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Preparation of polymer with controlled molecular weight up to high conversion using methyl 2-bromomethylacrylate as a chain transfer agent in radical polymerization

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Summary

Radical polymerizations of methyl methacrylate (MMA) and styrene (St) in benzene up to high conversions were carried out in the presence of 2.5 and 2.0 mol% of methyl 2-bromomethylacrylate (MBMA) relative to the monomers, respectively. Number average molecular weight ($\bar{M}_n$) of poly(MMA) was reduced by chain transfer with MBMA to ca. 3000, and polydispersity ($\bar{M}_w/\bar{M}_n$) remained at 1.55–1.71 throughout the polymerization. $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of poly(MMA) obtained in the absence of MBMA were ca. 200000 and 1.74–2.16, respectively, depending on conversion. The 2-carbomethoxyallyl group formed by fragmentation of MBMA radical was quantitatively introduced at the ω-end of the polymer. Chain transfer which is much less affected by an increase in viscosity of the polymerization system than bimolecular termination of the polymer radical primarily limited $\bar{M}_n$ of the poly(MMA). While $\bar{M}_n$ of poly(St) was lowered by MBMA, increases in $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ with conversion were observed. Although the carbomethoxyallyl end-group was almost inactive toward poly(MMA) radical, addition of poly(St) radical to the allyl end group occurred to enhance $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$.

Introduction

Radical polymerization is a typical chain reaction consisting of elementary reactions. ESR studies of radical polymerizations of methyl methacrylate (MMA) [1–3] and styrene (St) in bulk [4] have revealed that the absolute values of the rate constants for the elementary reactions except for propagation rate constant (k_p) of St change with conversion to different extents. Proceeding of bulk polymerization of MMA resulted in considerable changes in termination rate constant (k_t) from the initial stage of the polymerization and k_p at ca. 80% conversion or above [1–3]. Molecular weight and polydispersity ($\bar{M}_w/\bar{M}_n$) of poly(MMA) increased significantly with conversion [5,6]. Although the dependence of the individual rate constants for the elementary reactions on conversion is considered to affect the chain transfer constant (C_{tr}) [7], radical polymerization involving unimolecular reactions with respect to polymer radical such as chain transfer and primary radical termination as the dominant chain stopping events may bring about much less increases in $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ up to high conversions.

Recently, some 2-(substituted methyl)acrylic esters such as methyl 2-alkylthiomethylacrylate and methyl 2-bromomethylacrylate (MBMA) as well as α-(substituted methyl)styrenes and acrylonitriles have been drawn attention as efficient chain transfer agents through the addition-fragmentation

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mechanism in radical polymerization [8-13]. We have shown that the bromo and 2-carbomethoxyallyl end-groups are quantitatively introduced at the α- and ω-terminuses of poly(MMA) and poly(St) prepared by the polymerizations in the presence of MBMA and that contribution of bimolecular termination as chain stopping process becomes extremely small [13]. As emphasized by Meijs *et al.* [8], chain transfer through the addition-fragmentation mechanism allows to introduce functional groups at the α- and ω-terminuses, although hydrogen or halogen may be bound to the ω-end of polymer by chain transfer to mercaptan or polyhalomethane.

To control the molecular weight and end groups simultaneously with the chain transfer over a wide conversion range, C_{tr} should be close to unity otherwise concentration ratio of monomer to chain transfer agent would be changed with conversion [8]. The C_{tr}'s of MBMA for MMA, St, and methyl acrylate (MA) polymerizations have been obtained as 0.93, 2.34, and 2.93, respectively [13]. However, Meijs *et al.* [9] have reported 1.45 and 2.33 as the C_{tr}'s of ethyl 2-bromomethylacrylate in the polymerizations of MMA and MA. These values were determined by the Mayo equation [14] at low conversions, and an advantage of the bromomethylacrylate as the chain transfer agent of which the C_{tr} is close to unity has not been exemplified over a wide conversion range.

Considering the efficient chain transfer to MBMA, we intended to adjust the molecular weight of the polymer throughout the polymerization of MMA under the conditions where the chain transfer is of primary importance for chain stopping. For comparison, St polymerization in the presence of MBMA was examined. Because the addition of a propagating radical to MBMA can be a chemical step-controlled reaction over a wide conversion range as well as propagation, the contribution of a slower diffusion-controlled termination may diminish further as the conversion increases. The molecular weight and the content of the end group of the resultant polymer were measured at different conversions. To avoid a considerable influence arising from the change in the physical state of the polymerization mixtures on the rate constants, solution polymerizations of MMA and St in the presence of MBMA were carried out.

Experimental

MMA, ethyl methacrylate (EMA), and St were commercially obtained and were distilled under reduced pressure before use. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. MBMA was synthesized by bromination of methyl 2-hydroxymethylacrylate with tribromophosphine [15]. Dimethyl 4-methyl-1-pentene-2,4-dicarboxylate (MMAD) was synthesized by a catalytic chain transfer of MMA as described in the literature [16] using benzylbis(dimethylglyoximato)(pyridine)cobalt(III) [17] instead of a porphiline complex of cobalt(III). MMAD was isolated from the reaction mixture by passing a silica gel column using benzene as eluent and was distilled under reduced pressure. Structure of MMAD was verified by ^{1}H NMR spectroscopy.

The polymerizations of MMA and St were run in the presence and absence of MBMA in benzene at 60°C. For isolation of poly(MMA) and poly(St), n-hexane and methanol were used as precipitants, respectively. The polymerizations of EMA and St in the presence of MMAD were also carried out similarly. Number- and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) was measured by a TOSOH high performance liquid chromatograph equipped with columns for gel permeation chromatography (GPC). GPC curves of instantaneously formed polymers in narrow conversion ranges were obtained as differences between the curves for different conversions [18]. ^{1}H NMR spectra were taken by a JEOL GX 400 spectrometer, and deuterochloroform was used as a solvent.

Results and Discussion

MMA Polymerization

The polymerization of MMA in the absence and presence of a small amount of MBMA proceeded at almost the same initial rate, and a considerable decrease in $\bar{M}_n$ was induced by coexistence of MBMA as shown in Table 1. The first order kinetic plot in Fig. 1 shows acceleration of the polymerization by the gel effect in the absence of MBMA. The polymerization in the presence of MBMA obeys the first order kinetics with respect to MMA up

Table 1. The polymerization of MMA in the presence and absence of MBMA up to high conversions in benzene at 60°C

Time (h)	[MBMA] = 0.125 mol/L[a]				In the absence of MBMA[a]		
	Convn. (%)	$\bar{M}_n$ (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)	$\bar{P}_n$[b]	Convn. (%)	$\bar{M}_n$ (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)
1	6.0	2900	1.58	41.2	-	-	-
2	11.9	2900	1.61	-	16.5	212000	1.74
4	23.0	3200	1.55	-	30.4	192000	1.78
6	34.8	2900	1.68	-	42.3	166000	1.98
8	42.8	3000	1.64	-	56.4	178000	1.89
9	49.8	3100	1.65	43.4	-	-	-
10	58.4	3100	1.71	-	71.1	190000	1.98
12	64.4	3200	1.67	-	91.6	224000	2.12
14	63.8	3200	1.69	-	100.0	205000	2.16
15	70.2	3200	1.71	43.2			

[a] [MMA] = 5.0 mol/L and [AIBN] = 5.0 x 10^{-3} mol/L. [b] $\bar{P}_n$ of poly(MMA) determined by ^{1}H NMR spectroscopy.

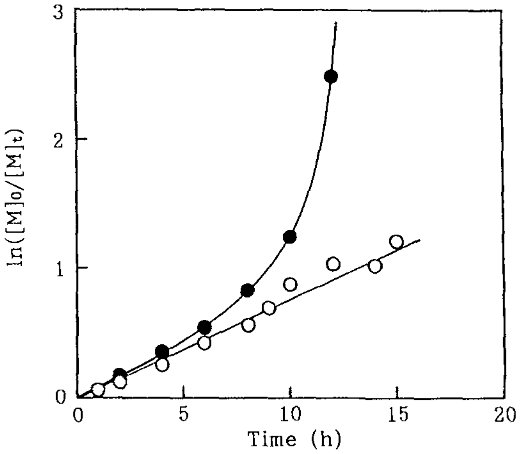

Fig. 1. First-order plot for the polymerization of MMA in the absence (●) and presence of MBMA (○) at 60°C: [MMA] = 5.0 mol/L, [MBMA] = 0.125 mol/L, and [AIBN] = 5.0 x 10^{-3} mol/L

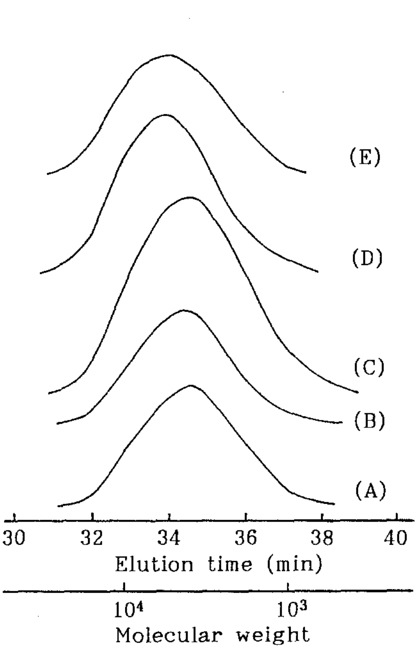

Fig. 2. GPC curves of poly(MMA) formed by the polymerization in the presence of MBMA in the conversion ranges of 0–11.9 (A), 11.9–34.8 (B), 34.8–42.8 (C), 42.8–58.4 (D), and 58.4–70.2% (E)

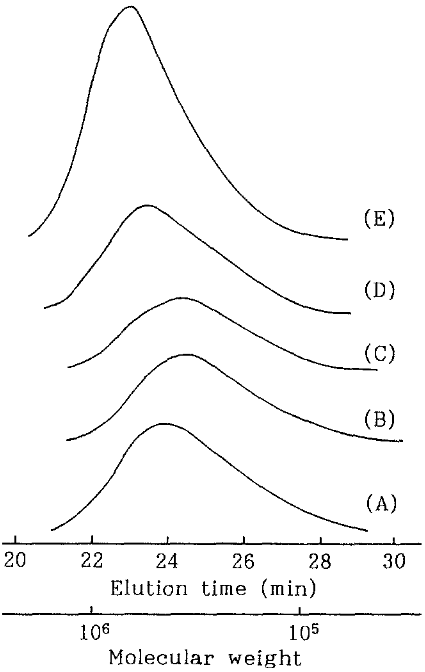

Fig. 3. GPC curves of poly(MMA) formed in the conversion ranges of 0–16.5 (A), 16.5–30.4 (B), 30.4–42.3 (C), 56.4–71.1 (D), and 71.1–100% (E)

to high conversions, and no gel effect was observed.

While the bulk polymerization of MMA is suppressed at ca. 80% conversion by solidification of the polymerization mixture [1–3], the polymerization in benzene attained almost 100% conversion. Table 1 also shows $\bar{M}_n$ of the polymers isolated at different conversions. During the polymerization in the absence of MBMA, a slight decrease in $\bar{M}_n$ induced by a decrease in monomer concentration at 30–70% conversions was followed by a subsequent gradual increase in $\bar{M}_n$. It is expedient to estimate contribution of the gel effect on $\bar{M}_n$ from the GPC elution curves of the instantaneously formed polymers in narrow conversion ranges [18]. Figs. 2 and 3 show the GPC curves of the poly(MMA) obtained in various conversion ranges as differences between the pairs of the GPC curves from which the cumulative $\bar{M}_n$ could be obtained.

The rate determining step of the addition-fragmentation chain transfer is considered to be the addition to MBMA, because no MBMA unit is incorporated in the polymers [13]. Polymerizations and copolymerizations of methyl 2-chloromethylacrylate [19] and methyl 2-phenoxymethylacrylate [20] yielded the polymers and copolymers bearing the 2-carbomethoxyallyl end-group, because the slower fragmentation of the poly(2-chloromethylacrylate) and poly(2-phenoxymethylacrylate) radicals than that of the MBMA radical competes with propagation. Although a decrease in k_t with conversion is anticipated for the polymerization of MMA in the absence of MBMA, $\bar{M}_n$ primarily determined by competition of propagation and the addition to MBMA could not be affected by the change in k_t value. Although $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the polymer isolated at various conversions remained constant for the polymer in the presence of MBMA as in Table 1, the GPC elution curve in Fig. 2 demonstrate almost constant $\bar{M}_n$ irrespective of conversion except for the final stage of the polymerization. The ^{1}H NMR spectra of the poly(MMA) isolated at different conversions during the polymerization in the presence of MBMA exhibited the resonances characteristic to the olefinic protons of the substituted allyl end-group at 5.48, 5,50, and 6.20 ppm [21] as previously studied in detail [13], and intensity ratios of these resonances confirmed quantitative introduction of the bromo and carbomethoxyallyl end-groups.

To inspect the reactivity of MBMA as a chain transfer agent with C_{tr} close to unity, number average degree of polymerization ($\bar{P}_n$) of poly(MMA) was estimated according to the Mayo equation using numerical values of k_p, k_t, the rate constant for decomposition of AIBN (k_d), initiation efficiency (f), and the rate constant for chain transfer (k_{tr}).

$$\frac{1}{\bar{P}_n} = \frac{k_t[\mathrm{M}\cdot]^2 + k_{tr}[\mathrm{M}\cdot][\mathrm{MBMA}]}{k_p[\mathrm{M}\cdot][\mathrm{M}]} = \frac{(k_t R_i)^{0.5}}{k_p[\mathrm{M}]} + \frac{k_{tr}[\mathrm{MBMA}]}{k_p[\mathrm{M}]}$$

$$= \frac{1}{P_{n0}} + C_{tr} \cdot \frac{[\mathrm{MBMA}]}{[\mathrm{M}]}$$

Substitution of k_p = 510 $\pm$ 100 L/mol·s [1], k_t = (4.2 $\pm$ 0.4) x 10^7 L/mol·s [1], C_{tr} = 0.93 [13], and $R_i = 2fk_d[\mathrm{AIBN}]$ = 4.56 x 10^{-8} mol/L·s [22] at 60°C into the Mayo equation results in $\bar{P}_n$ = 42.0. Actually, $\bar{P}_n$ is determined by solely the second term of the right hand side of this equation, since the first term, 5.43 x 10^{-4}, is about 1/43 of the second term, 2.33 x 10^{-2}, in magnitude. As Table 1 shows, $\bar{M}_n$ of the poly(MMA) prepared in the presence of MBMA was 2900 at 6.0% conversion. The estimate by the Mayo equation is apparently larger than the experimental value determined by GPC. However, we have shown that the $\bar{M}_n$ of the poly(MMA) in the range of 2000-3000 determined by GPC was less than those measured by vapor pressure osmometry and estimated based on the amount of the end-group [13]. Moreover, $\bar{P}_n$ determined by the NMR spectroscopy coincides with the estimate of the Mayo equation as discussed later on, and the validity and the adequacy of the numerical values are approved.

Intensity ratios of total of the resonances of the methoxy and bromomethyl protons to the resonances of the olefinic protons permit to estimate $\bar{P}_n$ given in Table 1, and $\bar{P}_n$ consistent with the estimate of the Mayo equation corroborates that only an extremely small portion of the terminus was formed by bimolecular termination. Conformity with almost the same $\bar{M}_n$ of poly(MMA) irrespective of conversion, the intensity ratio of the resonances also remained constant. It is confirmed that formation of the poly(MMA) with constant $\bar{M}_n$ throughout the polymerization in the presence of a small amount of MBMA.

St Polymerization

Results of the St polymerization in the presence of MBMA are summarized

Table 2. The polymerization of St in the presence of MBMA in benzene at 60°C[a]

Polymerization time (h)	Conversion (%)	Polymer $\bar{M}_n$ (GPC)	Polymer $\bar{M}_w/\bar{M}_n$ (GPC)
20	12.0	2500	1.46
30	18.6	2500	2.03
40	28.9	3300	2.92

[a] [St] = 3.48 mol/L, [MBMA] = 0.07 mol/L, and [AIBN] = 6.1 x 10^{-3} mol/L

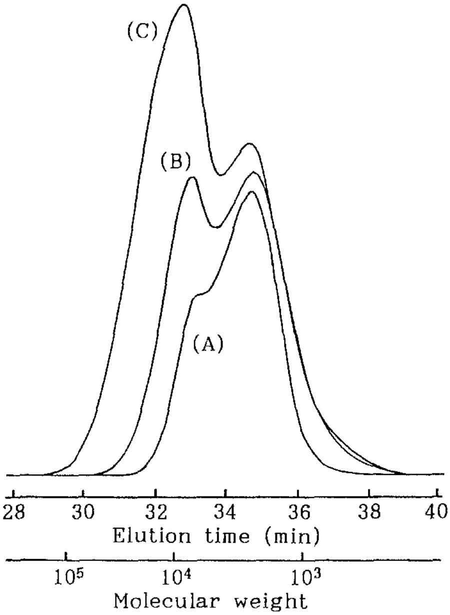

Fig. 4. Normalized GPC elution curves of the poly(St) isolated at 12.0 (A), 18.6 (B), and 28.9% conversions (C) at 60°C: [St] = 3.48 mol/L, [MBMA] = 0.07 mol/L, and [AIBN] = 6.1 x 10^{-3} mol/L

in Table 2. Although a decrease in St concentration brought about a decrease in $\bar{M}_n$ of the instantaneously formed polymer [18], cumulative $\bar{M}_n$ of the whole polymeric product increased with conversion simultaneously with $\bar{M}_w/\bar{M}_n$. The greater C_{tr} of MBMA for St polymerization, 2.34 [13], may result in the increase in instantaneous $\bar{M}_n$, since a faster consumption of MBMA than St leads to a decrease in [MBMA]/[St] ratio with conversion. Fig. 4 exhibits the GPC elution curves of the poly(St) obtained at different stages of the polymerization, which are normalized to conversion, and an additional GPC peak appears in a higher molecular weight range at conversions higher than 12.0%.

We have obtained GPC curves of poly(St) prepared at different conversions in bulk in relation to the changes in the absolute value of k_p with $\bar{M}_n$ of the polymer radical [18]. No significant change in $\bar{M}_n$ was observed below 30% conversion consistent with the constant k_p and k_t. Formation of the higher molecular weight poly(St) during the polymerization in the presence of MBMA seems to be rendered by a decrease in [MBMA]/[St] as the conversion increased, because of C_{tr} greater than unity, 2.34. However, solely the decrease in [MBMA]/[St] is not sufficient to predict the considerable changes in the GPC curve in Fig. 4.

According to the Mayo equation at C_{tr} = 2.34 using the absolute values of the rate constants [18], $\bar{M}_n$ = 2200 is obtained under the conditions of [St] = 3.48 mol/L and [MBMA] = 0.07 mol/L. [St] and [MBMA] are estimated to be 2.44 and 0.021 mol/L at 30% conversion, and $\bar{M}_n$ of the instantaneously formed poly(St) may be 5200. Fig. 4 shows formation of the poly(St) of which $\bar{M}_n$ is higher than 10000, indicating that further addition of the polymer radical to the carbon-carbon double bond of the end-group.

Copolymerization of EMA and St with MMAD

Results of the copolymerizations of EMA and St (M_2) with MMAD (M_1) as a model of the unsaturated end-group are shown in Table 3. Slow addition of poly(MMA) radical to MMAD and a low reactivity of the resulting MMAD radical have been reported by Tanaka *et al.* [23]. Since the almost inactive nature of the radical from MMAD in MMA polymerization has been shown by a high steady state concentration of the MMAD radical which allowed detection by ESR spectroscopy [23], MMAD could be involved in poly(MMA) to an extremely small extent.

Tanaka *et al.* [23] could not obtain poly(St) by the polymerization in the presence of 10 mol% of MMAD relative to St. This finding may indicate taking place of the copolymerization of St with MMAD, and a higher reactivity of MMAD toward poly(St) radical than poly(MMA) radical is expected. Table 3 also shows the results of the St polymerization in the presence of smaller amounts of MMAD, 3 and 6 mol%; MMAD reduced the conversion after the polymerization for 5 h and $\bar{M}_n$ of poly(St). These findings suggest that MMAD is involved in a reaction with poly(St) radical conformity with the r_1 = 0.000 and r_2 = 0.975 for the copolymerization of St (M_2) with MMAD (M_1) [24]. Probably, a low reactivity of the MMAD radical toward St leads to the decreases in the polymerization rate and $\bar{M}_n$ of the polymer. Therefore, a further reaction of the allylic end-group from MBMA bound to poly(St) chain could result in the increases in $\bar{M}_n$

Table 3. The copolymerization of MMAD (M_1) with EMA and St (M_2) in benzene at 60°C[a]

M_2	[M_1] (mol/L)	Time (h)	Conversion (%)	$\bar{M}_n$ (GPC)	$\bar{M}_w/\bar{M}_n$ (GPC)
None	5.30[b]	20.0	0[c]	–	–
EMA	0	3.5	35.8	131000	1.90
	0.15	3.5	32.2	66000	2.19
	0.30	3.5	29.4	45000	2.23
	0.90	3.5	20.3	29000	1.87
St	0	5.0	11.6	40600	1.70
	0.09	5.0	4.5	15400	1.58
	0.18	5.0	3.3	11500	1.54

[a] [M_2] = 3.0 mol/L and [AIBN] = 1.0 x 10^{-2} mol/L. [b] Bulk polymerization. [c] No n-hexane insoluble product.

and $\bar{M}_w/\bar{M}_n$ of the poly(St) at conversions higher than 10%.

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