3
24.4	22.3	5:1	36	1:0.23	2000	1.3
24.4	22.3	10:1	29	1:0.20	1900	1.4

[a] Reaction conditions: CuBr, 0.38 mmol; PMDETA, 0.38 mmol; MBP, 0.38 mmol; 92 °C, 21 h. [b] Determined by ^{1}H NMR integration. [c] Determined by SEC in $CHCl_3$ relative to poly(styrene).

ligand had no significant effect on polymerization; i.e., similar polymer yields, compositions, molecular weights, and molecular weight distributions were obtained. In addition, varying the ligand-to-copper ratio (1:1, 5:1, and 10:1) did not affect the reaction (Table 5).

Mechanistic Aspects. The copper-mediated copolymerizations display some of the characteristics of a controlled polymerization system. Kinetic plots of molecular weight vs conversion for the polymerization of methyl acrylate with norbornene were constructed for low molecular weight and high molecular weight polymers. Figure 2 shows the dependence of molecular weight and molecular weight distribution on total monomer conversion for the low molecular weight copolymer. The number-average molecular weight (M_n) increased linearly with total monomer conversion while the polydispersity index remained below 1.2. At higher conversions, there is slight curvature, presumably because the long reaction times caused some chain termination. In the same vein, for the higher molecular weight copolymer, the molecular weight distribution was below 1.5 for conversions up to 50%. When the conversion was greater than 50%, the polydispersity index increased to 1.6.

Finally, the "controlled" nature of this system allowed for the synthesis of unique block terpolymers. This is illustrated by the synthesis of poly[(methyl acrylate-*co*-ethene)-*b*-(methyl acrylate-*co*-norbornene)] 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 (500 psi, single charge). We have previously demonstrated the controlled nature of the copper-mediated acrylate/ethene copolymerization.[9] Following the first step, the reaction vessel was vented and flushed with nitrogen gas, and a polymer sample was taken out for ^{1}H NMR analysis and molecular weight measurements. The amount of ethene incorporated (2 mol %) was determined from ^{1}H NMR integration of the methoxy group of the acrylate vs the total aliphatic region containing resonances from both the acrylate and ethene units.[9] Norbornene was then added to the reaction vessel under nitrogen, and a second polymerization cycle was carried out. The molecular weight of the final polymer was determined. The molecular weight (M_n) increased from 5700 for the poly(methyl acrylate-*co*-ethene) formed after the first step to 13 300 for the final poly[(methyl acrylate-*co*-ethene)-*b*-(methyl acrylate-*co*-norbornene)]. The corresponding molecular weight distributions (M_w/M_n) were 1.18 and 1.46, respectively. The relatively high polydispersity of the terpolymer suggests that not all the growing chains formed after the first step remain living during the second copolymerization cycle. The co- and terpolymer of methyl acrylate, ethene, and norbornene were analyzed by NMR spectroscopy. The ^{1}H

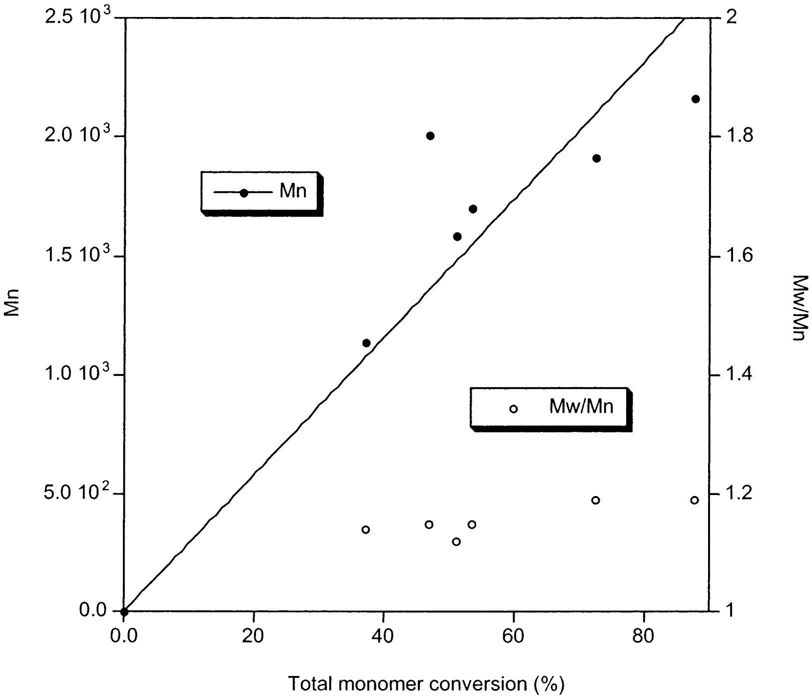


Figure 2. Dependence of molecular weight and molecular weight distribution on total monomer conversion for a low molecular weight copolymer of methyl acrylate and norbornene. Reaction conditions: CuBr, 0.77 mmol; PMDETA, 0.77 mmol; MBP, 0.77 mmol; anisole, 134.3 mmol; methyl acrylate, 44.4 mmol; and norbornene, 44.8 mmol; 90 °C.

NMR spectrum of the acrylate–ethene copolymer showed a resonance at 1.09 ppm due to the incorporation of ethene into the polymer. The incorporation of norbornene into the terpolymer was also confirmed by ^{1}H and ^{13}C NMR spectroscopies. In the latter, resonances were observed at 174.7, 51.6, 41.1, and 34.4 ppm, corresponding to runs of acrylate units. Additional resonances were observed for the acrylate–ethene sequence (31.9 and 24.5 ppm) and the acrylate–norbornene sequence (29.8, 28.4, and 21.5 ppm). The resonances in the terpolymer agreed well with those reported for copolymers of methyl acrylate and ethene and methyl acrylate and norbornene.[9]

Conclusions

We have demonstrated the unprecedented copolymerization of methyl acrylate with norbornene derivatives by atom transfer radical polymerization (ATRP). The polymerizations were run under mild reaction conditions to afford random copolymers as was verified by ^{1}H and ^{13}C NMR spectroscopies, MALDI mass spectrometry, and size exclusion chromatography (SEC). While the copolymerizations were not significantly affected by the specific initiator and/or ligand employed, the copolymer molecular weight increased with increasing monomer-to-initiator ratio. The copper-mediated system also displays some characteristics of a controlled polymerization system as illustrated by a linear plot of M_n vs conversion and the synthesis of block terpolymers of methyl acrylate with ethene and norbornene.

Experimental Procedure

General. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on a Bruker PX-300 (300 MHz), a Bruker CX-300 (300 MHz), or a Bruker RX-400 (400 MHz) spectrometer using chloroform-*d* as the solvent. Chemical shifts were reported in δ ppm downfield from TMS. Molecular weights and molecular weight distributions were determined on a Waters size exclusion chromatography (SEC) system 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 D), a Waters 410 differential refractometer, and a Waters 486 tunable absorbance detector. SEC samples were run in $CHCl_3$ at ambient temperature and calibrated to polystyrene standards.

The freeze–thaw–pump technique was used for deoxygenation of reagents. Methyl acrylate (99%) was purchased from Aldrich and vacuum-distilled and deoxygenated prior to use. Methyl 2-bromopropionate (MBP) (98%), ethyl 2-bromopropionate (EBP) (99%), ethyl 2-bromoisobutyrate (EBiB) (98%), *N,N,N′,N′,N″*-pentamethyldiethylenetriamine (PMDETA) (99%), and 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA) (97%) were purchased from Aldrich, dried over CaH_2, and distilled and deoxygenated before use. CuBr (99.999%), 2,2′-azobis(isobutyronitrile) (AIBN) (98%), 5-methylene-2-norbornene (90%), were purchased from Aldrich and deoxygenated before use. Norbornene (99%) was purchased from Acros Organics and deoxygenated before use. *n*-Butylnorbornene and ethyl ester norbornene were donated by BF Goodrich and distilled and deoxygenated before use. Chemical grade ethene was purchased from MG Industries. Anisole and PhCl were dried over CaH_2 and distilled and deoxygenated before use. All the reactions described were carried out in an inert atmosphere.

Polymerization of Methyl Acrylate with Norbornene Derivatives by Atom Transfer Radical Polymerization (ATRP). Homopolymerization of Methyl Acrylate. CuBr (0.055 g, 0.38 mmol), PMDETA (0.080 mL, 0.38 mmol), EBP (0.050 mL, 0.38 mmol), and methyl acrylate (2.00 mL, 22.2 mmol) were placed in a round-bottom flask. The flask was capped with a rubber septum and removed from the drybox. After stirring for 15 h at 90 °C, the flask was cooled to room temperature. The crude product was dissolved in $CHCl_3$ and purified by filtration through alumina to remove the metal compound. The solvent was removed, and the product was dried under vacuum overnight to yield 1.9 g (99%). M_w (M_w/M_n) = 5300 (1.1).

Attempted Homopolymerization of Norbornene. The polymerization was carried out following a procedure analogous to the one employed for the homopolymerization of methyl acrylate. Norbornene (2.00 g, 21.2 mmol) was employed to yield 0.1 g (5%).

Copolymerization of Methyl Acrylate with Norbornene. In a drybox, CuBr (0.055 g, 0.38 mmol), PMDETA (0.080 mL, 0.38 mmol), methyl acrylate (1.78 mL, 19.7 mmol), and norbornene (1.80 g, 19.1 mmol) were placed in a round-bottom flask and stirred until the solution became homogeneous. MBP (0.064 g, 0.38 mmol) was then added to the flask. The flask was capped with a rubber septum and removed from the drybox. After stirring for 21 h at 90 °C, the flask was cooled to room temperature. The crude product was dissolved in CHCl$_3$ and purified by filtration through alumina to remove the metal compound. The solvent was removed, and the product was dried under vacuum to yield 1.3 g (37%, based on total monomer feed). Polymer composition = 1:0.26 methyl acrylate:norbornene.

^{1}H NMR (CDCl$_3$) (ppm): 3.68 (s, br), 2.5−0.71 (m, br). ^{13}C-{^{1}H} NMR (CDCl$_3$) (ppm): 176.5−175.1, 175.0, 51.8, 48.8, 46.5, 43.0, 41.4, 40.0−33.8, 31.1−29.5, 28.7. 21.7. M_w (M_w/M_n) = 3700 (1.4).

Copolymerization of Methyl Acrylate with 5-*n*-Butyl-2-norbornene. The polymerization was carried out following a procedure analogous to the one employed for the copolymerization of methyl acrylate and norbornene. Methyl acrylate (1.57 mL, 17.4 mmol) and *n*-butylnorbornene (2.60 g, 17.3 mmol) were employed to yield 2.2 g (54%, based on total monomer feed). Polymer composition = 1:0.27 methyl acrylate: *n*-butyl norbornene.

^{1}H NMR (CDCl$_3$) (ppm): 3.67 (s, br), 2.66−0.33 (m, br). ^{13}C-{^{1}H} NMR (CDCl$_3$) (ppm): 175.4−175.0, 52.0−51.5, 41.8−41.3, 40.5−32.7, 31.2, 23.1, 14.4. M_w (M_w/M_n) = 3300 (1.4).

Copolymerization of Methyl Acrylate with 5-Methylene-2-norbornene. The polymerization was carried out following a procedure analogous to the one employed for the copolymerization of methyl acrylate and norbornene. Methyl acrylate (1.88 mL, 20.9 mmol) and 5-methylene-2-norbornene (2.34 mL, 21.7 mmol) were employed to yield 1.6 g (39% yield based on total monomer feed). Polymer composition = 1:0.63 methyl acrylate:5-methylene-2-norbornene.

^{1}H NMR (CDCl$_3$) (ppm): 3.68 (s, br), 2.84−0.57 (m, br). M_w (M_w/M_n) = 3500 (1.6).

Copolymerization of Methyl Acrylate with 5-Ethyl Ester-2-norbornene. The polymerization was carried out following a procedure analogous to the one employed for the copolymerization of methyl acrylate and norbornene. Methyl acrylate (1.46 mL, 16.3 mmol) and ethyl ester norbornene (2.70 g, 16.2 mmol) were employed to yield 1.0 g (24% yield based on total monomer feed). Polymer composition = 1:0.22 methyl acrylate:ethyl ester norbornene.

^{1}H NMR (CDCl$_3$) (ppm): 4.08 (m, br), 3.61 (s, br), 2.90−0.79 (m, br). M_w (M_w/M_n) = 1700 (1.3).

Polymerization of Methyl Acrylate with Norbornene Derivatives by Conventional Free Radical Polymerization. Copolymerization of Methyl Acrylate with Norbornene. A solution of AIBN (0.05 g, 0.03 mmol) in PhCl (2 mL) was placed in a round-bottom flask equipped with a magnetic stirrer. A solution of methyl acrylate (1.04 mL, 11.6 mmol) and norbornene (1.00 g, 10.6 mmol) in PhCl (2 mL) was added to the flask. The flask was capped with a rubber septum and removed from the drybox. After stirring for 21 h at 60 °C, the flask was cooled to room temperature. The polymer was precipitated from MeOH, the MeOH was decanted, and the polymer was dried under vacuum to yield 1.0 g (50% yield based on total monomer feed). Polymer composition = 1:0.32 methyl acrylate:norbornene.

^{1}H NMR (CDCl$_{3)}$ (ppm): 3.67 (s, br), 2.59−0.72 (m, br). M_w (M_w/M_n) = 91 600 (2.0).

Copolymerization of Methyl Acrylate with 5-*n*-Butyl-2-norbornene. The polymerization was carried out following a procedure analogous to the one employed for the copolymerization of methyl acrylate and norbornene. Methyl acrylate (0.73 mL, 8.1 mmol) and butyl norbornene (1.3 g, 8.7 mmol) were employed to yield 0.8 g (40% yield based on total monomer feed). Polymer composition = 1:0.29 methyl acrylate: norbornene.

^{1}H NMR (CDCl$_3$) (ppm): 3.68 (s, br), 2.63−0.43 (m, br). M_w (M_w/M_n) = 87 200 (1.9).

Copolymerization of Methyl Acrylate with 5-Methylene-2-norbornene. The polymerization was carried out following a procedure analogous to the one employed for the copolymerization of methyl acrylate and norbornene. Methyl acrylate (0.94 mL, 10.5 mmol) and 5-methylene-2-norbornene (1.12 mL, 10.4 mmol) were employed to yield 1.3 g (65% yield based on total monomer feed). The polymer was insoluble, and therefore, the polymer composition and molecular weight were not determined.

Copolymerization of Methyl Acrylate with 5-Ethyl Ester-2-norbornene. The polymerization was carried out following a procedure analogous to the one employed for the copolymerization of methyl acrylate and norbornene. Methyl acrylate (0.67 mL, 7.0 mmol) and ethyl ester norbornene (1.3 g, 7.9 mmol) were employed to yield 0.5 g (26.3% yield based on total monomer feed). Polymer composition = 1:0.24 methyl acrylate:ethyl ester norbornene.

^{1}H NMR (CDCl$_3$) (ppm): 4.13 (m, br), 3.67 (s, br), 2.84−0.78 (m, br). M_w (M_w/M_n) = 76 200 (1.6).

Mechanistic Studies of the Copolymerization of Methyl Acrylate with Norbornene by Atom Transfer Radical Polymerization. Data for the Plot of Molecular Weight vs Conversion for Copolymerization of Methyl Acrylate with Norbornene. In a drybox, CuBr (0.11 g, 0.77 mmol), PMDETA (0.16 mL, 0.77 mmol), anisole (14.60 mL, 134.3 mmol), methyl acrylate (4.00 mL, 44.4 mmol), and norbornene (4.20 g, 44.8 mmol) were placed in a round-bottom flask. The solution was allowed to stir until it became homogeneous. MBP (0.127 g, 0.77 mmol) was then added to the flask. The flask was capped with a rubber septum and removed from the drybox. The reaction mixture was stirred at 90 °C. Under a nitrogen flow, aliquots were taken from the reaction mixture at the desired reaction times. The samples were dissolved in CHCl$_3$ and purified by filtration through alumina to remove the metal compound. The solvent was removed, and the products were dried under vacuum.

Synthesis of Block Terpolymers of Methyl Acrylate, Ethene, and Norbornene by Sequential Addition. CuBr (0.055 g, 0.38 mmol), PMDETA (0.080 mL, 0.38 mmol), and methyl acrylate (15.77 mL, 191.7 mmol) were placed in a glass liner equipped with a magnetic stirrer. The solution was stirred until it became homogeneous. MBP (0.064 g, 0.38 mmol) was then added to the glass liner. The resultant solution was placed in a 125 mL Parr steel autoclave, removed from the drybox, and charged with ethene (500 psi, single charge). After stirring for 1 h at 95 °C, the autoclave was cooled to room temperature and unreacted ethene was released. The autoclave was flushed with nitrogen gas by three cycles of charge and release. A polymer sample was removed from the autoclave under a flow of nitrogen gas, and norbornene (7.30 g, 76.5 mmol) was then syringed into the autoclave. Polymerization was resumed at 90 °C for an additional 17 h. The products were dissolved in CHCl$_3$ and purified by filtration through alumina to remove the metal compound. The solvent was removed, and the products were dried under vacuum to yield the following:

Step 1: ∼2% ethene incorporation; M_n (M_w/M_n) = 5700 (1.18).

Step 2: ∼1% ethene and ∼10% norbornene incorporation; M_n (M_w/M_n) = 13 300 (1.47).

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