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Copolymerizations of macromonomer prepared by addition-fragmentation chain transfer polymerization of methyl acrylate trimer

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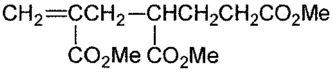
SUMMARY

An oligomer of the methyl acrylate unsaturated trimer bearing 2-carbomethoxy-2-propenyl ω-end group (M_n = 1300, M_w/M_n = 1.7, and functionality > 0.7) was copolymerized as a macromonomer (0.02 mol/L) with styrene (1.0 mol/L) in benzene at 60 °C. The amounts of monomer and macromonomer in the feed simultaneously decreased with increasing time to indicate copolymer formation, and the macromonomer was found to be as reactive as styrene toward poly(styrene) radicals. The M_ns of the copolymers were 13900-22000 depending on conversion. No resonance due to the unsaturated ω-end group bound to the poly(styrene) chain was detected by ^{1}H-NMR spectroscopy, indicating that no fragmentation of adduct radical of the end group to expel the poly(methyl acrylate trimer) radical. Polymerization of ethyl methacrylate (1.0 mol/L) in the presence of the macromonomer (0.02 mol/L) resulted in a mixture of the unreacted macromonomer and homopolymer of ethyl methacrylate. No end group bound to the poly(ethyl methacrylate) was detected by ^{1}H-NMR spectroscopy, excluding the possibility of addition fragmentation chain transfer to the macromonomer to expel an oligomer radical of the methyl acrylate trimer. Addition of the poly(methacrylate) radical to the macromonomer is extremely slow under the present conditions of copolymerization.

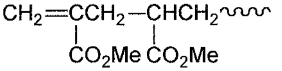
INTRODUCTION

It has been known that efficient addition-fragmentation chain transfer (AFCT) using some α-(substituted methyl)acrylic esters [1] such as α-(bromomethyl)acrylates [2-4], α-(alkylsulfenylmethyl)acrylates [5], and α-(arylsulfonylmethyl)acrylates [6] reduce the polymer molecular weight accompanied by introduction of the substituted propenyl ω-end group almost quantitatively. We studied the polymerizations of styrene (St), methyl acrylate (MA), and methyl methacrylate (MMA) in the presence of methyl α-(bromomethyl)acrylate (MBMA) [2] and the respective polymers bearing the 2-carbomethoxy-2-propenyl end group were submitted to further reaction with polymer radicals [7]. It was found that the carbomethoxypropenyl group as the ω-end group of poly(MA) (PMA) and poly(St) (PSt) is as reactive as common monomers such as MA and St toward their propagating radicals, and that the radical from the end group can add to these monomers. Therefore, PMA and PSt bound to the carbomethoxypropenyl end group are radically copolymerizable macromonomers (MCMs), although they do not homopolymerize. The propenyl end group bound to poly(MMA) (PMMA) is feasible to addition of PMA radicals and the adduct radical formed almost exclusively undergoes β-fragmentation to yield the unsaturated end group bound to PMA chain and PMMA radical [7]. Actually, PMMA bearing the substituted propenyl end group does not copolymerize with MA. Addition of PSt radicals to the end groups bound to PMMA is followed by β-fragmentation of adduct radicals to give PSt bearing the carbomethoxypropenyl end group and by addition of adduct radical to St to form copolymer [7].

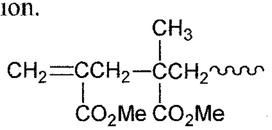
The MA unsaturated dimer (MAD) [8,9] and trimer (MAT) [10,11] are homopolymerizable AFCT agents that form the polymers bearing the propenyl end group as a result of β-fragmentation of the propagating radicals. MAD and MAT are as reactive as acrylic ester toward poly(acrylate) radicals in copolymerizations, and the propagating radicals of MAD and MAT are much less reactive than poly(acrylate) radicals toward MAD and MAT, respectively [9,11]. An increase in the size of the α-substituent from MAD to MAT apparently facilitates β-fragmentation of the respective propagating radicals. However, MAD and MAT, which are structurally similar to the carbomethoxypropenyl end group, are less efficient as AFCT agents than MBMA at 60 °C. The adduct radical from the end group bound to PMMA chain is anticipated to undergo faster fragmentation than the adduct radical from the end group bound to PMA because of formation of a more stable radical, a tertiary carbon centered radical, than a secondary carbon centered radical. The MAT radicals would also expel secondary carbon center radicals upon fragmentation.


$CH_2{=}\underset{\substack{|\\ CO_2Me}}{C}CH_2{-}\underset{\substack{|\\ CO_2Me}}{C}HCH_2CH_2CO_2Me$

Methyl acrylate trimer (MAT)


$CH_2{=}\underset{\substack{|\\ CO_2Me}}{C}CH_2{-}\underset{\substack{|\\ CO_2Me}}{C}HCH_2\sim\sim$

PMA bound to end group


$CH_2{=}\underset{\substack{|\\ CO_2Me}}{C}CH_2{-}\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CO_2Me}}{C}}CH_2\sim\sim$

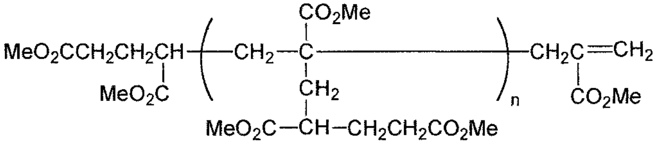
PMMA bound to end group

β-Fragmentation of the MAT radical has to be facilitated for efficient preparation of macromonomers. The fragmentation rate constant is increased more than the propagation rate constant by raising the temperature because of higher activation energy for fragmentation (a unimolecular reaction) than propagation (a bimolecular reaction) [8-11]. MAT polymerization, which involves sterically hindered propagation and sterically accelerated β-fragmentation of the propagating radicals [11], is advantageous over the MAD polymerization with regards to introduction of the unsaturated end group for macromonomer formation [9]. Therefore, high temperature polymerization of MAT was expected to be an efficient method to prepare *radically copolymerizable macromonomer by radical polymerization.*

This paper deals with copolymerizations of MCM, which was obtained as a result of competition between propagation and fragmentation of the MAT radicals, with St and ethyl methacrylate (EMA).

EXPERIMENTAL

MCM of poly(MAT) (PMAT) (M_n = 1300 and M_w/M_n = 1.7) corresponding to approximately pentamer of MA including the end group, was prepared by radical polymerization at 130 °C using *tert*-butyl peroxide as initiator [11]. The end functionality was 0.7 based on the following structure where n ≈ 4 [7,8]. However, the end functionality could be underestimated because PSt standards were employed for GPC measurement of PMAT which has a branched structure.



$MeO_2CCH_2CH_2CH(CO_2Me){-}\left(CH_2{-}C(CO_2Me)(CH_2{-}CH(CO_2Me){-}CH_2CH_2CO_2Me)\right)_n{-}CH_2C(=CH_2)CO_2Me$

St and EMA were commercially available and were distilled under reduced pressure before use. Commercial 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol.

St (M_1) and MAT (M_2) copolymerizations in benzene were carried out using Pyrex ampoules sealed under vacuum at 60 °C, and the copolymer compositions were calculated from intensity ratio of the ^{1}H-NMR resonances due to the methoxy group of the MAT unit and the phenyl group of the St unit. The r_1 and r_2 values were obtained by a non-linear least squares procedure [12]. St or EMA (M_1) and MCM (M_2) copolymerization was carried out at 60 °C. After copolymerization, the unreacted monomer and solvent were evaporated from the polymerization mixture using a rotary evaporator. A preparative HPLC was employed to remove remaining solvent and monomer, and the mixture of polymer formed and MCM were submitted for ^{1}H-NMR and GPC analysis. The conversion of MCM was determined based on the intensity ratio of the ^{1}H-NMR resonances due to the methoxy groups of the polymer and MCM to those due to the unsaturated methylene groups of MCM. Monomer conversion was calculated from the initial weight of MCM and the MCM content in the polymer-MCM mixture after HPLC purification. The compositions of the St-MCM copolymers were calculated from the intensity ratio of the ^{1}H-NMR resonances due to the phenyl group of the St unit and the methoxy group of the MCM unit after subtraction of the contribution the unreacted MCM with consideration of the end functionality = 0.7.

A Japan Analytical Industry LC-908 equipped with JAIGEL columns using chloroform as eluent was employed for removal of unchanged monomer from polymerization mixture. GPC measurement was performed using a Tosoh 8000 series HPLC equipped with TSK-gel columns, and PSt standards were used for calibration. ^{1}H-NMR spectra were recorded on a JEOL JNM-A 400 spectrometer. Deuteriochloroform and tetramethylsilane were used as solvent and internal standard, respectively.

RESULTS AND DISCUSSION

Copolymerization with St

The r_1 and r_2 for the St-MAT copolymerization were evaluated to be 0.66 and 0.10, respectively (Figure 1). The r_1 and r_2 values indicate that MAT is more reactive than St toward PSt radicals by a factor of 1/0.66 = 1.52 and that St is more reactive than MAT toward PMAT radicals by a factor of 1/0.10 = 10. Table 1 shows the results of the St polymerization in the presence of a small molar amount of MCM. Independent formation of PSt can be ruled out in accordance with ordinary radical binary copolymerization because of simultaneous consumption of MCM as mentioned later.

The ^{1}H-NMR spectra of MCM and its copolymer with St are shown in Figure 2. MCM exhibits resonances due to the saturated MA units and the unsaturated end group. After the copolymerization, the resonances due to the St units appeared at 6.2-7.2 ppm. The remaining resonances are similar to those of MCM except for the intensity ratios of the resonances due to the methylene, methine, methoxy, and the unsaturated end groups.

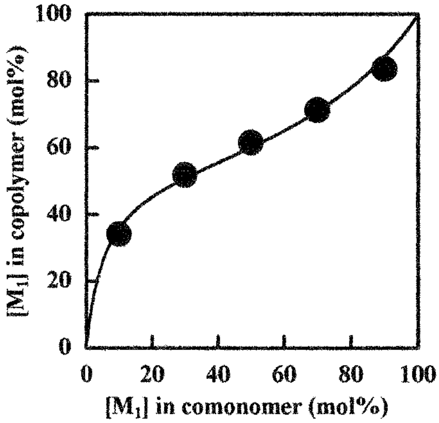


Figure 1. Comonomer-copolymer composition curve ($r_1 = 0.66$ and $r_2 = 0.10$) for St (M$_1$) -MCM (M$_2$) copolymerization in benzene at 60 °C: [M$_1$] + [M$_2$] = 2 mol/L, [AIBN] = 5 mmol/L.

Table 1. Results of copolymerization of MCM with St in benzene at 60 °C [a)]

Time (h)	Conversion of St (%)	Copolymer		MCM	
		M_n	M_w/M_n	M_n	M_w/M_n
0	-	-	-	1300	1.7
3	5.9	22000	1.7	1300	1.7
6	9.8	18800	1.5	1400	1.6
12	18.1	16500	1.6	1300	1.6
24	32.0	13900	1.6	1300	1.4

a) [MCM] = 0.02 mol/L, [St] = 1.0 mol/L, [AIBN] = 5.0 mmol/L.

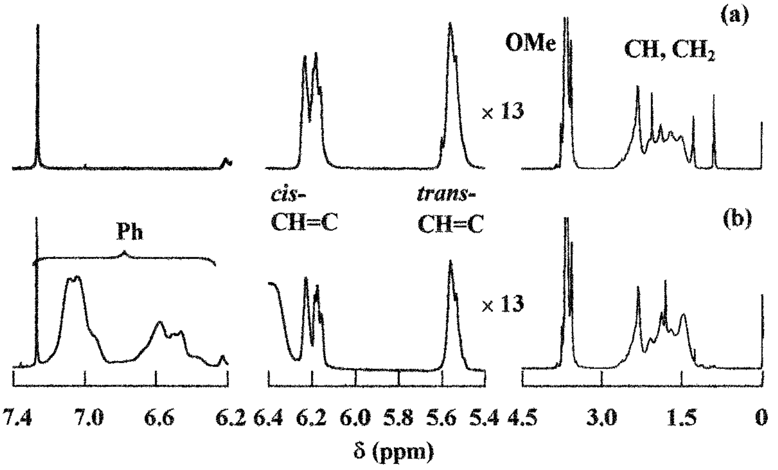
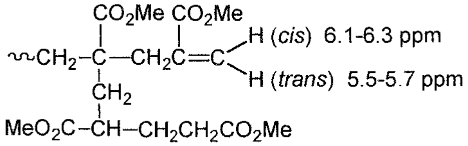


Figure 2. ^{1}H-NMR resonances of methylene, methine, methoxy, and olefinic of protons of MCM (a), and methylene, methine, methoxy, olefinic, and phenyl protons of MCM-St copolymer after polymerization for 6 h at 60 °C (b): [MCM] = 0.02 mol/L, [St] = 1.0 mol/L, and [AIBN] = 5.0 mmol/L.

The carbomethoxypropenyl ω-end group bound to different polymer chains can be regarded as methyl α-(substituted methyl)acrylates, and a linear relationship between the chemical shifts for the *cis*-protons (6.0-6.3 ppm) and for the *trans*-protons (5.1-6.0 ppm) is given by the following equation [14].

$$\delta \text{ for } \textit{cis}\text{-proton (ppm)} = 0.36 \times \delta \text{ for } \textit{trans}\text{-proton (ppm)} + 4.20$$

The olefinic protons of the propenyl end group bound to the MCM and St units show resonances at the following chemical shifts in agreement with prediction based on the above equation.



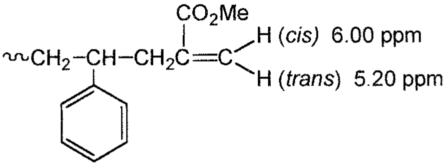
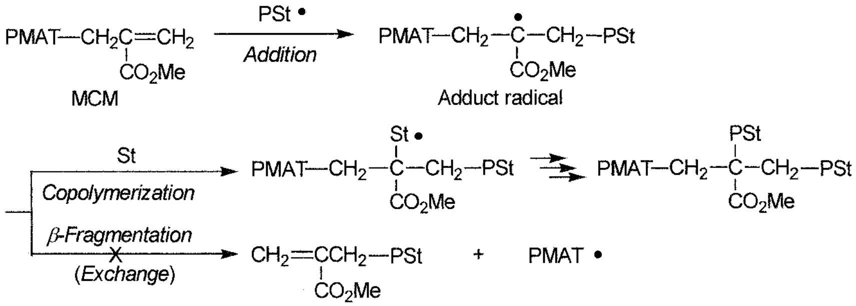


Figure 2 shows only one set of the resonances assigned to the *cis*- and *trans*-protons of MCM. No end group bound to St unit was detected in the expected chemical shift range, excluding the possibility of the exchange of the end group through fragmentation of the adduct radical (Scheme 1).



Scheme 1

Figure 3 shows pseudo first-order kinetic plots through the origin with respect of St and MCM. The ratio of the copolymerization rates with respect to MCM and St at the feed consisting of a large excess of St such as $[\mathrm{St}]_0/[\mathrm{MCM}]_0 = 50$ (molar ratio) may be approximated by the following simplified copolymer composition equation:

$$\frac{d[\mathrm{St}]}{d[\mathrm{MCM}]} = \frac{[\mathrm{St}]_0\,(r_1[\mathrm{St}]_0 + [\mathrm{MCM}]_0)}{[\mathrm{MCM}]_0\,([\mathrm{St}]_0 + r_2[\mathrm{MCM}]_0)} = \frac{r_1[\mathrm{St}]_0}{[\mathrm{MCM}]_0}$$

Integration of this equation results in

$$\ln\frac{[\mathrm{St}]_0}{[\mathrm{St}]} = r_1 \ln\frac{[\mathrm{MCM}]_0}{[\mathrm{MCM}]}$$

The ratio of the slopes of the linear relationships in Figure 3, 0.5, is equal to the r_1 value for the copolymerization of St (M_1) with MCM (M_2): $r_1 = 0.5$ and $1/r_1 = 2.0$. MCM exhibits higher reactivity than St toward PSt radicals. The monomer reactivity ratios for the copolymerization with St (M_1) are $r_1 = 0.69$ and $r_2 = 0.18$ for M_2 = MAD

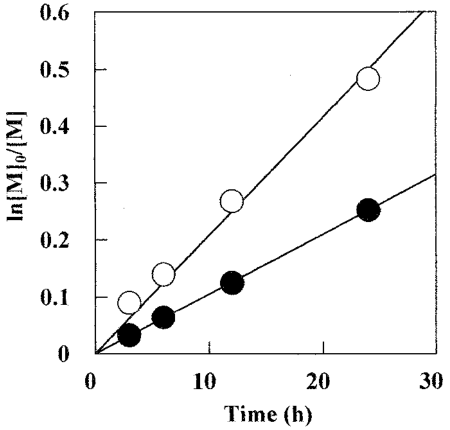


Figure 3. First-order kinetic plots with respect to St (●) and MCM (○) for copolymerization of St with MCM in benzene at 60 °C: [MCM] = 0.02 mol/L, [St] = 1.0 mol/L, and [AIBN] = 5.0 mmol/L.

[8], and $r_1 = 0.66$ and $r_2 = 0.10$ for M_2 = MAT. Although k_p for MAD is considerably greater than that for MAT [8,10], MAD and MAT exhibited almost the same reactive reactivities toward PSt radicals according to the r_1 values. MAD and MAT are more reactive than St by factors of 1/0.69 = 1.45 and 1/0.66 = 1.52, respectively. MCM is slightly more reactive than MAD and MAT. Considering that the functionality of MCM was estimated to be approximately 0.7, the r_1 value obtained based on functionality = 1 may be slightly overestimated. Steric hindrance arising from the oligomeric chain of MAT bound to the reacting C=C seems not to be significant.

Bimodal elution curves in Figure 4a which are $w(\log M)$ vs. $\log M$ plots show that the isolated polymeric material consists of the unreacted MCM and copolymer. The areas under curves have been normalized to be proportional to the weight of the polymer-MCM mixture. Although an increase in the St conversion brought about a gradual decrease in M_n of the copolymer (Table 1), the M_n and M_w/M_n of MCM remained constant at the original values. The decrease in M_n of the copolymer can be explained by a decrease in St and MCM concentrations.

Figures 4b and 4c illustrate the GPC elution curves after the copolymerization for

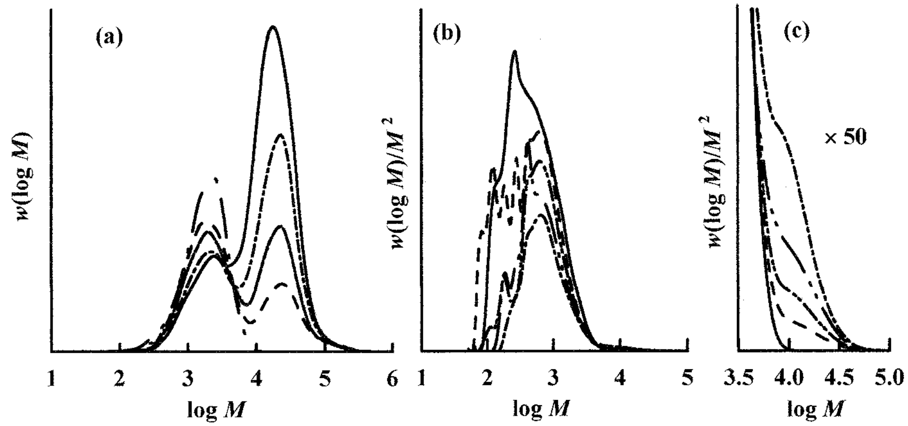


Figure 4. GPC elution curves of $w(\log M)$ vs. $\log M$ plot (a), $w(\log M)/M^2$ vs. $\log M$ plot (b), and expanded $w(\log M)/M^2$ vs. $\log M$ plot by 50 times (c) for copolymerization mixture after copolymerization of MCM with St in benzene at 60 °C for 0 (· – ·), 3 (– –), 6 (- - -), 12 (-----), and 24 h (——): [MCM] = 0.02 mol/L, [St] = 1.0 mol/L, and [AIBN] = 5.0 mmol/L.

different times by $w(\log M)/M^2$ vs. $\log M$ plot. These figures show the molar basis molecular weight distributions, indicating consumption of MCM (Figure 4b) and formation of higher molecular weight polymer (Figure 4c). Although larger peaks in Figure 4a almost disappear in Figures 4b and 4c because of higher M_ns of the product copolymers than MCM (Table 1), the amount of copolymer increased with increasing time. If MCM acted as an AFCT agent, the PSt bearing the end group would be formed (Scheme 1). However, the unsaturated end group bound to PSt was not detected by ^{1}H-NMR spectroscopy, as was also the case in the St-MAD copolymerization [9].

The St-MCM copolymer composition obtained from the intensity ratio of the ^{1}H-NMR resonances due to the St and MCM units was [St]/[MCM] = 23 (molar ratio) on the average. The M_n of the segment containing 23 St units and one MCM unit may be 3700, and the St-MCM copolymer obtained (M_n = 18800) would consist of five such segments: $(St)_{115}\text{-}(MCM)_5$. Studies of the MCM copolymer based on absolute M_n measurement are now in progress.

Copolymerization with methacrylate

The copolymerization of MCM with EMA was carried out similarly to the copolymerization with St. The ^{1}H-NMR spectrum of the polymeric material isolated consisting of the unreacted MCM and the polymer formed exhibits the characteristic resonances due to MCM and the MAT units. If MCM copolymerized with EMA, the intensity ratio of the ^{1}H-NMR resonances of the olefinic protons to those of the methoxy protons would be changed by copolymerization of MCM. The decrease in the intensity ratio of the resonances would also be observed by the exchange of the end group from MCM to the poly(EMA) (PEMA) formed if the end group was not consumed by further addition of the EMA radical. However, the ratios of the resonances due to the unsaturated end group and the methoxy group before and after polymerization remained almost constant. GPC elution curves of the polymers

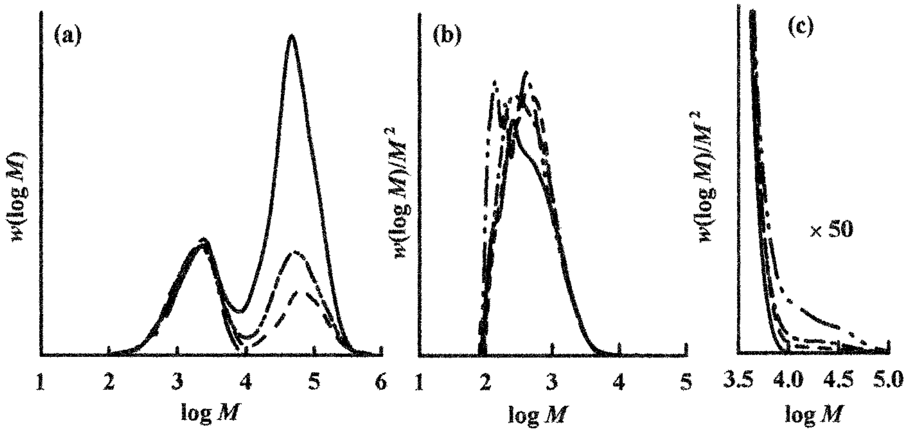


Figure 5. GPC elution curves of $w(\log M)$ vs. $\log M$ plot (a), $w(\log M)/M^2$ vs. $\log M$ plot (b), and expanded $w(\log M)/M^2$ vs. $\log M$ plot by 50 times (c) for polymerization mixture after polymerization of MCM in the presence of EMA in benzene at 60 °C for 0 (· – ·), 1.5 (– –), 3.0 (----), and 12 h (—) : [MCM] = 0.02 mol/L, [St] = 1.0 mol/L, and [AIBN] = 5.0 mmol/L.

obtained by the polymerizations of MCM in the presence of EMA are shown in Figure 5a, where an increase in the total area of the bimodal curve along the polymerization is normalized to be proportional to the EMA conversion. Unlike the GPC curves in Figure 4a, only the peak due to the higher molecular weight polymer increased and the peak due to MCM remained unchanged as shown in Figure 5a. The elution curves obtained by the $w(\log M)/M^2$-log M plot (Figures 5b and 5c) show formation of extremely small molar amounts of higher M_n polymers.

The low reactivity of the end group toward poly(methacrylate) radical was already suggested when methacrylic esters were polymerized in the presence of the MMA unsaturated dimer ($CH_2{=}C(CO_2Me)CH_2C(CH_3)_2CO_2Me$, MMAD) [15,16]. The presence of MMAD reduced the polymerization rate and the M_n of the polymer formed. In the case of the polymerization of EMA, a small amount of MCM might be involved as the end groups in the polymer of EMA. Addition of PEMA radical to the unsaturated end group of MCM was strongly suppressed because of the steric hindrance arising from the α-methyl and carbethoxy groups of the PEMA radical and the oligo(MAT) chain and the carbomethoxy group as the substituents of MCM.

CONCLUSIONS

MCM prepared by radical polymerization of MAT accompanied by AFCT at 130 °C can be used as a radically copolymerizable monomer for copolymerization with St. MCM was more reactive than St toward PSt radicals, and a copolymer consisting of St and MCM units was formed at [St]/[MCM] = 50 (molar ratio). The estimated copolymer composition was $(St)_{115}$-$(MCM)_5$. However, EMA did not copolymerize with MCM at the feed ratio of [EMA]/[MCM] = 50 (molar ratio); consumption of MCM was not observed by GPC. Steric hindrance arising from the α-methyl group of the EMA radical would render extremely slow addition to MCM bearing oligo(MAT) chain as the α-substituent. Studies of the MCM copolymer based on absolute M_n measurement are now in progress.

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