Controlled Random and Alternating Copolymerization of Methyl Acrylate with 1-Alkenes

Shengsheng Liu, Bin Gu, Heather A. Rowlands, and Ayusman Sen*

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

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ABSTRACT: Controlled random copolymerization of methyl acrylate (MA) with 1-alkenes was achieved through the reversible addition–fragmentation transfer (RAFT) technique using benzyl 1-pyrrolcarbodithioate as the transfer agent. NMR analysis reveals that RAFT agent-capped MA units are the predominant end groups. This allowed chain extension to synthesize the novel block copolymer, (MA-*co*-1-hexene)-*b*-PMA, by treating poly(MA-*co*-1-hexene) with AIBN in the presence of MA. The perfectly alternating copolymer of MA and ethene was obtained by using $AlCl_3$ as the complexing agent. Additionally, the first controlled alternating copolymerization of MA and ethene was achieved by degenerative transfer polymerization with iodoform as transfer agent.

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] 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. On the other hand, 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 alkenes can be copolymerized by copper-mediated atom transfer radical polymerization (ATRP),[2] 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.[3] In the area of metal-catalyzed copolymerization of polar and nonpolar alkenes, Brookhart reported the copolymerization of ethene and acrylates with cationic palladium(II) diimine compounds.[4] 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 in which acrylates units were "built in" the chain.[5] The acrylate incorporation was again low (<17%). Finally, nickel-[6] and copper-based[7] systems for the copolymerization of acrylates with ethene have been reported. While the 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.[2] More recently, Klumperman has reported the copolymerization of methyl methacrylate and 1-octene by ATRP.[8] One of the major disadvantages of using metal-based ATRP is that the resultant polymer contains traces of metal impurities and needs further purification. This limits their potential applications. Thus, there is a need for a non-metal-based system for controlled copolymerization of polar vinyl monomers with simple alkenes.

Alternating copolymers represent an interesting class of materials, with physical properties different from random and block copolymers. As described above, the radical-initiated alternating copolymerization of acrylates and 1-alkenes in the presence of Lewis acids has been reported.[3] However, the process is uncontrolled, affording products with a broad molecular weight distribution.

In this paper, we report the radical-initiated controlled random copolymerization of methyl acrylate (MA) with 1-alkenes (1-hexene, 1-octene, and 1-decene) by reversible addition–fragmentation chain transfer (RAFT). Copolymers with narrow polydispersity were formed. MA/1-hexene copolymer capped with the RAFT agent was chain-extended to synthesize the novel block copolymer, (MA-*co*-1-hexene)-*b*-PMA. Additionally, the controlled alternating copolymerization of MA with ethene was achieved by using alkyl iodide as degenerative transfer agent and $AlCl_3$ as the complexing Lewis acid. Although controlled alternating copolymerization of MA and styrene has been reported recently,[9] our work constitutes the first example of controlled alternating copolymerization of MA with an aliphatic 1-alkene.

Experimental Section

Materials. All chemicals and reagents were obtained from Aldrich unless stated otherwise. Methyl acrylate (MA, 99%) and 1-alkene (1-hexene, 97%; 1-octene, 98%; 1-decene, 94%) were distilled under vacuum from CaH_2 and stored under N_2. 2,2′-Azobis(isobutyronitrile) (AIBN, 98%) and $AlCl_3$ (99.99%) were used as received. CP grade ethene was supplied by Matheson Co. and used without further purification. The RAFT agent, benzyl 1-pyrrolcarbodithioate, was synthesized according to the literature procedure.[10] ^{1}H NMR ($CDCl_3$, ppm): 4.62 (s, 2H, *CH*$_2$PH), 6.35 (m, 2H, pyrrole), 7.40 (m, 5H, *CH*$_2$Ph), 7.73 (m, 2H, pyrrole).

Characterization. *Nuclear Magnetic Resonance (NMR).* NMR spectra were recorded at room temperature on a Bruker

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* To whom correspondence should be addressed. E-mail: asen@psu.edu.

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Table 1. Copolymerization of MA and 1-Alkene by RAFT and Degenerative Transfer Agent[a]

run	RAFT/AIBN (molar ratio)	1-alkene (g)	MA conv (%)	yield (g)	1-alkene incorp (mol %)	M_n	PDI (M_w/M_n)
1	5	0	88.4	4.2	0	33 000	1.28
2	10	0	52.4	2.5	0	24 900	1.16
3	0	1-hexene (3.0)	68.9	3.8	12.4	60 400	2.03
4	5	1-hexene (3.0)	56.9	3.6	10.8	43 700	1.49
5	10	1-hexene (3.0)	32.2	1.8	12.4	15 100	1.46
6	40	1-hexene (3.0)	16.4	1.0	20.2	4 400	1.07
7[b]	0	1-octene (2.0)	77.6	1.6	17.1	50 000	2.04
8[b]	5	1-octene (2.0)	67.5	1.7	16.5	9 400	1.34
9[b]	10	1-octene (2.0)	38.2	0.9	13.5	5 200	1.10
10[c]	5	1-octene (1.3)	42.5	2.1	14.3	8 000	1.29
11[c]	10	1-octene (1.3)	38.2	1.9	14.5	3 600	1.33
12	0	1-decene (3.0)	82.7	3.9	10.5	64 000	2.33
13	5	1-decene (3.0)	76.9	4.5	11.9	33 400	1.64
14	10	1-decene (3.0)	49.3	3.1	16.0	24 200	1.47
15	20	1-decene (3.0)	28.7	1.7	13.8	5 200	1.23
16	10/1 (CHI_3)	1-hexene (3.0)	45.8	2.5	12.0	11 100	1.78
17	20/1 (CHI_3)	1-hexene (3.0)	39.9	2.2	12.1	5 800	1.70
18[b]	5/1 (ethyl iodoacetate)	1-octene (1.3)	n.d.	n.d.	n.d.	8 900	2.08
19[b]	10/1 (ethyl iodoacetate)	1-octene (1.3)	n.d.	n.d.	n.d.	4 500	2.31

[a] Conditions: AIBN, 3 mg; MA, 4.8 g; PhCl, 10 mL; 60 °C, 20 h. [b] AIBN, 9.5 mg; MA, 2.0 g. [c] AIBN, 9.5 mg; MA, 4.0 g; 9 h.

DPX-300 spectrometer opening at 300 MHz for ^1H NMR and 75.4 MHz for ^{13}C NMR spectra. $CDCl_3$ was used as solvent. The chemical shifts are referenced relative to the solvent.

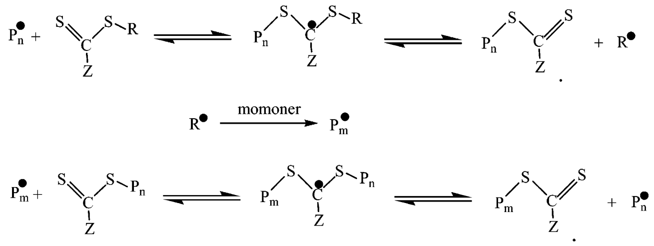
Gel Permeation Chromatography (GPC). Molecular weights and polydispersities were measured on a Shimadzu size exclusion chromatograph (SEC) using a flow rate of 1 mL/min and a three-column bed (Styragel HR 7.8 × 300 mm columns with 5 μm bead size: 100−10 000, 500−30 000, and 5000−6 000 000 Da), a Shimadzu RID 10A differential refractometer, and SPD-10A UV−vis detector. SEC samples were run in $CHCl_3$ at ambient temperature and calibrated to polystyrene standards obtained from Aldrich.

Synthesis of MA and 1-Alkene Copolymer by RAFT. In a typical experiment (Table 1, run 8), in a N_2-filled dry glovebox, a round-bottom flask equipped with a magnetic stir bar was charged with chlorobenzene (10 mL), MA (2.00 g, 23.3 mmol), 1-octene (2.00 g, 17.9 mmol), benzyl 1-pyrrolcarbodithioate (0.068 g, 0.29 mmol), and AIBN (0.0095 g, 0.058 mmol). The flask was then placed in an oil bath at 60 °C for 20 h. Following the reaction, the flask was cooled to room temperature. The contents of the flask were then poured into 500 mL of acidic methanol. The precipitated polymer was washed and dried under vacuum. Composition of the copolymer was determined from the integration ratio of the resonances at 3.66 ppm for a $-OCH_3$ unit of methyl acrylate and 0.82 ppm for a methyl unit of 1-alkene. Yield: 1.7 g; 1-octene: 16.5 mol %. ^1H NMR ($CDCl_3$, ppm): 0.82 ($-CH_3$ in 1-octene), 1.0−2.0 ($-CH_2$ in MA and $-CH_2$/-CH in 1-octene), 2.30 (−CH in MA), 3.66 ($-COOCH_3$). $M_n = 9400$, $M_w/M_n = 1.34$.

Chain Extensions To Synthesize Poly(methyl acrylate-*co*-1-hexene)-*b*-poly(methyl acrylate). Run 1. A round-bottom flask was charged with benzyl 1-pyrrolcarbodithioate-terminated poly(methyl acrylate-*co*-1-hexene) (0.12 g, 0.077 mmol, $M_n = 4400$, $M_w/M_n = 1.07$, 1-hexene mol % = 20.2), methyl acrylate (1.50 g, 17.4 mmol), chlorobenzene (10 mL), and AIBN (1.8 mg, 0.011 mmol). The flask was then placed in an oil bath at 60 °C for 8 h. Following the reaction, the contents of the flask were poured into 500 mL of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 0.45 g. $M_n = 13\,900$, $M_w/M_n = 1.21$.

Run 2. A round-bottom flask was charged with benzyl 1-pyrrolcarbodithioate-terminated poly(methyl acrylate-*co*-1-hexene) (0.050 g, 0.032 mmol, $M_n = 4400$, $M_w/M_n = 1.07$, 1-hexene mol % = 20.2), methyl acrylate (2.00 g, 23.2 mmol), chlorobenzene (10 mL), and AIBN (1.5 mg, 0.009 mmol). The flask was then placed in an oil bath at 60 °C for 15 h. Following the reaction, the contents of the flask were poured into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 1.60 g. $M_n = 77\,700$, $M_w/M_n = 1.38$.

Scheme 1



Kinetic Study of MA/1-Octene RAFT Copolymerization. In a N_2-filled dry glovebox, a round-bottom flask equipped with a magnetic stir bar was charged with chlorobenzene (10 mL), MA (4.00 g, 46.5 mmol), 1-octene (1.30 g, 11.6 mmol), benzyl 1-pyrrolcarbodithioate (0.068 g, 0.29 mmol), and AIBN (0.0095 g, 0.058 mmol). The flask was then placed in an oil bath at 60 °C. The samples were taken using a syringe for GPC and NMR analysis to determine molecular weight, PDI, and monomer conversion.

Alternating Copolymerization of Methyl Acrylate and Ethene in the Presence of $AlCl_3$ by Degenerative Transfer Polymerization. Chlorobenzene (10 mL), MA (2.00 g, 23.2 mmol), $AlCl_3$ (3.10 g, 23.2 mmol), and AIBN and CHI_3 solution (AIBN, 0.016 g, 0.098 mmol; CHI_3, 0.384 g, 0.98 mmol; chlorobenzene, 2 mL) were added to a 300 mL glass-lined, stainless steel autoclave equipped with a stirring bar. The autoclave was taken out from the glovebox and then charged with ethene (800 psi). The reaction was allowed to stir at 60 °C for 14 h. The contents were poured into a large amount of acidic methanol. The precipitated polymer was washed and dried under vacuum. Yield: 0.52 g. $M_n = 5700$, $M_w/M_n = 1.38$. ^1H NMR ($CDCl_3$, ppm): 1.10−1.60 ($-CH_2$), 2.26 (−CH), 3.65 ($-OCH_3$).

Results and Discussion

Controlled RAFT Copolymerization of MA and 1-Alkenes. RAFT polymerization[11] is one of the most powerful of the living/controlled polymerizations with many attractive features, such as tolerance for a wide range of functionality, applicability to different reaction conditions (bulk, solution, emulsion, suspension), and compatibility with conventional free radical processes. The mechanism involves a series of reversible addition−fragmentation steps (Scheme 1). As with ATRP and NMP processes, these reversible addition−fragmentation steps allow a dynamic equilibrium to be established between active propagating radicals and dormant polymeric (thiocarbonyl)sulfanyl compounds.

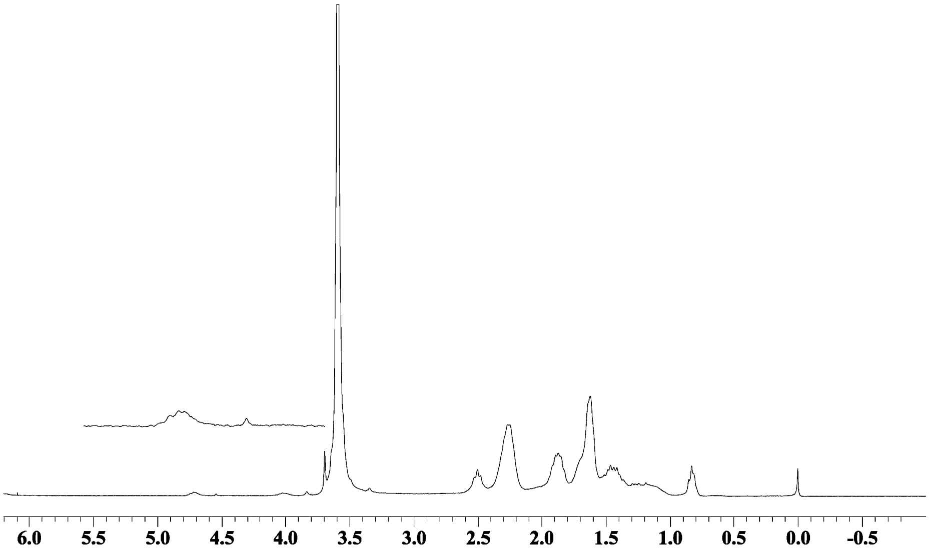


Figure 1. ^{1}H NMR (300 MHz) spectrum of poly(MA-*co*-1-hexene) prepared by RAFT polymerization (1-hexene mol % = 20.2).

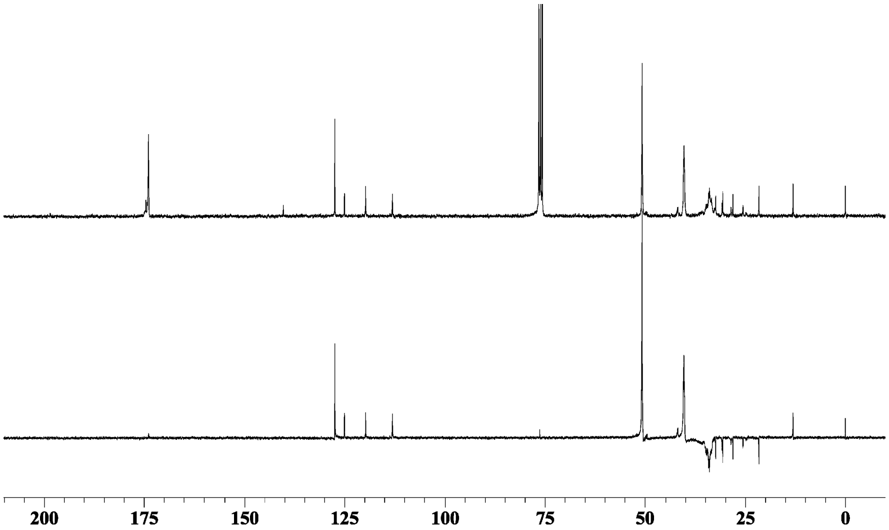


Figure 2. ^{13}C NMR (upper, 75.4 MHz) and DEPT135 NMR (lower) of poly(MA-*co*-1-octene) (1-octene mol % = 16.5).

Using benzyl 1-pyrrolcarbodithioate as the RAFT agent, our results for methyl acrylate and 1-alkene (1-hexene, 1-octene, 1-decene) copolymerization are summarized in Table 1. As shown, the MA conversion and polymer molecular weight decrease with increasing molar ratio of the RAFT agent to AIBN, a typical characteristic of controlled polymerization. For example, under otherwise similar reaction conditions, the MA conversion and number-average molecular weight for MA/1-hexene copolymerization were 68.9% and 60 400, 56.9% and 43 700, 32.2% and 15 100, and 16.4% and 4400, respectively, when the RAFT agent to AIBN ratio was 0, 5, 10, and 40. The slower polymerization rate with added RAFT agent can be attributed to the formation of a dynamic equilibrium between the active propagating radicals and dormant polymeric (thiocarbonyl)-sulfanyl compounds, resulting in a lower concentration of the former. Comparison of runs 1 and 4, as well as runs 2 and 5, demonstrates that the MA conversion in MA homopolymerization is significantly higher than that for MA/1-hexene copolymerization for identical RAFT/AIBN ratios. Thus, MA conversion decreased from 88.4% to 56.9% (RAFT/AIBN = 5) and from 52.4% to 32.2% (RAFT/AIBN = 10). As expected, for both homo- and copolymerization of MA with 1-alkenes, the polymer polydispersity decreases with increasing RAFT agent/AIBN ratio. However, a higher ratio of RAFT agent is required to obtain the same level of polydispersity for copolymerization reactions compared to MA homopolymerization. For example, under similar conditions, the use of RAFT/AIBN ratio of 5 led to PMA with PDI 1.16 (run 2), while the PDI was 1.46 for copolymerization with MA/1-hexene copolymer (run 5) and 1.47 for MA/1-decene copolymer (run 14). One reason may be the coupling of the intermediate RAFT radical and the relatively unstable secondary radical derived from the 1-alkene. This process would be expected to be irreversible, leading to higher polydispersity. Nevertheless, this side reaction is not too significant, presumably because the cross-polymerization with acrylate is significantly faster than irreversible termination. Thus, the copolymerizations are still “controlled” with a polydispersity index as narrow as 1.07 for lower molecular weight MA/1-hexene copolymers; as shown in Figure 4, the polydispersity starts to increase with increasing molecular weight. For comparison, degenerative transfer copolymerizations were also performed using either CHI_3 or ethyl iodoacetate. As is evident from Table 1,

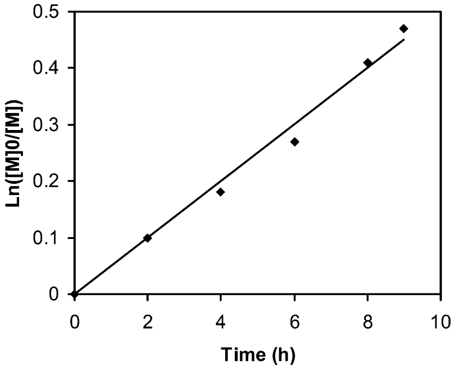


Figure 3. Polymerization kinetics of methyl acrylate with 1-octene. [MA] = 4.65 M, [1-octene] = 1.16 M, [RAFT] = 0.029 M, [AIBN] = 0.0058 M, 60 °C.

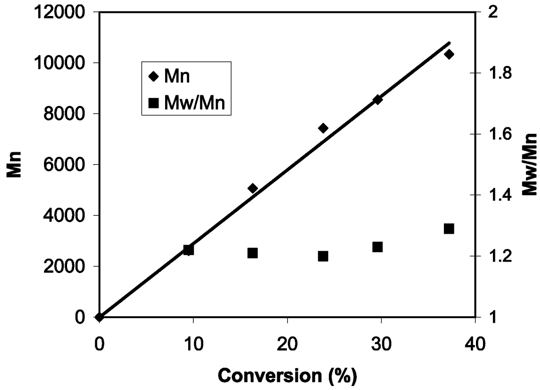


Figure 4. Dependence of molecular weight, M_n, and molecular weight distribution, M_w/M_n, on overall conversion for the copolymerization of methyl acrylate with 1-octene. [MA] = 4.65 M, [1-octene] = 1.16 M, [RAFT] = 0.029 M, [AIBN] = 0.0058 M, 60 °C.

although the molecular weight decreased as the degenerative transfer agent is increased, the polydispersity remains high.

Figure 1 shows the 300 MHz ^{1}H NMR spectrum of poly(MA-*co*-1-hexene) prepared by RAFT polymerization (RAFT/AIBN = 40). The peak at 0.82 ppm is assigned to the CH_3 units of 1-hexene. The chemical shifts at 3.66 and 2.28 ppm are assigned to the OCH_3 and CH units, respectively, of MA. The resonances at 1.0−2.0 ppm are due to the CH_2 units of MA and CH_2/CH units of 1-hexene. The chemical shifts from the RAFT agent, benzyl 1-pyrrolcarbodithioate, incorporated as copolymer end groups are also visible. The peaks at 6.28 and 7.32 ppm were assigned to CH_2 units of the pyrrole moiety. The triplet at 2.50 ppm is due to the benzyl CH_2 units. The multiple peaks at 4.71 ppm clearly demonstrate that the pyrrolcarbodithioate fragment is attached to the MA methine terminus of the polymer chains. The above chemical shifts of end groups from the copolymer are very similar to those from PMA.[12] On the basis of ^{1}H NMR analysis, one can conclude that the predominant end groups are the RAFT agent-capped MA units. This is important for chain extension in the synthesis of block copolymers (see below) since an MA-terminated polymer radical rather than the less stable secondary alkyl radical will be generated when the poly(MA-*co*-1-hexene) is treated with AIBN.

The 75.4 MHz ^{13}C NMR and DEPT135 NMR spectra of poly(MA-*co*-1-octene) are presented in Figure 2. In addition to the chemical shifts from runs of MA units, 175.5 (−C(O)O), 52.1 ($-OCH_3$), 41.8 (−CH−), and 35.3 ppm ($-CH_2-$), the chemical shifts from 1-octene units in MMO and MOM sequences are observed at 14.6 (CH_3) and 23−35 ppm. The chemical shifts for the RAFT agent are at 114.6 and 121.3 ppm for the pyrrole moiety and 141.8 (C-1), 128.9 (C-2 and C-3), 126.6 ppm (C-4) for phenyl carbons in the benzyl unit. The evidence from the ^{13}C NMR spectra for attachment of the RAFT agent to the polymer chains is consistent with the ^{1}H NMR results.

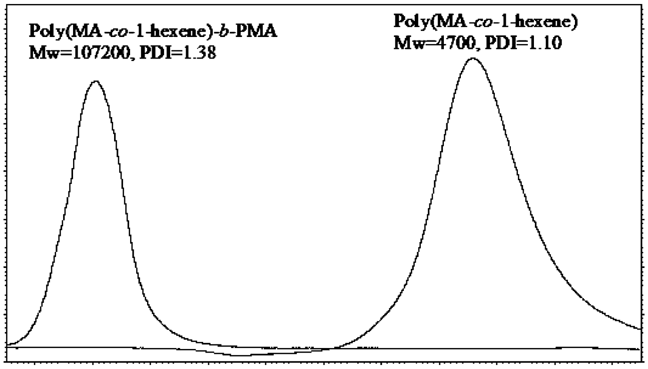


Figure 5. GPC traces of poly(MA-*co*-1-hexene)-*b*-PMA (left) and poly(MA-*co*-1-hexene) (right).

Table 2. Alternating Copolymerization of MA and 1-Alkene with $AlCl_3$/AIBN

run	1-alkene	$AlCl_3$/MA (molar ratio)	yield (g)	1-alkene (mol %)	M_n	PDI (M_w/M_n)
1[a]	ethene	1/1	2.75	50.0	80 600	2.40
2[a]	ethene	0.2/1	2.43	47.0	55 900	2.36
3[a]	ethene	0.1/1	2.23	47.3	39 400	2.15
4[b]	1-hexene	1/1	1.51	73.8	39 500	2.17
					1 300	1.26
5[b]	1-hexene	0.5/1	1.55	50.1	66 200	2.19

[a] Conditions: MA, 2 g; ethene, 800 psi; AIBN, 0.016 g; PhCl, 10 mL; 60 °C, 18 h. [b] Conditions: MA, 1 g; 1-hexene, 1.95 g; AIBN, 0.016 g; PhCl, 10 mL; 60 °C, 18 h.

The RAFT copolymerization of MA with 1-alkenes displays the characteristics of a "living" system. As shown in Figures 3 and 4, the MA/1-octene copolymerization follows first-order kinetics for overall monomer conversion and molecular weight increases linearly with overall conversion while the polydispersities remain below 1.3. The living/controlled free radical polymerizations can provide products with controlled molecular weight and narrow molecular weight distribution; more importantly, the polymer prepared by living/controlled system can be retreated with monomers for chain extension to form block copolymers. Indeed, the synthesis of block copolymers is widely used to demonstrate the "living" nature of a polymerization.[13] The poly(methyl acrylate-*co*-1-hexene) (1-hexene mol % = 20.2, M_n = 4400, PDI = 1.07) was employed as a macro-RAFT agent in chain extension reactions to form poly(methyl acrylate-*co*-1-hexene)-*b*-poly(methyl acrylate). The polymer was added to AIBN/MA solution in chlorobenzene (Run 1: poly(MA-*co*-1-hexene), 0.077 mmol; AIBN, 0.011 mmol; MA, 17.4 mmol. Run 2: poly(MA-*co*-1-hexene), 0.032 mmol; AIBN, 0.009 mmol; MA, 23.2 mmol). The mixtures were heated at 60 °C for 8 and 15 h to afford the final products with molecular weights (M_n) 13 900 (M_w/M_n = 1.21) and 77 700 (M_w/M_n = 1.38), respectively. The polydispersities of the final products are much lower than that for a conventional radical process, implying efficient chain initiation by the RAFT macromer. Moreover, the complete separation of GPC traces for poly-

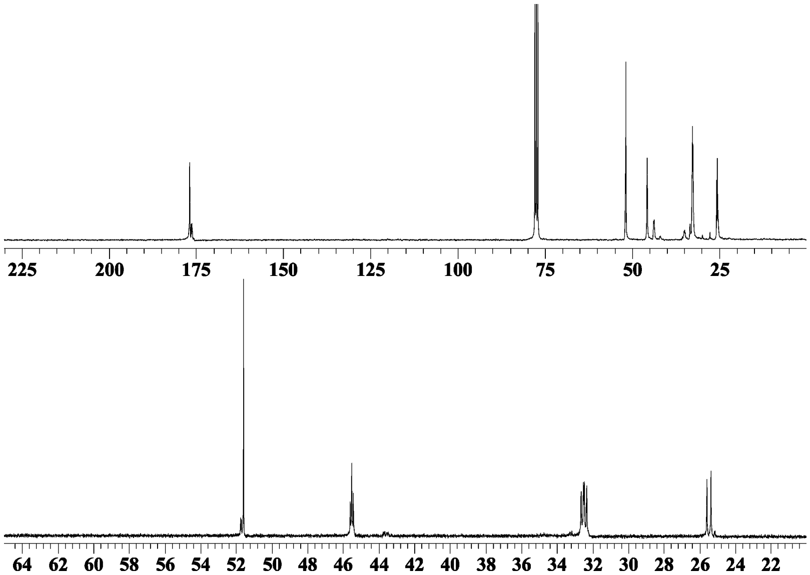
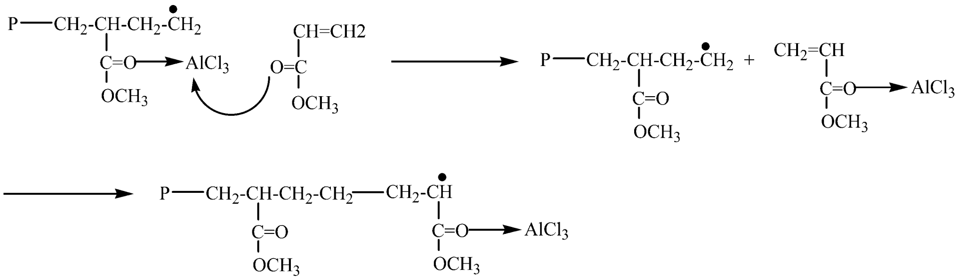


Figure 6. ^{13}C NMR (75.4 MHz) spectra of alternating copolymer of MA and ethene prepared with different molar ratios of $AlCl_3$/MA: upper, $AlCl_3$/MA = 0.2/1 (0−230 ppm); lower, $AlCl_3$/MA = 1/1 (20−65 ppm).

Scheme 2



(MA-*co*-1-hexene) and poly(MA-*co*-1-hexene)-*b*-PMA as shown in Figure 5 demonstrates that all of the end groups of poly(MA-*co*-1-hexene) were reactivated during the block copolymer synthesis.

Alternating Copolymerization of MA and 1-Alkenes. Table 2 summarizes the alternating copolymerization of MA/ethene and MA/1-hexene using $AlCl_3$ as the complexing Lewis acid. In contrast to the conclusion by Logothetis that $AlCl_3$ does not allow appreciable incorporation of the 1-alkene, as shown in Table 2, alternating copolymer of MA and ethene can be obtained using $AlCl_3$ as complex agent with 1:1 molar ratio of $AlCl_3$ and MA. Although the molecular weight of the product decreases with decreasing $AlCl_3$ ratio, the ethene content in the copolymer is still close to 50 mol % with $AlCl_3$:MA ratio of 0.1, implying that the alternating sequences are still predominant in the copolymer since ethene units are not likely to be incorporated consecutively into polymer chains in a free radical polymerization. The fact that an alternating copolymer can be prepared using a $AlCl_3$:MA ratio that is significantly less than 1 suggests facile $AlCl_3$ exchange between MA units in the polymer and monomeric MA as shown below (Scheme 2).

For MA/1-hexene copolymerization with 1:1 ratio of MA to 1-hexene, the bimodal GPC trace suggests a mixture of products generated by different polymerization mechanisms. The high molecular weight fraction (M_n = 39 400, PDI = 2.17) is the radical-initiated MA/1-hexene alternating copolymer, while the low molecular weight fraction is poly(1-hexene) (M_n = 1300, PDI = 1.26) produced by a cationic process. The latter was verified by carrying out a cationic polymerization of 1-hexene with $AlCl_3$ under similar conditions, except for the exclusion of MA and AIBN. The product obtained was essentially identical (M_n = 1500, PDI = 1.23) with the poly(1-hexene) obtained previously. Reducing the ratio of $AlCl_3$/MA to 0.5 resulted in the disappearance of poly(1-hexene) in the product, and only the alternating copolymer was obtained.

Figure 6 shows the ^{13}C NMR spectra of alternating copolymers of MA and ethene (upper: $AlCl_3$/MA = 0.2/1; lower: $AlCl_3$/MA = 1/1). In the spectrum of the alternating copolymer prepared with a lower ratio of $AlCl_3$ (upper spectrum), in addition to the major resonances from alternating MA−E sequences at 176.0 (−C(O)−), 51.9 (−OCH_3), 45.8 (−CH−), 32.7 (−CH_2−), 25.7 ppm (−CH_2−), the small peaks were observed at 43.8 and 35.1 ppm attributable to CH and CH_2 units in MEM sequences and at 29.8 and 27.7 ppm attributable to CH_2 units in MEE sequences. The presence of consecutive MA and ethene units suggests nonperfect alternation similar to that observed when BF_3 is used as the complexing agent.[3a] It is interesting to note these resonances are not detectable in Figure 6 (lower spectrum) for copolymer formed with a 1:1 ratio of $AlCl_3$ and MA. Thus, $AlCl_3$ is superior to BF_3 as a complexing agent for the alternating MA/1-alkene copolymerization.

Controlled Alternating Copolymerization of MA and Ethene. The results of the copolymerization of MA and ethene with $AlCl_3$/AIBN in the presence of different control agents are summarized in Table 3. The molecular weight and molecular weight distribution of the product decrease with increasing amount of the degen-

Table 3. Alternating Copolymerization of MA and Ethene with $AlCl_3$/AIBN in the Presence of Control Agents[a]

run	control agent (CA)	CA/AIBN (molar ratio)	yield (g)	M_n	PDI (M_w/M_n)
1	0	0	2.75	80 600	2.40
2	CHI_3	3.5	1.88	20 000	1.90
3	CHI_3	5	2.10	15 900	1.75
4	CHI_3	10	1.46	9 000	1.43
5	CHI_3	20	0.52	5 700	1.38
6	ethyl iodoacetate	5	2.26	30 600	2.37
7	ethyl iodoacetate	10	1.87	33 500	1.90
8	RAFT	5	0.56	51 600	1.96
9	RAFT	10	n.d.	37 900	2.25

[a] Conditions: MA, 2 g; ethene, 800 psi; $AlCl_3$, 3.1 g; AIBN, 0.016 g; PhCl, 10 mL; 60 °C, 18 h.

erative transfer agent, CHI_3. The M_n decreases from 80 600, 15 900, 9000, to 5700, and molecular weight distribution drops off from 2.40, 1.75, 1.43, to 1.38 as the CHI_3/AIBN ratio increases from 0, 5, 10, to 20, displaying the some control of polymerization. The use of ethyl iodoacetate or the RAFT agent, benzyl 1-pyrrolcarbodithioate, however led to less controlled behavior with high molecular weight and broad polydispersity for the resultant material. It is possible that the reactivity of the RAFT agent is adversely affected by the coordination of its thiocarbonyl group to $AlCl_3$.

Conclusion

In conclusion, we have demonstrated the controlled random copolymerization of methyl acrylate and 1-alkenes through reversible addition−fragmentation transfer (RAFT) technique using benzyl 1-pyrrolcarbodithioate as transfer agent. NMR analyses of the copolymers reveal that RAFT agent-capped MA units are the predominant end groups, which allows chain extension to synthesize the block copolymer poly(MA-*co*-1-hexene)-*b*-PMA when poly(MA-*co*-1-hexene) was treated with AIBN. The strictly alternating copolymer of MA and ethene without detectable sequences of consecutive MA and ethene units was obtained by using $AlCl_3$ as the complexing agent. The first example of controlled alternating copolymerization of MA and ethene was achieved by degenerative transfer polymerization with iodoform as the transfer agent.

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