Macromonomer Synthesis Using Oligomers of ω-Unsaturated Methacrylate as Addition−Fragmentation Chain Transfer Agents: Increased Efficiency by Manipulation of Steric Hindrance

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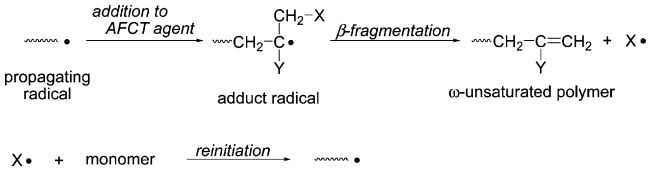
ABSTRACT: The benzene solution polymerizations of ethyl methacrylate (EMA), cyclohexyl acrylate (CHA), and styrene (St) in the presence of ω-unsaturated methyl methacrylate oligomers (MMA-*n*; n = 2−4) and cyclohexyl methacrylate oligomers (CHMA-*n*; n = 2 and 3) as addition−fragmentation chain transfer (AFCT) agents have been studied to synthesize macromonomers efficiently by radical polymerization. The number of unsaturated end groups per chain (f) was used as an index to evaluate the effectiveness of the AFCT agents. In the EMA and St polymerizations, greater steric hindrance of the α-substituent of the AFCT agent and higher temperatures yielded polymers with higher f, and the level of retardation decreased with increasing f. CHA polymerization in the presence of MMA-*n* at 60 °C resulted in high-f polymer, although accompanied by marked retardation. Polymer structure analysis revealed that backward β-fragmentation of the EMA adduct radical, resulting in regeneration of the propagating radical and the AFCT agent, is a significant reaction mode of the adduct radical.

Introduction

Macromonomers bearing unsaturated end groups (e.g., 2-substituted-2-propenyl end groups) that are reactive toward addition of propagating radicals of monomers such as methacrylates, acrylates, and styrene (St) have attracted attention as useful precursors for synthesis of branched or graft polymers by conventional free radical polymerization.[1−5] Macromonomer synthesis by conventional radical polymerization, and the reactions of these macromonomers, have been widely studied in recent years.[1,5−10] The approach has the advantage of its lenient conditions compared to living ionic polymerizations. Catalytic chain transfer (CCT) polymerization[11,12] is one of the most effective methods to prepare macromonomers in radical polymerization. However, effective CCT polymerization resulting in carbon−carbon double bonds feasible to propagating radical addition is restricted to the homopolymerization and copolymerization of α-methylvinyl compounds such as methyl methacrylate (MMA) and α-methylstyrene.[9,10] The polymerization of acrylates and St at high temperature has been also shown to yield macromonomers via formation of midchain radicals followed by β-fragmentation.[8,9,13]

Addition−fragmentation chain transfer (AFCT) is known to be compatible with a variety of conjugate monomers such as methacrylates, acrylates, and St, and a number of α-(substituted methyl)vinyl compounds (CH_2═$C(CH_2X)Y$) have been reported as AFCT agents.[10,14−21] Furthermore, the variation of the chain transfer constant (C_{tr}) among monomers except for nonconjugated monomers is relatively small in comparison with conventional chain transfer agents such as carbon tetrachloride.[22] Addition of a propagating radical to the double bond of the AFCT agent is followed by β-fragmentation of the adduct radical, and the radical expelled by β-fragmentation adds to monomer to reinitiate the polymerization as shown in Scheme 1, where X· represents expelled radical. To effectively obtain polymers bearing ω-unsaturated end groups, AFCT is required to be the main end forming event instead of bimolecular termination.

Scheme 1



Methyl α-(bromomethyl)acrylate, a typical AFCT agent, has large C_{tr} values for polymerization of MMA, methyl acrylate (MA), and St at 60 °C:[17] 0.93, 2.93, and 2.34, respectively.[15] ^{1}H NMR studies have revealed that 2-carbomethoxy-2-propenyl end groups are introduced almost quantitatively at the ω-ends of poly(MMA) and poly(St).[17] Ethyl α-(bromomethyl)acrylate also has a large C_{tr} value for the polymerization of MMA at 60 °C, C_{tr} = 1.5.[23] Further examples include α-(alkylsulfenylmethyl)acrylates[24] and α-(arylsulfonylmethyl)acrylates,[20] which function as highly reactive AFCT agents introducing 2-carboalkoxy-2-propenyl end groups. Investigations of AFCT involving C−C bond cleavage during the β-fragmentation step are much more scarce than those of the typical AFCT systems where C-heteroatom bond cleavage occurs. ω-Unsaturated MMA oligomers (MMA-*n*), which do not homopolymerize due to its bulky α-substituent, act as an AFCT agent.[1,3,19,25−28] However, the C_{tr} value of methyl α-(2-methyl-2-carbomethoxypropyl)acrylate (ω-unsaturated MMA dimer; MMA-2) for MMA is small (C_{tr} = 0.013 at 60 °C), and the functionality of the resulting poly(MMA) in the presence of MMA-2 has not been quantified.[19]

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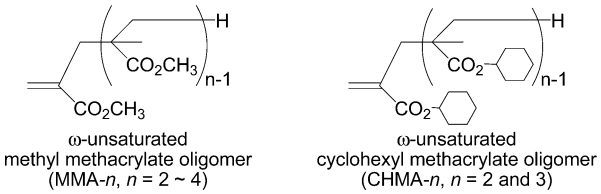
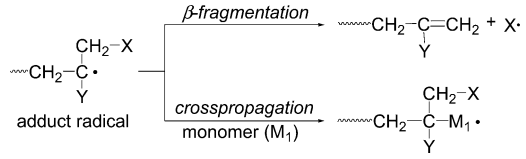
Scheme 2



Scheme 3



We previously studied the reactivity of ω-unsaturated MMA oligomers (MMA-*n*; $n = 2-5$) and ω-unsaturated cyclohexyl methacrylate oligomers (CHMA-*n*; $n = 2$ and 3) (Scheme 2) toward addition of the *tert*-butoxy radical employing the nitroxide trapping method.[29] It was revealed that the addition to MMA-*n* is suppressed by up to a factor of 4 in comparison with addition to MMA. The double bond of CHMA-*n* is as reactive as that of MMA-*n* toward addition of highly reactive radicals such as the *tert*-butoxy radical, indicating that CHMA-*n* has potential as an efficient AFCT agent.

This study deals with the polymerization of methacrylates, acrylates, and St in the presence of the ω-unsaturated methacrylate oligomers (RMA-*n*) MMA-*n* ($n = 2-4$) and CHMA-*n* ($n = 2$ and 3) as AFCT agents, where β-fragmentation proceeds via C−C bond cleavage. Detailed kinetic analyses were carried out, focusing on the competition between the two main reaction modes of the adduct radicals: β-fragmentation and addition to monomer (cross-propagation) (Scheme 3). The effects of steric hindrance of the α-substituent of the AFCT agent and the reaction temperature were also investigated, with the overall objective being efficient macromonomer preparation.

Experimental Section

Materials. MMA-*n* ($n = 2-4$) and CHMA-*n* ($n = 2$ and 3) were prepared by CCT polymerization of MMA and CHMA, respectively,[30] and were purified as described in our previous report.[29] Commercial ethyl methacrylate (EMA) (supplied by Kishida), cyclohexyl methacrylate (CHMA) (Kishida), cyclohexyl acrylate (CHA) (Kishida), and St (Kishida) were distilled under reduced pressure before use. Commercially available 2,2′-azobis(isobutyronitrile) (AIBN) (Wako) and 1,1′-azobis-(cyclohexane-1-carbonitrile) (ACN) (Wako) were used after recrystallization from methanol. *tert*-Butyl peroxide (TBP) (Kishida) was used without further purification. Solvents were purified by conventional methods.

Polymerization Procedure. A typical experiment was carried out as follows: 2 mL of benzene stock solution containing EMA (6.0 mol L^{-1}) and AIBN (0.02 mol L^{-1}), 0.3 mL of benzene stock solution containing MMA-2 (2.0 mol L^{-1}), and 1.7 mL of benzene were placed in a Pyrex glass tube, and polymerization was carried out under vacuum after three freeze−thaw cycles. After polymerization at 60 °C for 3.5 h, the EMA conversion was determined by integration of the ^{1}H NMR resonances due to the methyleneoxy groups of the unreacted monomer (4.2 ppm) and of the polymer (4.0 ppm): EMA conversion = 27.6%. Benzene was subsequently evaporated off, and the polymer was isolated by preparative HPLC (as opposed to precipitation) in order to avoid any loss of oligomeric products. After drying under vacuum overnight, the polymer was characterized by GPC and ^{1}H NMR spectroscopy.

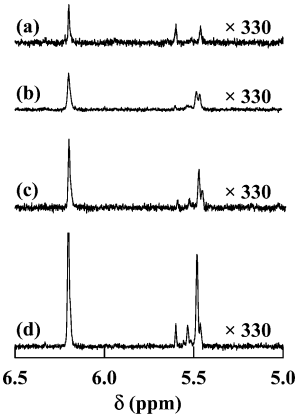


Figure 1. ^{1}H NMR spectra of poly(EMA)s obtained at 60 °C in the absence of MMA-2 (a) and in the presence of MMA-2: [MMA-2] in feed = 4.8 mol % (b), [MMA-2] in feed = 9.1 mol % (c), and [MMA-2] in feed = 23.1 mol % (d).

The ^{1}H NMR resonances due to the methyneoxy groups of the unreacted monomer (4.8 ppm) and of the polymer (4.7 ppm) were used for determination of CHMA and CHA conversions. In the case of St polymerization, the conversion was determined by gravimetry using methanol as precipitant. After the polymer was weighed, the filtrate was combined with the polymer to avoid any loss of oligomeric products, followed by evaporation of the solvent and separation of polymer from unreacted monomer and AFCT agent by preparative HPLC.

Measurements. Molecular weights were obtained by gel permeation chromatography (GPC), a Tosoh 8000 series GPC system equipped with TSK-gel columns G5000H_{HR}, GMultipoerH_{XL}-M, GMH_{HR}-L (5 μm particle sizes; exclusion limits are 4×10^6, 2×10^6, and 4×10^6, respectively) connected in this order and with differential refractometer (RI-8082). Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL min^{-1}. Poly(St) standards (M_n = 500−1 090 000) were used for calibration. ^{1}H NMR spectra were recorded on a JEOL α-400 spectrometer at 400 MHz. Deuteriochloroform and tetramethylsilane were used as solvent and internal standard, respectively. A recycle preparative HPLC (Japan Analytical Industry LC-908) equipped with JAIGEL 2H and 1H columns (poly(St) gel; 15 μm particle size) connected in this order and with differential refractometer (RI-5) and UV detector (UV-310) was employed for isolation of polymers from the reaction mixtures. Chloroform was used as the eluent at a flow rate of 3.5 mL min^{-1} at room temperature.

Results and Discussion

Polymerization of Methacrylates. Benzene solution polymerizations of EMA (M_1) were carried out in the presence of MMA-2 (M_2) at 60 °C. ^{1}H NMR spectra of poly(EMA)s obtained in the absence and presence of M_2 show *trans*- and *cis*-olefinic protons of the end group at around 5.5 and 6.2 ppm, respectively (Figure 1).[5,31] The resonances of olefinic protons in Figure 1a are assigned to the 2-carbethoxy-2-propenyl end group generated by disproportionation, which is the dominant termination mode in methacrylate polymerization[32,33] (the *trans*-proton exhibits two peaks at 5.47 and 5.60 ppm due to tacticity of polymer).[31] Two new peaks appear at 5.48 and 5.53 ppm due to the 2-carbomethoxy-2-propenyl end group generated by AFCT (Figure 1b,c).[5] The peak intensities of the *trans*-protons due to disproportionation relative to AFCT decrease with increasing [M_2] in the feed, illustrating that the contribution of bimolecular termination as an end-forming event gradually decreases.

The results of the polymerizations are listed in Table 1. The number of M_2 units per polymer chain (N_{M_2}),

Table 1. Results of the Benzene Solution Polymerization of EMA (M_1) in the Presence of MMA-2 (M_2) at 60,[a] 90,[b] and 120 °C[c]

temp (°C)	$[M_2]$ in feed (mol %)	M_1 conv (%) (rel M_1 conv[d])	M_n(GPC) (rel DP[e])	f	N_{M_2}	CRP/FRG[f]
60	0.0	33.3 (1.00)	98000 (1.00)			
60	4.8	27.6 (0.83)	58000 (0.59)	0.45	$1_{.1}$	1.4_5
60	9.1	23.6 (0.71)	46000 (0.47)	0.47	$1_{.1}$	1.2_5
60	23.1	15.1 (0.45)	26000 (0.26)	0.53	$1_{.4}$	1.8_1
90	0.0	21.7 (1.00)	140000 (1.00)			
90	4.8	21.1 (0.97)	71000 (0.52)	0.52	0.9_2	0.7_6
90	23.1	15.3 (0.71)	23000 (0.17)	0.70	$1_{.1}$	0.6_1
120	0.0	10.2 (1.00)	210000 (1.00)			
120	4.8	10.1 (0.99)	70000 (0.33)	0.72	$1_{.1}$	0.6_4
120	23.1	9.7 (0.96)	19000 (0.09)	0.92	$1_{.2}$	0.3_2

[a] $[M_1] = 3.0$ mol L^{-1} and $[AIBN] = 0.010$ mol L^{-1} for 3.5 h. [b] $[M_1] = 3.0$ mol L^{-1} and $[ACN] = 0.004$ mol L^{-1} for 1 h. [c] $[M_1] = 3.0$ mol L^{-1} and $[TBP] = 0.007$ mol L^{-1} for 0.5 h. [d] Conversion of M_1 relative to the conversion in the absence of M_2. [e] Degree of polymerization (DP) relative to the DP in the absence of M_2. [f] Ratio of cross-propagation rate to β-fragmentation rate.

including as an end group, was obtained from the polymer composition and M_n(GPC) using eq 1.

$$N_{M_2} = F_2 \frac{M_n(\text{GPC})}{F_1 M_{M_1} + F_2 M_{M_2}} \quad (1)$$

where F_1 and F_2 represent the molar fractions of M_1 and M_2 in the polymer, respectively, and M_{M_1} and M_{M_2} are the molecular weights of monomeric M_1 and M_2, respectively. The f value represents the number of unsaturated end groups per polymer chain and is expressed as $f = M_n(\text{GPC})/M_n(\text{NMR})$. M_n(NMR) was calculated from the total integrations of the ^{1}H NMR resonances due to the olefinic protons from AFCT and disproportionation (the methyleneoxy protons of the EMA units (3.9−4.2 ppm) and the methoxy protons of the MMA-2 units (3.6−3.8 ppm)), assuming that each polymer chain contains one unsaturated ω-end group:

$$M_n(\text{NMR}) = \frac{[\text{OCH}_2] \times M_{M_1} + [\text{OCH}_3]/n \times M_{M_2}}{[\text{CH}_2{=}\text{C}]} \quad (2)$$

where $n = 2$ for MMA-2. The ratio of cross-propagation to β-fragmentation of the adduct radicals (CRP/FRG) was estimated assuming that the effect of bimolecular termination of the adduct radical can be neglected according to eq 3:

$$\frac{\text{CRP}}{\text{FRG}} = \frac{[M_2 \text{ unit}][\text{CH}_2{=}\text{C group}]}{[\text{CH}_2{=}\text{C group}]} \quad (3)$$

where $[M_2$ unit$]$ and $[CH_2{=}C$ group$]$ in mol % were calculated from the ^{1}H NMR resonances due to the methoxy and propenyl groups, respectively.

The EMA conversion clearly decreases with increasing $[M_2]$ in the feed (Table 1). This retardation is most likely to be a result of the addition of the adduct radical to EMA (cross-propagation) and β-fragmentation of the adduct radical from EMA and M_2 not being sufficiently fast. Evaluation of C_{tr} based on the Mayo method and the chain length distribution method may result in erroneous values when there is significant retardation as observed in many cases in this study. Therefore, the effectiveness of the AFCT agents was instead assessed by means of the value of f, which is equal to unity when each polymer chain contains one unsaturated end group. The value of f increases with increasing $[M_2]$ in the feed, but it was only 0.53 even at the highest $[M_2]$ (23.1 mol %), where the calculation of M_n(NMR) also includes the ω-unsaturated end groups formed by disproportionation. The value of N_{M_2} is close to unity, showing that each chain on the average contains one M_2 unit, either as an end group or as part of the polymer backbone. The value of CRP/FRG is larger than unity, indicating that cross-propagation is preferred to β-fragmentation under these conditions.

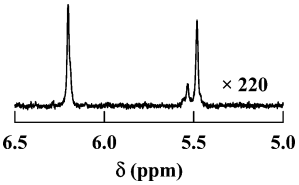


Figure 2. ^{1}H NMR spectrum of poly(EMA) obtained in the presence of 23.1 mol % [MMA-2] in the feed at 90 °C.

Effect of Reaction Temperature. Polymerization of EMA (M_1) in the presence of MMA-2 (M_2) was carried out at higher temperatures, 90 and 120 °C, with the expectation that a temperature increase would result in more significant acceleration of β-fragmentation of the adduct radicals (unimolecular reaction) relative to cross-propagation and bimolecular termination (bimolecular reactions). The ^{1}H NMR resonances of the end group generated by disproportionation were not observed at 90 °C in the presence of 23.1 mol % of M_2 in the feed (Figures 2). At 120 °C, disproportionation was not observed even at the lower feed content of 4.8 mol % of M_2, illustrating that an increase in temperature reduces the contribution of disproportionation to a negligible amount.

The f values increased with increasing $[M_2]$ in the feed and with increasing temperature, reaching as high as 0.92 at 120 °C without retardation (Table 1). The CRP/FRG values decreased as expected with increasing temperature, and β-fragmentation dominates over cross-propagation at both 90 and 120 °C. The N_{M_2} value is close to one and shows that a single M_2 unit is introduced as end group when the f value is close to unity. The relative decrease in M_n upon addition of the M_2 becomes significantly more pronounced as the temperature is increased; at 120 °C, the highest $[M_2]$ in the feed results in a greater reduction in M_n than at 60 °C by a factor of almost 3. This is consistent with the decreasing contribution of cross-propagation with increasing temperature.

Effect of Initiator Concentration. EMA (M_1) polymerization in the presence of MMA-2 (M_2) at 90 °C was carried out at two initiator concentrations differing by a factor of 13. The higher level of initiator concentration lead to lower values of M_n as well as a smaller relative decrease in M_n with increasing $[M_2]$ in the feed (Figure 3a). The f value was markedly higher (30−50%) at the lower initiator concentration over the whole range of the $[M_2]$ in the feed (Figure 3b) as a result of less contribution of bimolecular termination as an end-forming reaction.

Effect of AFCT Agents. MMA-3, CHMA-2, and CHMA-3 (M_2), which have bulkier α-substituents than MMA-2, were used as AFCT agents in EMA polymerization at 60 °C. The use of MMA-3 resulted in a higher f value with a sufficient reduction in M_n in comparison with MMA-2 (Table 2). However, in the presence of a

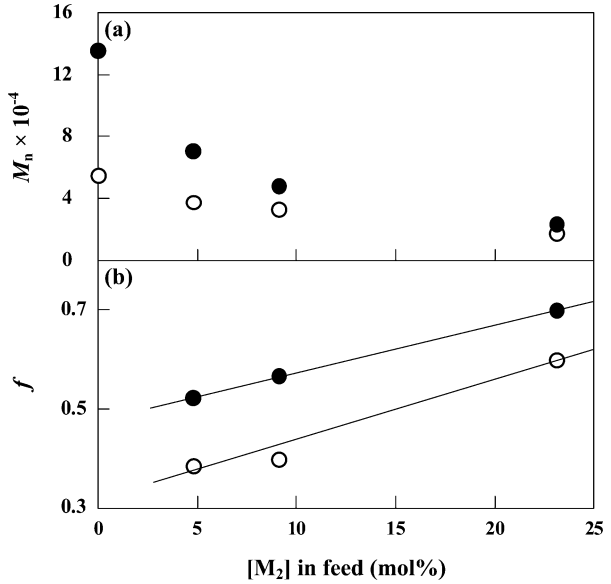


Figure 3. M_n values (a) and f values (b) for poly(EMA)s obtained in the presence of MMA-2 (M_2) at 90 °C with [ACN] = 0.004 mol L^{-1} for 1 h (●) and 0.05 mol L^{-1} for 20 min (○) in benzene at conversions of 23% or below.

Table 2. Results of the Benzene Solution Polymerization of EMA (M_1) in the Presence of RMA-*n* (M_2) at 60 °C[a]

[M_2] in feed (mol %)	rel M_1 conv[b]	M_n(GPC) (rel DP[c])	f	N_{M_2}	CRP/FRG[d]
MMA-3, 4.8[e]	0.77	11000 (0.13)	0.72	0.7_8	0.08_3
MMA-3, 23.1[e]	0.52	3800 (0.04)	0.81	0.9_5	0.1_7
CHMA-2, 13.0[f]	0.84	44000 (0.44)	0.64	0.7_7	0.2_1
CHMA-3, 4.8[f]	0.97	7200 (0.06)	0.68	0.7_0	0.02_2
CHMA-3, 23.1[f]	0.80	2100 (0.02)	0.82	0.8_2	≈0[g]

[a] [M_1] = 3.0 mol L^{-1} and [AIBN] = 0.010 mol L^{-1}. [b] Conversion of M_1 relative to the conversion in the absence of M_2. [c] Degree of polymerization (DP) relative to the DP in the absence of M_2. [d] Ratio of cross-propagation rate to β-fragmentation rate. [e] Polymerization for 3.5 h. [f] Polymerization for 3 h. [g] All M_2 units were introduced into the polymer as end groups. The values of [M_2 unit] − [CH_2═C group] calculated from the ^{1}H NMR spectrum were negative due to the limit of accuracy of the integration of the ^{1}H NMR resonances.

high concentration of MMA-3 in the feed (23.1 mol %), marked retardation was still observed. In the case of CHMA-2, the f value was slightly higher and the retardation was milder than for MMA-2; however, the polymer formed shows ^{1}H NMR resonances due to olefinic protons by both AFCT and disproportionation. The use of 23.1 mol % of CHMA-3 in the feed attained almost quantitative introduction of ω-unsaturated end groups (no disproportionation detected) and significantly reduced M_n (relative DP = 0.02) with only slight retardation. CHMA-3 resulted in similar f values and reductions in M_n as MMA-3 and has the advantage that it gives considerably less retardation than MMA-3. The CRP/FRG values for CHMA-*n* are lower than those of MMA-*n*, suggesting acceleration of β-fragmentation to relieve internal strain and suppression of cross-propagation of the adduct radical from CHMA-*n* due to steric congestion caused by the ester cyclohexyl group.

Polymer Composition. The molar fraction of M_2 in the polymer obtained at 60 °C is plotted vs the molar fraction of M_2 in the feed in Figure 4. The polymer formed in the presence of RMA-3 contains a larger amount of M_2 units than RMA-2, and the content of CHMA-3 is higher than that of MMA-3. We previously showed that addition of the *tert*-butoxy radical to RMA-*n*

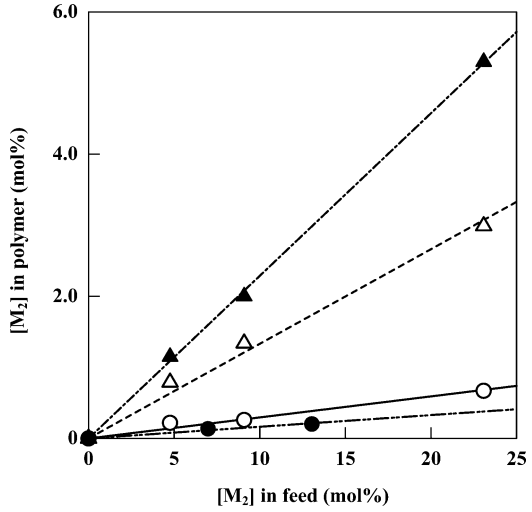
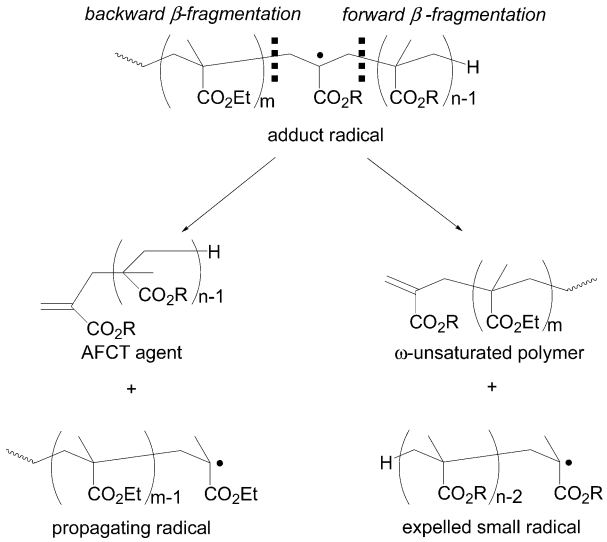


Figure 4. M_2 contents in poly(EMA) obtained in the presence of MMA-2 (○), MMA-3 (△), CHMA-2 (●), and CHMA-3 (▲) (M_2) in benzene at 60 °C.

Scheme 4. Backward and Forward β-Fragmentation of the Adduct Radical



(MMA-*n*; n = 2−5 and CHMA-*n*; n = 2 and 3) is suppressed with increasing n.[29] It was therefore expected that the double bond of RMA-3 is less reactive toward propagating radicals than RMA-2, and thus [M_2] in polymer obtained in the presence of RMA-3 would be lower than that of RMA-2. However, this was not the case.

The adduct radicals formed are believed to undergo "backward" β-fragmentation (i.e., the reverse of the addition step) to some extent, regenerating the AFCT agent and the propagating radical as originally proposed by Moad et al.,[19] and this reduces the M_2 unit content in the polymer and the f value. The adduct radical has two C−C bonds which may cleave to expel a small radical ("forward" β-fragmentation) and the propagating radical ("backward" β-fragmentation), and these radicals are structurally similar (see Scheme 4). The adduct radicals seem to be reluctant to expel a smaller radical, and this results in greater contribution of backward β-fragmentation to the reactions of the RMA-2 adduct radicals than for RMA-3. Assuming that the rate of addition of a propagating radical to CHMA-3 is not higher than to MMA-3 (which appears reasonable), CHMA-3 has the advantage over MMA-3 as an AFCT

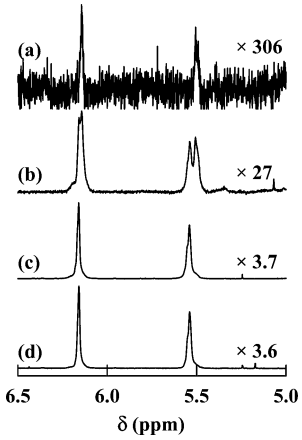


Figure 5. ^{1}H NMR spectra of poly(CHA)s obtained in the absence of MMA-2 (a) and in the presence of 4.8 mol % of [MMA-*n*] in the feed: $n = 2$ (b), $n = 3$ (c), and $n = 4$ (d).

agent that it minimizes backward β-fragmentation, and this may be rationalized in terms of the larger ester alkyl group of the expelled radical. However, MMA-2 and CHMA-2 do not show any significant differences with regards to the apparent extents of backward β-fragmentation. Polymerization of CHMA (M_1), which has a larger ester alkyl group than EMA, was carried out in the presence of MMA-2 (23.2 mol % in the feed) at 60 °C, and this resulted in a lower f (= 0.41) than for EMA ($f = 0.53$) under comparable conditions. This is consistent with the adduct radical being more reluctant to expel a radical having a smaller ester alkyl group. Backward β-fragmentation of the adduct radical can explain the considerable differences between the M_n's of the polymers obtained in the presence of RMA-2 and RMA-3 and also accounts for the very minor effect of n on retardation.

Our discussion based on the polymer composition is consistent with the previous report by Moad et al.,[19] who suggested that the backward β-fragmentation in competition with forward β-fragmentation of the adduct radical from MMA-2 is more significant than that from MMA-*n* ($n \geq 3$) in the polymerization of MMA.

Polymerization of CHA. Polymerizations of CHA (M_1) were carried out in the presence of MMA-*n* ($n = 2-4$) (M_2) at 60 °C in benzene. ^{1}H NMR spectra of poly(CHA)s obtained in the absence and presence of M_2 show the *trans*- and *cis*-olefinic protons at around 5.5 and 6.1 ppm, respectively (Figure 5). The polymerization of acrylates is known to be accompanied by the formation of midchain radicals by intramolecular and/or intermolecular hydrogen abstractions of propagating radicals.[34−36] Subsequent β-fragmentation of the midchain radical generates ω-unsaturated polymer while expelling a radical having the structure of the propagating radical. The resonances of the olefinic protons in Figure 5a are assigned to those of the 2-carbocyclohexyloxy-2-propeynyl end group generated via β-fragmentation of midchain radicals.[8] The *trans*-olefinic protons in Figure 5b exhibit two peaks due to unsaturated end groups formed by AFCT (5.54 ppm)[5] and the β-fragmentation of midchain radicals (5.51 ppm). The intensity of the peak resulting from β-fragmentation of midchain radicals in Figure 5b is much greater than in Figure 5a; it appears that β-fragmentation of midchain radicals is somehow promoted in the presence of MMA-2. This is supported by the fact that the number of unsaturated end groups from β-fragmentation of midchain radicals per chain in the copolymerization of CHA and MMA at high temperature shows close correlation with the content of the CHA−CHA−MMA sequence as the feed ratio of CHA is varied.[37] However, the effect is much stronger in the current study. The *trans*-olefinic proton in the case of MMA-3 and MMA-4 shows only one peak caused by AFCT in Figures 5c,d, illustrating that formation of midchain radical followed by β-fragmentation is not accelerated in the presence of M_2 under these conditions. This is not surprising in view of the fact that the M_2 units are introduced only at the polymer ends as will be described later, and the CHA−CHA−MMA-*n* ($n = 3$ and 4) sequence is hardly obtained.

Table 3. Results of the Benzene Solution Polymerization of CHA (M_1) in the Presence of MMA-*n* (M_2) at 60 °C[a]

[M_2] in feed (mol %)	M_1 conv (%) (rel M_1 conv[b])	M_n(GPC) (rel DP[c])	f	N_{M_2}	CRP/FRG[d]
none	60.4 (1.00)	99000 (1.00)	0.42[e]		
MMA-2, 4.8	13.4 (0.22)	14000 (0.14)	1.1	4.9	3.7
MMA-2, 20.0	3.4 (0.06)	2400 (0.02)	1.0	3.1	2.1
MMA-3, 4.8	20.5 (0.34)	3000 (0.03)	0.72	1.0	0.44
MMA-3, 20.0	2.5 (0.04)	800 (0.01)	0.72	1.0	0.42
MMA-4, 4.8	19.7 (0.33)	3000 (0.03)	0.80	1.0	0.38
MMA-4, 20.0	8.9 (0.15)	1200 (0.01)	0.92	1.2	0.38

[a] $[M_1] = 1.0$ mol L^{-1}, $[M_2] = 0.25$ mol L^{-1}, and [AIBN] = 0.010 mol L^{-1}. [b] Conversion of M_1 relative to the conversion in the absence of M_2. [c] Degree of polymerization (DP) relative to the DP in the absence of M_2. [d] Ratio of cross-propagation rate to β-fragmentation rate. [e] Calculated from ^{1}H NMR resonances due to vinyl protons formed by β-fragmentation of midchain radical.

As shown by the f value being close to unity, the 2-carbalkoxy-2-propenyl end groups were introduced almost quantitatively, and M_n was controlled by the concentration of M_2 and also depended on n (Table 3). However, the behavior of MMA-2 as an AFCT agent is inherently different from that of MMA-3 and MMA-4, and in the case of MMA-2, unsaturated end groups are formed not only by AFCT but also by β-fragmentation of midchain radicals. The contribution of cross-propagation relative to β-fragmentation for MMA-2 is markedly higher than for MMA-3 and MMA-4, and MMA-2 units are introduced not only as end groups but also as monomer units along the polymer backbone as shown by CRP/FRG and N_{M_2}, respectively, leading to much higher M_n values than for MMA-3 and MMA-4. The sterically less congested radical center of the adduct radical from MMA-2 allows cross-propagation accompanied by significant retardation with increasing [M_2]. Considerable retardation (but less than for MMA-2) was also observed for MMA-3 and MMA-4, where the adduct radicals hardly undergo cross-propagation as shown by N_{M_2} being close to unity and CRP/FRG being much smaller than for MMA-2, leading to introduction of M_2 units only at polymer ends. The absolute rates of both cross-propagation and β-fragmentation of these adduct radicals appear to be low. Although a higher temperature might reduce the level of retardation through faster β-fragmentation, further investigations have not been carried out for the reason that an increase in temperature is expected to result in increased contribution of midchain radicals.

The molar fraction of M_2 in the (co)polymer for CHA is plotted vs the molar fraction of M_2 in feed in Figure 6, showing how the M_2 content in the (co)polymer for CHA is close to that in the feed and much higher than for EMA. This suggests that the rate constant for addition of propagating radicals to the AFCT agents are similar to the propagation rate constant. The fact that

Table 4. Results of the Benzene Solution Polymerization of St (M_1) in the Presence of RMA-*n* (M_2) at 60[a] and 120 °C[b]

$[M_2]$ in feed (mol %)	temp (°C)	conv (%) (rel conv[c])	M_n(GPC) (rel DP[d])	*f*	N_{M_2}	CRP/FRG[e]
none	60	10.6 (1.00)	30000 (1.00)			
MMA-2, 5.7	60	3.1 (0.29)	9200 (0.31)		$5._5$	
MMA-3, 4.8	60	2.7 (0.25)	2700 (0.09)	0.52	$1._3$	$2._7$
MMA-3, 23.1	60	n.d.[g]	1300 (0.04)	0.77	$1._7$	$1._2$
none	120	8.0 (1.00)	87000 (1.00)			
MMA-2, 4.8	120	3.8 (0.48)	6700 (0.08)	0.72	$2._6$	$1._5$
MMA-2, 23.1	120	0.8 (0.10)	3800 (0.04)	0.69	$3._4$	$4._0$
MMA-3, 4.8	120	5.6 (0.70)	2100 (0.02)	0.85	0.8_7	0.02_0
MMA-3, 23.1	120	n.d.[f]	630 (0.001)	0.78[g]	0.8_2	0.05_0

[a] $[M_1] = 3.0$ mol L^{-1} and $[AIBN] = 0.010$ mol L^{-1} for 5 h. [b] $[M_1] = 3.0$ mol L^{-1} and $[TBP] = 0.007$ mol L^{-1} for 1 h. [c] Conversion of M_1 relative to the conversion in the absence of M_2. [d] Degree of polymerization (DP) relative to the DP in the absence of M_2. [e] Ratio of cross-propagation rate to β-fragmentation rate. [f] Precipitation was not obtained in methanol due to low molecular weights. [g] Separation of polymer from reaction mixture was not completely successful due to low molecular weights of polymer being close to molecular weight of MMA-3.

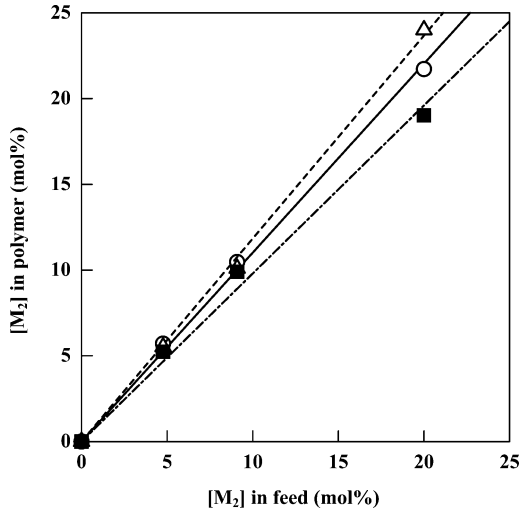


Figure 6. M_2 contents in the poly(CHA) obtained in the presence of MMA-2 (○), MMA-3 (△), and MMA-4 (■) in benzene for 1 h at 60 °C: $[CHA] = 1.0$ mol L^{-1} and $[AIBN] = 0.01$ mol L^{-1}.

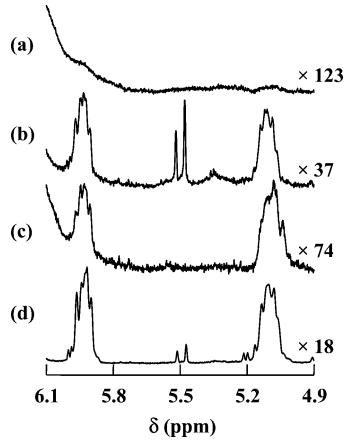


Figure 7. ^{1}H NMR spectra of poly(St)s obtained in the presence of MMA-*n*: [MMA-2] in feed = 5.7 mol % at 60 °C (a), [MMA-3] in feed = 4.8 mol % at 60 °C (b), [MMA-2] in feed = 4.8 mol % at 120 °C (c), and [MMA-3] in feed = 4.8 mol % at 120 °C (d).

the molar fraction of M_2 in the (co)polymer does not show any marked change with increasing *n* of MMA-*n* illustrates only minor, if any, contribution of backward β-fragmentation. Forward β-fragmentation of the adduct radical (expelled radical is a tertiary carbon-centered radical) would be favored and more rapid than backward β-fragmentation (expelled radical is a secondary carbon-centered radical).

Polymerization of St. Polymerizations of St (M_1) were carried out in the presence of MMA-*n* (*n* = 2 and 3) (M_2) at 60 and 120 °C. No peaks assignable to olefinic protons were observed in the ^{1}H NMR spectrum of poly(St) obtained in the presence of MMA-2 at 60 °C (Figure 7a), indicating that all the adduct radicals undergo cross-propagation and/or bimolecular termination. Slower cross-propagation in comparison with homopropagation of St results in a lower M_n in the presence of M_2 (Table 4). The use of MMA-3 at 60 °C generated polymer bearing 2-carbomethoxy-2-propenyl end groups by AFCT as shown in Figure 7b, where the resonances of the *trans*- and *cis*-olefinic protons were

Table 5. Effectiveness of AFCT Agents

M_1	characteristic	observed order	remarks
EMA	*f* at 60 °C	MMA-2 < CHMA-2 ≪ MMA-3 < CHMA-3	suppression of crosspropagation and acceleration of β-fragmentation by α-substituent of AFCT agent
	retardation at 60 °C	RMA-2 ≈ RMA-3 MMA-*n* > CHMA-*n*	reversibility of addition to AFCT agent reduces effect of *n* acceleration of total β-fragmentation by ester alkyl group of AFCT agent
	f (MMA-2)	60 < 90 < 120 °C	more acceleration of β-fragmentation than cross-propagation and bimolecular termination
	retardation (MMA-2)	60 > 90 > 120 °C	faster β-fragmentation
CHA	*f* at 60 °C	MMA-2 ≈ MMA-3 ≈ MMA-4 ($f \approx 1$)	end formation via midchain radicals ($n = 2$) and fast AFCT relative to bimolecular termination ($n = 3$ and 4)
	retardation at 60 °C	significant retardation in all cases	slow crosspropagation and β-fragmentation
St	*f* at 60 °C	MMA-2 ($f = 0$) ≪ MMA-3	suppression of cross-propagation and acceleration of β-fragmentation by α-substituent
	retardation at 60 °C	significant retardation in all cases	slow cross-propagation and β-fragmentation (no β-fragmentation for MMA-2)
	f (MMA-*n* (*n* = 2 and 3))	60 ≪ 120 °C	more acceleration of β-fragmentation than cross-propagation and bimolecular termination
	retardation (MMA-*n* (*n* = 2 and 3))	60 > 120 °C	faster β-fragmentation

detected at around 5.1 and 5.9 ppm, respectively.[38] The polymerizations at 120 °C in the presence of MMA-*n* resulted in higher *f* values than at 60 °C. At this high temperature, MMA-3 operates as a very efficient AFCT agent with high values of *f* and a significant reduction in M_n. An increase in steric congestion around the adduct radical center by use of MMA-3 as opposed to MMA-2 promotes β-fragmentation and suppresses cross-propagation as shown by the N_{M_2} value being close to unity and the much lower values of CPR/FRG. At 120 °C, the extent of cross-propagation of the adduct radical is close to negligible for MMA-3. It appears as if cross-propagation is more likely to occur in the case of St polymerization compared with CHA and EMA, as exemplified by the values of CPR/FRG for MMA-2 and MMA-3 at $[M_2] = 4.8$ mol % in Tables 1−4. Similar findings have been reported for the polymerization of St and MA in the presence of poly(MMA) bearing 2-carbomethoxy-2-propenyl end group.[5]

The extent of retardation can be correlated with the degree of cross-propagation relative to β-fragmentation of the adduct radicals; lower values of CPR/FRG (N_{M_2} approaching unity) lead to less retardation. The extent of retardation by MMA-3 at 120 °C is lower than in the other cases because the adduct radical fragments more rapidly at this high temperature (relative to cross-propagation, since the activation energy of the former is higher) and hardly undergoes cross-propagation. β-Fragmentation of the adduct radical from MMA-3 generates the 4,2-bis(carbomethoxy)-4-methyl-2-pentyl radical, which is expected to be at least as reactive as the propagating radical, and therefore slow reinitiation is not expected to contribute to the retardation observed. Furthermore, low molecular weight polymer was generated when using MMA-3, and it is possible that some oligomeric products did not precipitate, resulting in underestimation of the conversion. (At [MMA-3] = 23.1 mol %, the polymer formed could not be successfully precipitated in methanol.)

The content of M_2 in the poly(St) obtained at 60 °C is much higher than for poly(EMA) and qualitatively similar to that observed for poly(CHA); i.e., the molar fraction of M_2 in the polymer was similar to that in the feed and did not vary significantly with *n*. Thus, backward β-fragmentation is of minor importance as was also the case for CHA, contrary to what was observed for EMA.

Conclusions

Synthesis of macromonomers by AFCT polymerization involving C−C bond cleavage has been investigated. The effectiveness of MMA-*n* ($n = 2-4$) and CHMA-*n* ($n = 2, 3$) as AFCT agents in the polymerizations of EMA, CHA, and St was assessed by evaluation of the number of unsaturated end groups per chain (*f*), which is accessible by comparison of M_n from GPC and ^{1}H NMR. The effectiveness of the AFCT agents in terms of their *f* values and the extent of retardation are summarized in Table 5. In the polymerizations of EMA and St, high values of *f* close to unity with only mild retardation could be achieved by manipulation of the degree of steric hindrance of the α-substituent of AFCT agents and the reaction temperature. In the polymerizations of CHA at 60 °C, high values of *f* were obtained regardless of *n* of MMA-*n*, but marked retardation was observed in all cases. Careful analysis of ^{1}H NMR spectra of olefinic protons revealed that under certain conditions disproportionation and β-fragmentation of midchain radicals contribute to formation of unsaturated end groups in poly(EMA) and poly(CHA), respectively. The polymer composition revealed that the methacrylate polymerizations involve backward β-fragmentation of the adduct radical, leading to regeneration of the propagating radical and the AFCT agent, and this process results in a lower M_2 content in the polymer and a lower *f* value. The contribution of backward β-fragmentation is significantly greater for RMA-2 than for RMA-3. However, in the case of St and CHA polymerization, backward β-fragmentation is less or of no significance due to the structure of the propagating radicals (secondary carbon-centered radical as opposed to tertiary for EMA). It is concluded that efficient macromonomer synthesis can be achieved in AFCT polymerization of methacrylates, St, and acrylates by manipulation of the level of steric hindrance of the AFCT agents.

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