$Mn_2(CO)_{10}$-Induced Controlled/Living Radical Copolymerization of Methyl Acrylate and 1-Hexene in Fluoroalcohol: High α-Olefin Content Copolymers with Controlled Molecular Weights

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ABSTRACT: A highly active manganese complex [$Mn_2(CO)_{10}$] efficiently induced the controlled/living radical copolymerizations of a conjugated polar vinyl monomer, methyl acrylate (MA), and an unconjugated nonpolar olefin, 1-hexene (1-Hex), in the presence of ethyl 2-iodoisobutyrate (EMA−I) as an initiator under weak visible light at 40 °C to give the copolymers with controlled molecular weights. The further use of protic fluoroalcohols as solvents enhanced the copolymerization without losing the molecular weight control to result in a high 1-Hex content up to 50 mol %, for which the predominant alternating sequences were confirmed by the ^{13}C NMR analysis of the copolymers. The kinetic analysis of the copolymerizations revealed an increase in the reactivity of the MA-radical to the 1-Hex monomer in the fluoroalcohol [$1/r_{MA} = 0.49$ in $(CF_3)_2CHOH$ vs 0.081 in toluene], which can be attributed to the 1:1 hydrogen-bonding interaction between the MA unit and the fluoroalcohol as suggested by the ^{13}C NMR analysis of the MA−fluoroalcohol mixtures [$K_{assn} = 2.21$ L/mol for $(CF_3)_2CHOH$]. Thus, a combination of a highly active $Mn_2(CO)_{10}$ catalyst and a protic fluoroalcohol solvent is effective for the alternating controlled/living radical copolymerization of acrylic monomers and α-olefins.

Introduction

The copolymerization of polar acrylic monomers and nonpolar hydrocarbon olefins is one of the most fascinating topics in vinyl addition polymerizations because novel or improved properties can be imparted into the products even from the simple commodity monomers. However, copolymers containing both monomer units in moderate amounts are generally difficult to form due to their highly different reactivities in all vinyl addition polymerizations. In radical polymerizations, acrylates can be readily polymerized while the reactivity of the nonpolar olefins is extremely low due to the less reactive unconjugated double bond and the less stable alkyl radical species.[1] The conventional radical copolymerization of the two monomers thus results in mostly polyacrylates containing a small amount of nonpolar olefin units. In contrast, for metal-catalyzed coordination polymerizations, which are highly effective for ethylene and α-olefins, the polar acrylic monomers generally deteriorate the metal catalysis to inhibit the polymerizations. However, in recent years, late transition metal olefin polymerization catalysts proved to be active even in the presence of polar groups in order to incorporate a small amount of the polar acrylic monomers into the polyolefins.[2−4]

For radical copolymerizations, there have been several reported methods for enhancing the copolymerizations. One of the most effective methods is to add strong Lewis acids,[5] such as AlR_nCl_{3-n},[6−11] BF_3,[12] $SnCl_4$,[11,13] $ZnCl_2$,[14−20] etc., for increasing the copolymerizability of nonpolar olefins with polar monomers, such as acrylonitrile, acrylates, and methacrylates. Although the detailed mechanisms of these copolymerizations have not yet been completely clarified, the enhanced reactivity seems to be due to the coordination of the Lewis acids to the carbonyl groups of the acrylic monomer and its growing radical species, which decreases the electron density of the vinyl group and the growing radical to enhance the cross-propagation to the relatively electron-rich nonpolar olefin monomer and its propagating radical species, respectively. These strong Lewis acids can generate nearly complete alternating copolymers although it needs strict anhydrous conditions, low temperatures, large excess of the olefin monomers, etc. Another accompanying problem with these Lewis acid−based systems is the contamination of the metal residues in the polymer products. Recently, Sen et al. alleviated some of these problems using the relatively water-tolerant rare-earth metal Lewis acid like $Sc(OTf)_3$,[21] Brønsted acid like pyridinium triflate,[22] and solid acidic Al_2O_3[23] for the copolymerizations of acrylates and nonpolar olefins while the effectiveness on the copolymerizability was relatively small for some compounds. Although trifluoroacetic acid was employed for the copolymerizations between highly electron-deficient polar monomers, such as α-cyanoacrylate and acrylonitrile, and ethylene, the effects were unknown for the acrylate−α-olefin copolymerizations.[19,20,24] Thus, more effective radical copolymerization systems based on metal-free compounds are awaited from various aspects.

Another important controlling factor of the copolymerization is the homogeneity of the comonomer distributions and chain lengths among each polymer chain. Such well-defined copolymers can theoretically be prepared by living copolymerizations, in which all the polymer chains continue their chain growths throughout the polymerizations. In radical polymerizations, recent years have seen significant developments in the controlled/living radical polymerizations by a variety of initiating systems, all of which are based on the reversible activation of covalent species into growing radical species.[25−28] These systems can be applicable for various conjugated vinyl monomers, such as (meth)acrylic monomers and styrenes, while the appropriate reagents and reaction conditions are dependent on the types of monomers in most cases. In contrast to the conjugated monomers, there are a few effective controlled/living radical polymerization systems for unconjugated or less conjugated monomers like vinyl chloride, vinyl esters, vinyl amides, etc., mainly due to the difficulty in the reversible activation of the relatively strong covalent bonds into the unstable growing radical species for these monomers. Furthermore, typical unconjugated monomers like ethylene and α-olefins are hardly homopolymerized even by controlled/living radical

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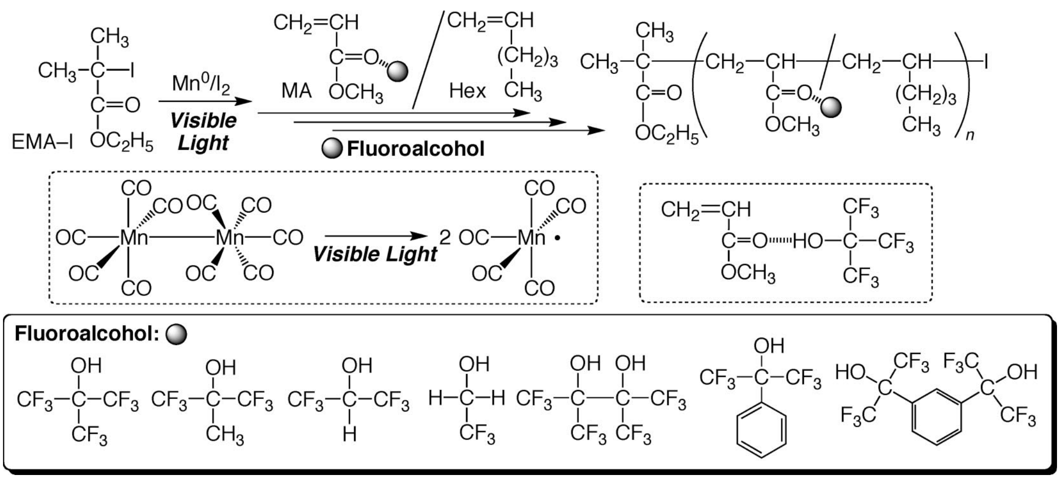
Scheme 1. Controlled/Living Radical Copolymerization of Methyl Acrylate and 1-Hexene with $Mn_2(CO)_{10}$



polymerization systems as in conventional radical polymerizations. In contrast, their copolymerizations with acrylates proceed with several highly active controlled/living radical polymerization systems to give the copolymers with controlled molecular weights although the contents of the nonpolar monomers are quite low (∼10%).[21,26,29−34] Recently, $AlCl_3$[34] and $Sc(OTf)_3$[21] were added to the reversible addition-fragmentation chain-transfer (RAFT) polymerizations of methyl acrylate (MA) and ethylene or 1-hexene (1-Hex) in order to attain a high olefin content in addition to the molecular weight control. However, the obtained copolymers showed relatively broad molecular weight distributions (MWDs) ($M_w/M_n \sim 1.7$) in comparison to those obtained using the RAFT system in the absence of the Lewis acids as well as relatively small 1-Hex (maximum ∼ 25%) compared to those obtained with $Sc(OTf)_3$ in the absence of the RAFT agent. This indicates that the Lewis acid gives some adverse effects on the molecular weight control by the RAFT agent via an unfavorable interaction for the RAFT process and vice versa. These results also suggest that a more suitable combination should be developed for attaining both the molecular weight control and a high olefin content: i.e., most probably a versatile, highly active, and tolerant controlled/living radical polymerization and a novel acidic mediator effective for the copolymerization.

Quite recently, we developed a highly active manganese-induced controlled/living radical polymerizations of various monomers including unconjugated monomers like vinyl acetate (VAc) and conjugated vinyl monomers like acrylates and styrene.[35] This polymerization is triggered by the photochemical homolysis of the Mn−Mn bond in $Mn_2(CO)_{10}$ via the $\sigma-\sigma^*$ transition under weak visible light to produce the highly active manganese radical $[^{\bullet}Mn(CO)_5]$,[36,37] which then activates the C−I bond of an appropriate alkyl iodide initiator and the dormant species derived from VAc as well as acrylates and styrene to induce fast and efficient polymerizations even at 40 °C. More recently, we utilized this system for the controlled/living radical copolymerization of conjugated (MA) and unconjugated (VAc) monomers and succeeded in the spontaneous formation of well-defined block copolymers consisting of the gradient copolymer [poly(MA-*grad*-VAc)] and homopolymer [poly(VAc)] segments.[38] These results indicate that the manganese system would be one of the highly versatile and active systems for the controlled/living radical polymerizations of various monomers.

Another recent breakthrough in the controlling radical polymerization is triggered by the use of protic fluoroalcohols for the stereospecific radical polymerizations, in which the acidic and bulky fluoroalcohols coordinate to the carbonyl groups of the monomer units like VAc[39] and methacrylates[40] to induce the syndiospecific propagation via steric repulsion around the growing polymer terminals. Although the fluoroalcohols have not been used for the copolymerizations between acrylic and nonpolar monomers, some protic solvents are known to change the monomer reactivity ratios.[19,20,24,41] These results suggest that the acidic fluoroalcohols would become novel effective solvents for enhancing the copolymerizations.

In this study, we first investigated the controlled/living radical copolymerization of MA and 1-Hex with the $Mn_2(CO)_{10}$-based initiating systems in toluene (Scheme 1). We further examined the use of fluoroalcohols as solvents for enhancing the copolymerization via a possible hydrogen-bonding interaction with the carbonyl substituents in the MA units due to the high acidity of the fluoroalcohols. This study revealed that a combination of $Mn_2(CO)_{10}$ and fluoroalcohols is quite effective in affording the copolymers with controlled molecular weights and high α-olefin contents (up to ∼50%) even at 40 °C. This study was further directed to the detailed analysis of the monomer sequences in the copolymers, the monomer reactivity ratios in the copolymerizations, and the interaction between the fluoroalcohols and MA by the model reactions.

Experimental Section

Materials. Methyl acrylate (Tokyo Kasei, >99%) and 1-hexene (Tokyo Kasei, >95%) were distilled from calcium hydride under reduced pressure before use. Toluene (Kishida, >99%) was distilled from sodium benzophenone ketyl and bubbled with dry nitrogen over 15 min just before use. 1,1,1,3,3,3-Hexafluoro-2-propanol (Wako, >99%), $PhC(CF_3)_2OH$ (Wako, >99%), m-$C_6H_4[C(CF_3)_2OH]_2$ (Wako, >97%), and 2,2,2-trifluoroethanol (Aldrich, >99%) were distilled from calcium hydride and bubbled with dry nitrogen for 15 min immediately before use. $(CF_3)_2C(CH_3)OH$ (fluorochem, >98%) and $[(CF_3)_2COH]_2$ (fluorochem, >97%) were bubbled with dry nitrogen and used without further purification. $(CF_3)_3COH$ (Aldrich, >99%) was used as received. Ethyl 2-iodoisobutyrate (EMA−I) was prepared according to the literature.[42] $Mn_2(CO)_{10}$ (Aldrich, 98%) and iodine (Kishida, >99.8%) were used as received and handled in unlighted glovebox (VAC Nexus) under a moisture- and oxygen-free argon atmosphere ($O_2 < 1$ ppm). 2,2′-Azobisisobutyronitrile (AIBN) (Kishida, >99%) was purified by recrystallization from methanol.

Polymerization. Polymerization was carried out by the syringe technique under dry nitrogen in oven-dried and sealed glass tubes. A typical example for MA and Hex copolymerization with EMA−I/$Mn_2(CO)_{10}$ is given below. $Mn_2(CO)_{10}$ (46.3 mg, 0.119 mmol) was mixed with toluene (2.72 mL), MA (0.53 mL, 5.89 mmol), 1-Hex

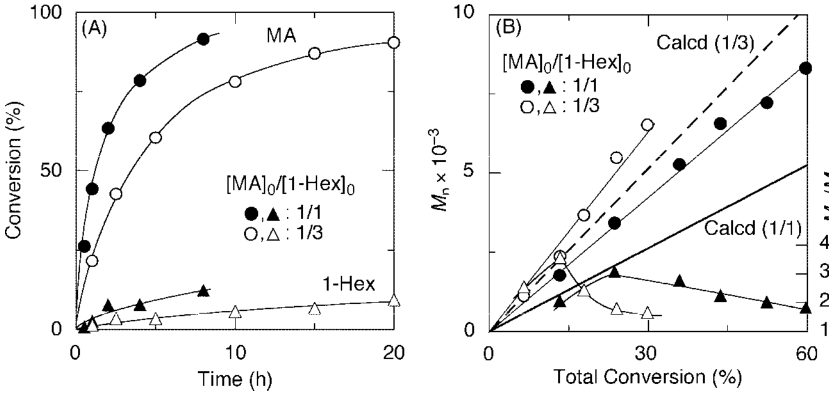


Figure 1. Copolymerization of methyl acrylate and 1-hexene with ethyl 2-iodoisobutyrate/$Mn_2(CO)_{10}$ in toluene at 40 °C under visible light; [methyl acrylate]$_0$/[1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$/[$Mn_2(CO)_{10}$]$_0$ = 2000/2000/40/40 mM (●,▲) or 1000/3000/20/20 mM (○,△).

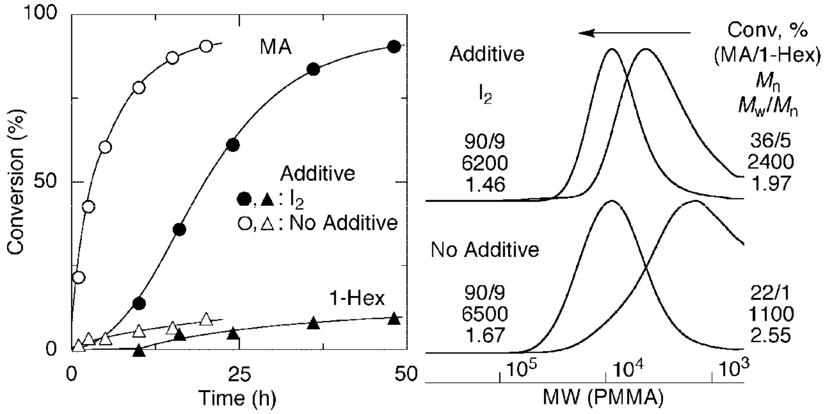


Figure 2. Copolymerization of methyl acrylate and 1-hexene with ethyl 2-iodoisobutyrate/$Mn_2(CO)_{10}$ in the presence (●,▲) or absence (○,△) of I_2 in toluene at 40 °C under visible light; [methyl acrylate]$_0$/[1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$/[$Mn_2(CO)_{10}$]$_0$/[I_2]$_0$ = 1000/3000/20/20/0 or 5.0 mM.

(2.20 mL, 17.7 mmol), I_2 (0.30 mL of 100 mM solution in toluene, 0.030 mmol) and EMA−I (0.135 mL of 880 mM solution in toluene, 0.119 mmol) sequentially in this order under light shielding condition. The total volume of the reaction mixture was thus 5.88 mL. Immediately after mixing, aliquots (0.7 mL each) of the solution were distributed via a syringe into baked glass tubes, which were then sealed by flame under nitrogen atmosphere. The tubes were immersed in thermostatic water bath at 40 °C under the 27 W fluorescent light with diffuser [3M filter light ($\lambda > 400$ nm)].[35] In predetermined intervals, the polymerization was terminated by cooling the reaction mixture to −78 °C. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR spectroscopy with toluene as an internal standard (48 h, 90.3% for MA and 9.4% for 1-Hex, respectively). The quenched reaction mixture was diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (∼5 g) to remove the metal-containing residues. After the absorbent was separated by filtration, the filtrate was washed with aqueous citric acid solution and water, and evaporated to dryness under reduced pressure, and vacuum-dried to give the product polymers (74.9 mg, 63% yield; M_n = 6200, M_w/M_n = 1.46).

Measurements. Monomer conversion was determined from the concentration of residual monomer measured by ^{1}H NMR spectroscopy with toluene as an internal standard. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 25 °C on a Varian Gemini 2000 or a JEOL ECS−400 spectrometer, operating at 400 MHz (^{1}H) or 100 MHz (^{13}C), respectively. The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of polymers were determined by size-exclusion chromatography (SEC) in THF at 40 °C on two polystyrene gel columns [Shodex K-805 L (pore size: 20−1000Å; 8.0 mm i.d. × 30 cm) × 2; flow rate 1.0 mL/min] connected to a JASCO PU-2080 precision pump and a JASCO RI-2031 detector. The columns were calibrated against 8 standard poly(methyl methacrylate) (PMMA) samples (Shodex; M_p = 202−1950000; M_w/M_n = 1.02−1.09).

Results and Discussion

1. Controlled/Living Radical Copolymerization of MA and 1-Hex with R−I/$Mn_2(CO)_{10}$ in Toluene: Molecular Weight Control.

MA and 1-Hex were first copolymerized in toluene with $Mn_2(CO)_{10}$ in conjunction with ethyl 2-iodoisobutyrate (EMA−I) as an initiator under weak visible light at 40 °C, in which the initial charge ratios of the two monomers were [MA]$_0$/[1-Hex]$_0$ = 1/1 or 1/3. The copolymerizations smoothly proceeded irrespective of the monomer feed ratios (Figure 1A). In both cases, MA was almost quantitatively consumed, whereas the consumption of 1-Hex ceased after the depletion of the counterpart comonomer as in the conventional radical copolymerizations.

Figure 1B shows the M_n and M_w/M_n of the obtained poly[MA-*co*-(1-Hex)]. The M_n, which were based on the PMMA calibration by SEC, increased in direct proportion to the total monomer conversions and were slightly higher than the calculated values assuming that one initiator (EMA−I) molecule generates one polymer chain. The molecular weight distributions (MWDs) were rather broad but became narrower (M_w/M_n ∼ 1.6) as the copolymerization proceeded. These results suggest that the Mn-based system is also applicable for the copolymerization of MA and 1-Hex to provide the moderate molecular weight control even at a high initial concentration of the unconjugated monomer, 1-Hex.

The improvement of the molecular weight control was further investigated by the addition of molecular iodine (I_2) to the copolymerization system. Previously, I_2 was employed as an additive for controlling the highly active iron(I)-based controlled/

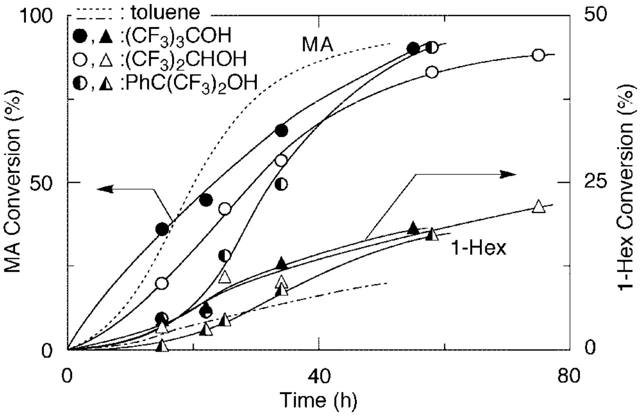


Figure 3. Time−conversion curves for the copolymerization of methyl acrylate and 1-hexene with ethyl 2-iodoisobutyrate/$Mn_2(CO)_{10}$/I_2 in $(CF_3)_3COH$ (●,▲), $(CF_3)_2CHOH$ (○,△) or $PhC(CF_3)_2OH$ (◐,▲) at 40 °C under visible light; [methyl acrylate]$_0$/[1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$/[$Mn_2(CO)_{10}$]$_0$/[I_2]$_0$ = 1000/3000/20/20/5.0 mM. The dashed and dashed-and-dotted lines indicate the conversions of methyl acrylate and 1-hexene in toluene, respectively.

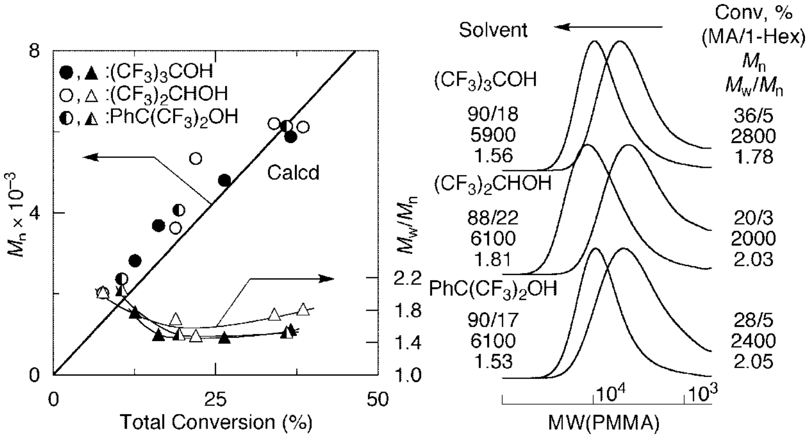


Figure 4. M_n, M_w/M_n and size-exclusion chromatograms of poly[(methyl acrylate)-*co*-(1-hexene)] obtained with ethyl 2-iodoisobutyrate/$Mn_2(CO)_{10}$/I_2 in $(CF_3)_3COH$ (●,▲), $(CF_3)_2CHOH$ (○,△) or $PhC(CF_3)_2OH$ (◐,▲) at 40 °C under visible light; [methyl acrylate]$_0$/[1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$/[$Mn_2(CO)_{10}$]$_2$/[I_2]$_0$ = 1000/3000/20/20/5.0 mM.

living radical polymerization of MA or acrylamide with R−I/$Fe_2Cp_2(CO)_{10}$, in which the added iodine worked for the rapid deactivation of the propagating radical species into the dormant C−I species.[43,44] Upon the addition of a small amount of I_2 (5.0 mM), the copolymerization was retarded similar to the iron-based systems for the homopolymerizations of acrylic monomers (Figure 2). The SEC curves of the copolymers obtained in the presence of I_2 also shifted to higher molecular weights and the MWDs became narrower than those in the absence of I_2. This is most probably attributed to the effective deactivation of the growing radical species by I_2 and/or the *in situ* formed manganese(I) iodide complex [I−$Mn(CO)_5$] from $Mn_2(CO)_{10}$,[45] which may also serve as an iodine atom donor to the growing radical species for the effective activation-deactivation process in the R−I/$Mn_2(CO)_{10}$-based polymerization.

2. Copolymerization in Fluoroalcohols: High α-Olefin Content Copolymers with Controlled Molecular Weights. The copolymerization of MA and 1-Hex ([MA]$_0$/[1-Hex]$_0$ = 1/3) was then investigated with EMA−I/$Mn_2(CO)_{10}$/I_2 in $(CF_3)_2CHOH$, $(CF_3)_3COH$, and $PhC(CF_3)_2OH$ (Figure 3). Although the consumption of MA was slightly slower in the fluoroalcohols than in toluene, MA was almost quantitatively consumed. Furthermore, the final conversions of 1-Hex were apparently higher in the fluoroalcohols [22% in $(CF_3)_2CHOH$, 18% in $(CF_3)_3COH$, and 17% in $PhC(CF_3)_2OH$] than in toluene (9%), which suggests that the fluoroalcohols most probably change the monomer reactivity ratios for the copolymerization of MA and 1-Hex to give the copolymers with a higher olefin content.

Figure 4 shows the M_n, M_w/M_n, and SEC curves of the MA/1-Hex-copolymers obtained with EMA−I/$Mn_2(CO)_{10}$/I_2 in the fluoroalcohols. Even in the fluoroalcohols, the M_n's of the copolymers increased in direct proportion to the monomer conversions and agreed well with the calculated values under the stated conditions. The MWDs obtained in $(CF_3)_3COH$ and $PhC(CF_3)_2OH$ were almost the same as those in toluene under the same conditions in the presence of I_2 while they were slightly broader in $(CF_3)_2CHOH$. A similar dependence of the MWDs on the fluoroalcohols was observed for the iodine transfer radical polymerization of VAc in the fluoroalcohols.[46] Thus, the controlled copolymerization of MA and 1-Hex with the Mn-based system also proceeded even in the protic fluoroalcohols thus inducing a higher 1-Hex consumption without any significant loss of the controllability of the molecular weights by the $Mn_2(CO)_{10}$ system. This suggests a good combination of the $Mn_2(CO)_{10}$-based system and the fluoroalcohols for the controlled/living radical copolymerization between acrylic and nonpolar monomers.

3. Copolymer Analysis. The structures of the copolymers obtained with EMA−I/$Mn_2(CO)_{10}$/I_2 in toluene and the fluoroalcohols were analyzed by ^1H and ^{13}C NMR spectroscopies. Figure 5 shows the ^1H NMR spectra of the copolymers obtained in toluene, $(CF_3)_2CHOH$, and $(CF_3)_3COH$.

The large signals were assigned to the main chain protons of the copolymers; the methyl ester (*c*), methylene (*a*), and methine (*b*) protons in the MA units absorb at 3.7, 1.4−2.0, and 2.2−2.6 ppm, respectively, and the methyl (*g*), methylene and methine (*d*, *e*, *f*) protons in the 1-Hex units absorb at 0.9 and 1.0−1.4

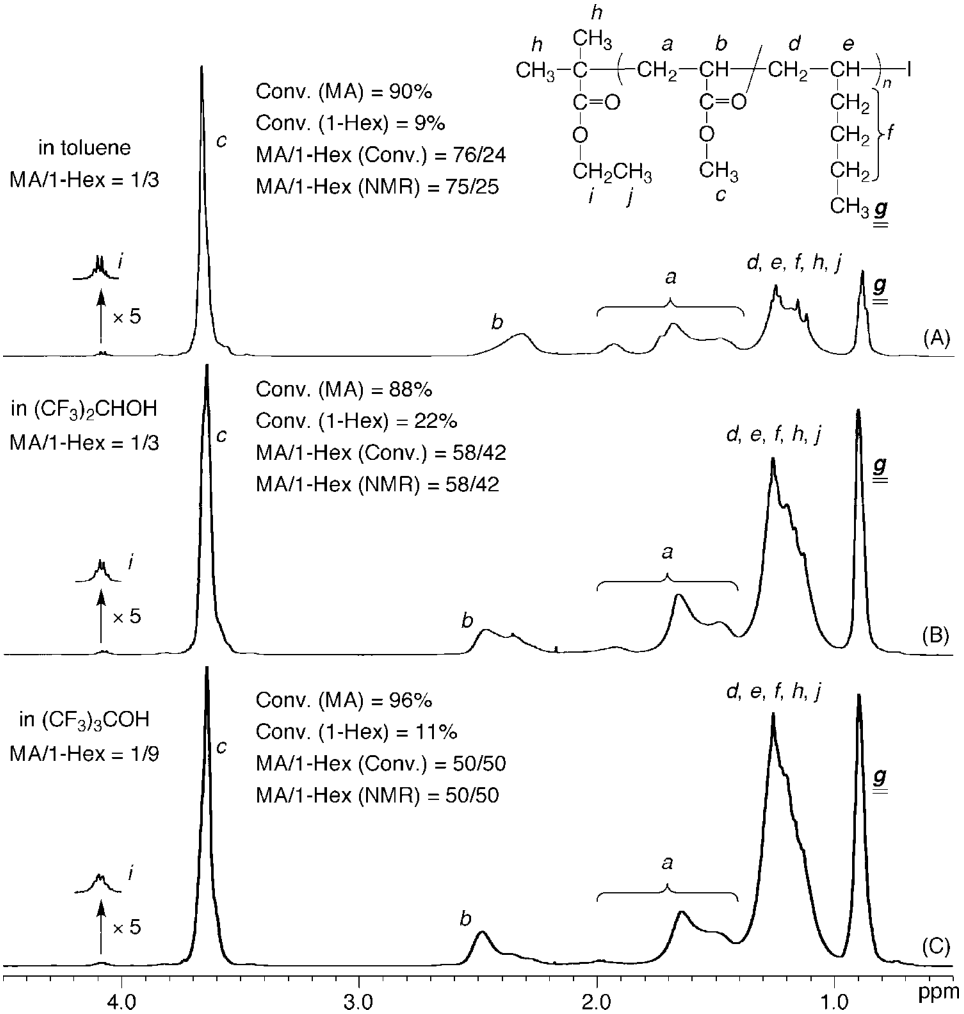


Figure 5. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 25 °C) of poly[(methyl acrylate)-*co*-(1-hexene)] obtained with ethyl 2-iodoisobutyrate/$Mn_2(CO)_{10}/I_2$ in toluene (A), $(CF_3)_2CHOH$ (B) or $(CF_3)_3COH$ (C) at 40 °C under visible light; [methyl acrylate]$_0$/[1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$/$[Mn_2(CO)_{10}]_0$/$[I_2]_0$ = 1000/3000/20/20/5.0 mM (A, B) or 400/3600/8.0/8.0/2.0 mM (C), respectively.

Table 1. Radical Copolymerization of Methyl Acrylate and 1-Hexene with EMA−I/$Mn_2(CO)_{10}$ in Various Solvents[a]

entry	$[MA]_0/[1\text{-Hex}]_0$	solvent	time (h)	convn, [b]% (MA/Hex)	M_n(calcd)[c]	M_n[d]	M_w/M_n[d]	MA/1-Hex[b]
1[e]	2000/2000	toluene	8	92/12	4700	7200	2.03	87/13
2		$(CF_3)_2CHOH$	70	91/35	5600	7300	1.68	69/31
3		$PhC(CF_3)_2OH$	50	92/37	5800	6400	1.55	76/24
4	1000/3000	toluene	48	90/9	5300	6200	1.46	75/25
5		$(CF_3)_2CHOH$	75	88/22	6800	6100	1.81	58/42
6		$(CF_3)_3COH$	55	90/18	5900	6400	1.56	58/42
7		$[(CF_3)_2COH]_2$	50	94/22	7100	6500	1.49	60/40
8		$(CF_3)_2C(CH_3)OH$	100	95/20	6800	6000	1.67	61/39
9		CF_3CH_2OH	77	93/13	5900	6300	1.70	63/37
10		$m\text{-}C_6H_4[C(CF_3)_2OH]_2$	45	95/19	6800	6800	1.50	63/37
11		$PhC(CF_3)_2OH$	58	90/17	6300	6100	1.53	64/36
12	400/3600	$(CF_3)_2CHOH$	245	85/9	7400	3900	1.87	50/50
13		$(CF_3)_3COH$	245	96/11	8500	4200	1.79	50/50
14[f]	2000/2000	toluene	53	86/11		37800	2.83	87/13
15[f]		$(CF_3)_2CHOH$	60	90/32		20700	2.90	71/29

[a] Polymerization conditions: [methyl acrylate]$_0$ + [1-hexene]$_0$ = 4.0 M, [methyl acrylate]$_0$/[ethyl 2-iodoisobutyrate]$_0$/$[Mn_2(CO)_{10}]_0$/$[I_2]_0$ = 1000/20/20/5, 40 °C under visible light. [b] The monomer conversion and the monomer composition ratio were determined by ^{1}H NMR. [c] M_n(calcd) = MW(methyl acrylate) × [methyl acrylate]$_0$/[ethyl 2-iodoisobutyrate]$_0$ × convn(MA) + MW(1-hexene) × [1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$ × convn(1-hexene) + MW(ethyl 2-iodoisobutyrate). [d] The number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography in THF [poly(methyl methacrylate) standard]. [e] [methyl acrylate]$_0$/[1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$/$[Mn_2(CO)_{10}]_0$/$[I_2]_0$ = 2000/2000/40/40/0. [f] [methyl acrylate]$_0$/[1-hexene]$_0$/[2,2′-azobisisobutyronitrile]$_0$ = 2000/2000/40 mM.

ppm, respectively. In addition to these large peaks, there are characteristic small signals that originated from the EMA−I; the ethyl ester (*i*) protons at the α-end were observed at 4.1 ppm. The M_n was calculated from the α-end signal (*i*/2) to the main-chain MA (*c*/3) and 1-Hex (*g*/3) units [M_n(NMR) = 6200; obtained in toluene], which was in good agreement with that by SEC [M_n(SEC) = 6200; obtained in toluene] against the PMMA calibration and was slightly higher than the calculated value [M_n(calcd) = 5200]. These results indicate that one molecule of EMA−I served as an initiator to form one polymer

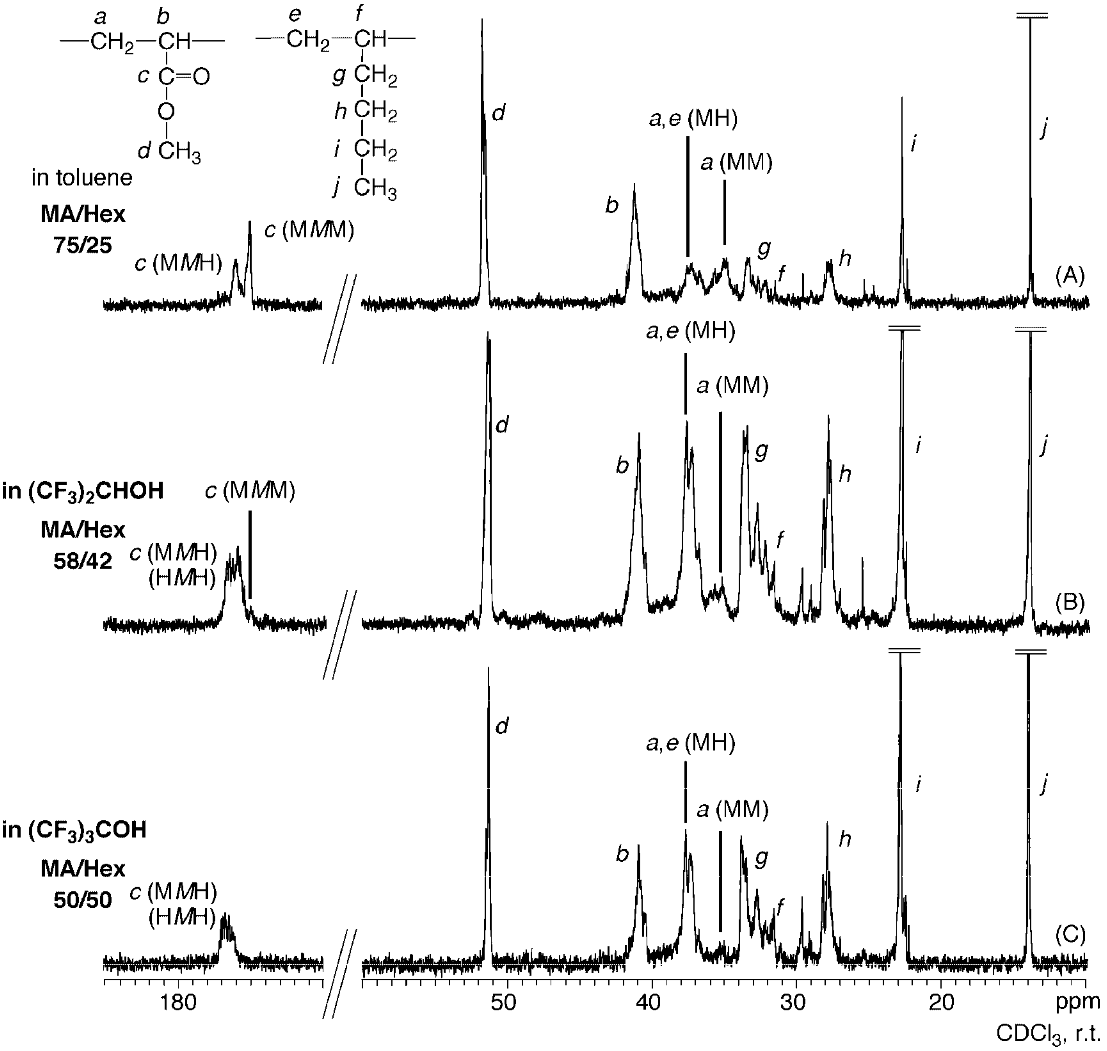


Figure 6. ^{13}C NMR spectra (100 MHz, $\mathrm{CDCl_3}$, 25 °C) of poly[(methyl acrylate)-*co*-(1-hexene)] obtained with ethyl 2-iodoisobutyrate/$\mathrm{Mn_2(CO)_{10}/I_2}$ in toluene (A), $\mathrm{(CF_3)_2CHOH}$ (B), or $\mathrm{(CF_3)_3COH}$ (C) at 40 °C under visible light; [methyl acrylate]$_0$/[1-hexene]$_0$/[ethyl 2-iodoisobutyrate]$_0$/[$\mathrm{Mn_2(CO)_{10}}$]0/[$\mathrm{I_2}$]$_0$ = 1000/3000/20/20/5.0 mM (A, B) or 400/3600/8.0/8.0/2.0 mM (C), respectively.

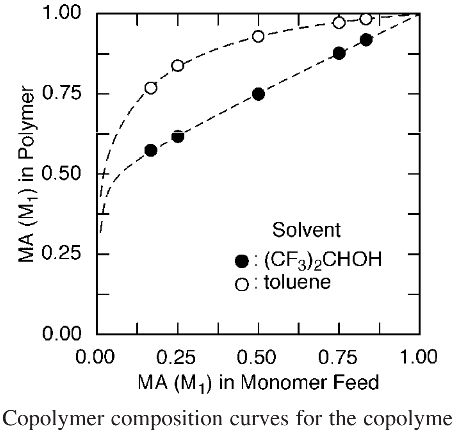


Figure 7. Copolymer composition curves for the copolymerization of methyl acrylate ($\mathrm{M_1}$) and 1-hexene ($\mathrm{M_2}$) in $\mathrm{(CF_3)_2CHOH}$ (●) or toluene (○) at 40 °C: [methyl acrylate]$_0$ = 0.67−3.33 M, [1-hexene]$_0$ = 3.33−0.67 M, [methyl acrylate]$_0$ + [1-hexene]$_0$ = 4.0 M, and [2,2′-azobisisobutyronitrile]$_0$ = 20 mM. The dashed lines indicate $r_1 = 2.06$, $r_2 = 0.01$ in $\mathrm{(CF_3)_2CHOH}$ and $r_1 = 12.3$, $r_2 = 0.005$ in toluene, respectively.

chain. Thus, the controlled/living radical copolymerization of MA and 1-Hex with EMA−I/$\mathrm{Mn_2(CO)_{10}/I_2}$ was further confirmed by the ^{1}H NMR analysis.

The copolymer compositions, i.e., the MA/1-Hex ratios, were then calculated from the peak intensities of the methyl ester (*e* for MA) and the pendent methyl (*g* for 1-Hex) protons, which agreed well with the values calculated from the initial charge ratio and conversions of the two monomers. Thus, all of the consumed monomers were incorporated into the copolymers. The signals of the 1-Hex units (*d*−*g*) of the copolymers obtained in the fluoroalcohols were much larger than those in toluene under the same conditions, where the MA/1-Hex ratios were 75/25 in toluene (Figure 5A) and 58/42 in $\mathrm{(CF_3)_2CHOH}$ (Figure 5B). These results indicate that the fluoroalcohols were effective for enhancing the 1-Hex incorporation.

To further investigate the comonomer sequences, the copolymers were also analyzed by ^{13}C NMR spectroscopy (Figure 6).[47] The signals originating from the alternating sequence were apparently dominated in $\mathrm{(CF_3)_2CHOH}$ (Figure 6B) [*a*,*e* (MH) for the diad and *c* (M*M*H and H*M*H) for the triad (M = MA, *H* = 1-Hex)], whereas that obtained in toluene (Figure 6A) showed almost the same peak areas of the MA−MA [*a* (MM) and *c* (M*M*M)] and MA−1-Hex sequence [*a*,*e* (MH) and *c* (M*M*H and H*M*H)]. These results indicate that the fluoroalcohols promote the cross-propagation between MA and 1-Hex to enhance the 1-Hex incorporation. This is most probably due to the hydrogen-bonding interaction between the protic fluoroalcohols and the carbonyl groups of the MA units to decrease the electron density of the vinyl group of MA and the growing MA radical, which facilitate the reaction with the nucleophilic

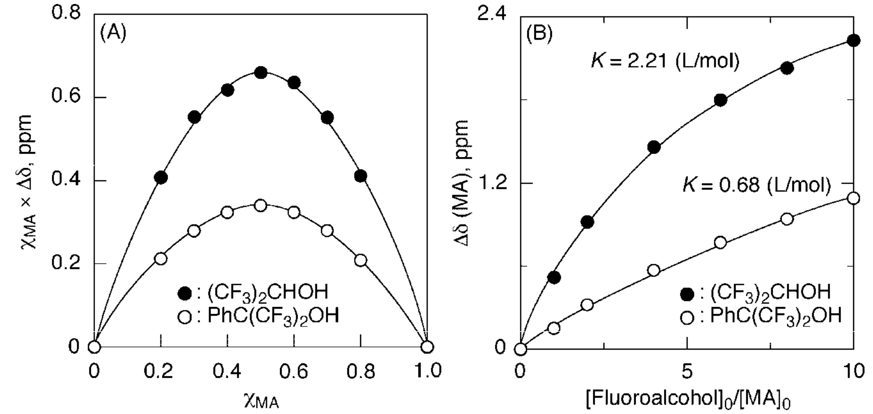


Figure 8. Job plots for the association of $(CF_3)_2CHOH$ (●) or $PhC(CF_3)_2OH$ (○) with methyl acrylate evaluated from the changes in chemical shift (ppm) of the carbonyl carbon of methyl acrylate ($[\text{methyl acrylate}]_0 + [\text{fluoroalcohol}]_0 = 1.0$ M, 100 MHz, $CDCl_3$, 40 °C). χ_{MA}: molar fraction of methyl acrylate (A) and NMR titration from the changes in the carbonyl carbon chemical shifts of methyl acrylate in $(CF_3)_2CHOH$ (●) or $PhC(CF_3)_2OH$ (○) ($[\text{methyl acrylate}]_0 = 100$ mM, $[\text{fluoroalcohol}]_0 = 100-1000$ mM, 100 MHz, $CDCl_3$, 40 °C) (B).

1-Hex radical and the electron-rich C=C bond of 1-Hex, respectively, as the metal Lewis acids do via coordination to the carbonyl goups.[21,34]

4. Effects of Fluoroalcohols on Copolymerizations of MA and 1-Hex. To clarify the effect of the fluoroalcohols on the copolymerizations, various fluoroalcohols were similarly employed as solvents for the copolymerization of MA and 1-Hex with EMA−I/$Mn_2(CO)_{10}/I_2$ at 40 °C (Table 1). While the 1-Hex contents in the copolymer products depended on the type of fluoroalcohols as well as on the comonomer feed ratios, all the fluoroalcohols improved the incorporation of 1-Hex. Among them, $(CF_3)_2CHOH$ ($pK_a = 9.3$)[48] and $(CF_3)_3COH$ ($pK_a = 5.2$)[48] proved most effective, in which the highest 1-Hex contents were achieved (MA/1-Hex = 58/42) with $[MA]_0/[1\text{-Hex}]_0 = 1/3$. A less protic alkyl fluoroalcohol, CF_3CH_2OH ($pK_a = 12.4$),[48] resulted in lower 1-Hex content (MA/1-Hex = 63/37). In contrast, bulky cumyl-type fluoroalcohols, such as $PhC(CF_3)_2OH$ ($pK_a = 8.8$)[49] and $m\text{-}C_6H_4[C(CF_3)_2OH]_2$, resulted in relatively low 1-Hex incorporations (MA/1-Hex = 64/36 and 63/37) although they were most effective in increasing the syndiospecificity in the polymerizations of vinyl acetate[46] and methyl methacrylate.[40] A similar enhancement of the 1-Hex incorporation by fluoroalcohols was also observed in the conventional free radical copolymerization with AIBN (entries 14 and 15 in Table 1). The copolymerization-enhancing effects are most probably related to the degrees of the interaction between the MA and fluoroalcohols, as will be discussed later.

The MWDs of the copolymers also depended on the solvents.[46] In particular, fluoroalcohols containing the C−H bonds adjacent to CF_3-group, such as $(CF_3)_2CHOH$ and CF_3CH_2OH, resulted in the copolymers with relatively broad MWDs ($M_w/M_n > 1.6$), which was most probably caused by some side reactions like hydrogen abstraction from the C−H bond by the highly active growing radical species of 1-Hex.

To attain still higher α-olefin contents, copolymerization at a higher 1-Hex feed ratio $[MA]_0/[1\text{-Hex}]_0 = 1/9$ was conducted in the most effective fluoroalcohols, $(CF_3)_3COH$ and $(CF_3)_2CHOH$, with EMA−I/$Mn_2(CO)_{10}/I_2$ at 40 °C (entries 12 and 13 in Table 1). The obtained copolymers showed an almost equivalent content of MA and 1-Hex (MA/1-Hex = 50/50). The ^1H NMR spectrum of the copolymers obtained in $(CF_3)_3COH$ obviously showed a different shape for peak b, which can be attributed to the methine protons of the MA−1-Hex sequence (Figure 5C). Furthermore, the ^{13}C NMR also showed the very predominant formation of the MA−1-Hex sequence [*a*,*e* (MH)] and minimal amount of the MA−MA sequence [*a* (MM)] (Figure 6C). These results indicate the formation of almost alternating copolymers between MA and 1-Hex in the fluoroalcohols under mild conditions. Thus, the fluoroalcohols proved highly effective for the copolymerizations of acrylic monomers and nonpolar olefins and compatible with the Mn-based controlled/living radical polymerization systems.

The monomer reactivity ratios of MA (M_1) and 1-Hex (M_2) in $(CF_3)_2CHOH$ and toluene were then determined by analyzing the AIBN-initiated radical copolymerizations of the two monomers at varying comonomer feed compositions at 40 °C ($[MA]_0 + [Hex]_0 = 4.0$ M, $[AIBN]_0 = 20$ mM) (Supporting Information). The obtained copolymer composition curves are shown in Figure 7. The monomer reactivity ratios were calculated by the Kelen−Tüdõs method (see also Supporting Information).[50] The r_2 values, close to zero, indicate almost no homopropagation of 1-Hex even in the fluoroalcohol as in toluene. However, the r_1 value was much lower in $(CF_3)_2CHOH$ ($r_1 = 2.06$) than in toluene ($r_1 = 12.3$). The reciprocal values of these were $1/r_1 = 0.49$ [in $(CF_3)_2CHOH$] and 0.081 (in toluene), indicating that the relative reactivity of the MA radical to 1-Hex increased by about 6 times in the fluoroalcohol. It can be most probably attributed to the hydrogen-bonding interaction of the fluoroalcohols with the carbonyl groups of the MA units, which enhances the cross-propagation to the electron-rich nonpolar monomer, 1-Hex.

5. Interaction of Fluoroalcohols with MA. To observe the possible interaction between the fluoroalcohols and MA, the mixtures of MA and $(CF_3)_2CHOH$ or $PhC(CF_3)_2OH$ were analyzed by ^1H and ^{13}C NMR spectroscopies.

Upon the addition of MA to the $CDCl_3$ solution of $(CF_3)_2CHOH$ or $PhC(CF_3)_2OH$ at 40 °C, the carbonyl carbon of MA shifted to a lower field, while the hydroxyl proton of the fluoroalcohols also shifted downfield via the hydrogen-bonding as in the case with VAc.[39,46] The stoichiometry of the interactions based on Job's method was evaluated and showed the 1:1 interaction between the monomer and the fluoroalcohols (Figure 8A). The equilibrium constants (K) of the complexes between MA and the fluoroalcohols were also determined by ^{13}C NMR titration experiments (Figure 8B). The K_{assn} values of MA−$(CF_3)_2CHOH$ and MA−$PhC(CF_3)_2OH$ were calculated to be 2.21 and 0.68 L/mol, respectively, which are consistent with the 1-Hex incorporation in the copolymerization. Thus, the acidic fluoroalcohols interact with the carbonyl groups of the MA units via hydrogen bonding in order to be effective for enhancing the cross-propagation.

Conclusion

The manganese-based initiating system proved effective for the controlled/living radical copolymerization of acrylic monomers and nonpolar α-olefins most probably due to the fact that the highly active manganese radical species [$^{\bullet}\mathrm{Mn(CO)_5}$] was generated from $\mathrm{Mn_2(CO)_{10}}$ at a controlled rate under weak visible light irradiation. Fluoroalcohols proved to have significant effects on enhancing the incorporation of the nonpolar monomer units via a hydrogen-bonding interaction with the carbonyl moieties of the acrylic monomer units resulting in the almost alternating copolymers when excess nonpolar olefins were employed. These two systems were compatible and thus the combination was highly effective for the synthesis of the high α-olefin content (up to 50 mol %) copolymers with controlled molecular weights under mild conditions.

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Supporting Information Available: Text giving the method of deteriming the monomer reactivitiy ratios, a table of copolymerization data, and figures showing plots of the data for determining monomer reactivity ratios in toluene and in $\mathrm{(CF_3)_2CHOH}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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