

Control of Molecular Weight and End Group of Polymer by Addition-Fragmentation Reaction with α -(Bromomethyl)acrylate and Allyl Bromide

Bunichiro YAMADA, Seiya KOBATAKE, and Takayuki OTSU

Department of Applied Chemistry, Faculty of Engineering, Osaka City University,
Sugimoto, Sumiyoshi-ku, Osaka 558, Japan

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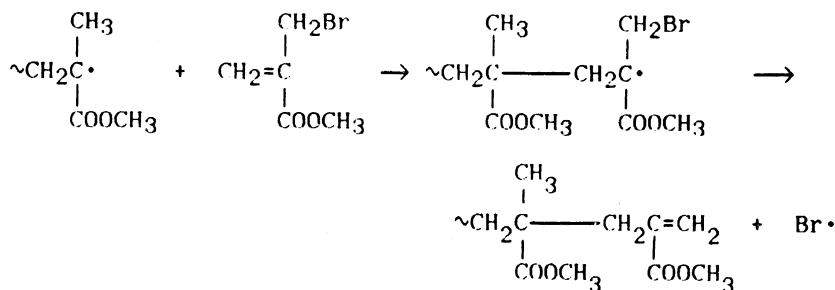
ABSTRACT: Allyl bromide as well as methyl α -(bromomethyl)acrylate functioned as an effective chain transfer agent through addition-fragmentation reaction in the radical polymerization of methyl methacrylate and methyl acrylate. The ^1H NMR spectra of the polymers revealed that the end groups of the polymer with the controlled molecular weight arise from addition of the polymer radical to the carbon-carbon double bond of the transfer agent accompanying subsequent scission of the carbon-bromine bond and reinitiation with bromine atom. However, allyl bromide was found to be almost ineffective in styrene polymerization, because of a low reactivity of the carbon-carbon double bond toward poly(styrene) radical.

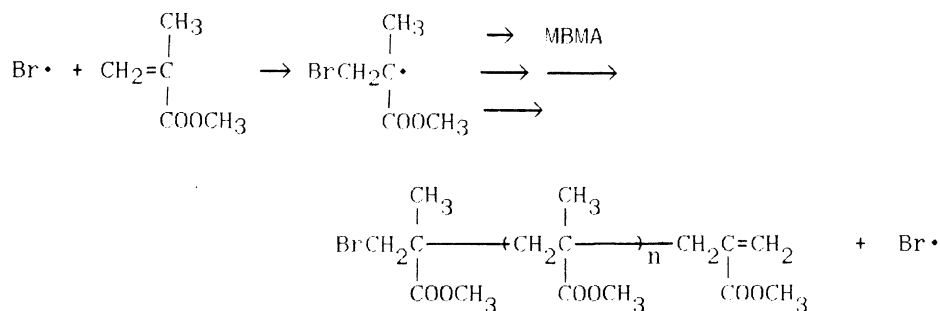
KEY WORDS Radical Polymerization / Chain Transfer / Methyl Methacrylate / Styrene / Methyl Acrylate / Allylic Compound /

Since radical polymerization is a typical chain reaction, efficient control of the chain length of polymer produced is not an easy task. Usually, chain transfer involving abstraction of hydrogen or halogen with propagating radical is utilized to adjust molecular weight of the polymer. Recently Meijs *et al.*¹⁻⁴ have found that α -thioalkoxymethyl vinyl monomers and related compounds function as effective chain transfer agents in the polymerizations of methyl methacrylate (MMA), styrene (St), and butyl acrylate through

addition-fragmentation reaction.

Independently, we have noted that ethyl and methyl α -(bromomethyl)acrylates (EBMA and MBMA) lacking of polymerization and copolymerization abilities are differentiated from α -(chloromethyl)- and α -(fluoromethyl)acrylates and that the addition-fragmentation reaction of EBMA and MBMA shortens the polymer chain of MMA.^{5,6} The polymers prepared have been shown to attach to the $\text{CH}_2=\text{C}(\text{COOCH}_3)\text{CH}_2$ as an end group⁷:





According to the above scheme, the reactivity of the carbon-carbon double bond of MBMA toward polymer radical is enhanced by the carbomethoxy group, whereas the rupture of the carbon-bromine bond would not be accelerated so much by the substituent. Although allyl bromide (AB) of which the carbon-carbon double bond can not be so reactive as MBMA, AB was considered to be feasible for the addition-fragmentation reaction resulting in the allyl end group. Consistent with this consideration formation of 4,4,4-trichloro-1-butene through β -elimination of bromine atom from an intermediate radical was noted by Kharasch in the addition of trichloromethyl radical to AB.⁸

The present study deals with further confirmation of the structure of the polymer controlled with MBMA, and the cleavage of the carbon-bromine bond of AB through the addition-fragmentation reaction was inspected on the basis of the ¹H NMR spectra of the polymers formed by radical polymerization in the presence of EBMA, MBMA, or AB.

EXPERIMENTAL

Materials

EBMA and MBMA were prepared by bromination of the α -(hydroxymethyl)acrylates.⁹ MMA, ethyl methacrylate (EMA), methyl acrylate (MA), ethyl acrylate (EA), St, AB, and benzyl bromide (BZB) were commercially available and were distilled under

atmospheric or reduced pressure in the stream of nitrogen before use.

Polymerization and Reduction

All the polymerizations in the presence and absence of the bromide were initiated with 2,2'-azobisisobutyronitrile (AIBN) in sealed tubes at 60°C. The polymer formed was precipitated by pouring the contents of the tube into an excess amount of *n*-hexane or methanol, and were purified by reprecipitation.

The bromine containing polymer was reduced with tributyltin hydride by refluxing a benzene solution of the polymer in the presence of a small amount of AIBN for 10 h. Chain transfer constant (C_s) was determined by the ordinary Mayo plot.

Measurement

Number and weight average molecular weights (\bar{M}_n and \bar{M}_w) were determined by a TOSO 8000 series GPC and were calibrated by standard poly(St). The molecular weight of poly(MMA) was also measured by a Knauer Vapour Pressure Osmometer, and toluene was used as a solvent. The ¹H NMR spectra of the polymers were taken on a JEOL GX400 spectrometer at 400 MHz. Deuteriochloroform was used as a solvent. Thermogravimetric analysis was run by using a Shimadzu TG 50 under nitrogen atmosphere at heating rate of 10°C min⁻¹, and initial degradation temperature (T_{init}) and maximum degradation rate temperature (T_{max}) were determined.

RESULTS AND DISCUSSION

Polymerization of MMA

Table I shows relevant results of the polymerization of MMA in the presence of MBMA, AB, and BZB. Since AB is about nine times less effective than MBMA in reducing \bar{M}_n , poly(MMA) of which \bar{M}_n is as low as the polymer prepared in the presence of MBMA was obtained using a larger amount of AB. The polymerization rate was slightly decreased by MBMA and AB within the concentration

range given in Table I. This table also shows the effect of BZB on the polymerization rate and \bar{M}_n of the polymer. In contrast to the significant effects of MBMA and AB, \bar{M}_n was little affected by BZB through bromine abstraction to a much less extent than MBMA and AB. The decreases in \bar{M}_n caused by MBMA and AB are deduced to arise from a chain transfer involving addition to the carbon-carbon double bond, and the bromine abstraction with the polymer radical could not be a main reaction.

Table I. Polymerization of MMA in the presence of MBMA, AB or BZB in benzene at 60°C: [MMA] = 3.76 mol l⁻¹, [AIBN] = 0.005 mol l⁻¹

Bromide	$\frac{[\text{Bromide}]}{[\text{MMA}]} \times 10^2$	$R_p/\% \text{ h}^{-1}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n
None	0	6.5	123	2.00
MBMA	0.41	6.4	18.3	1.90
MBMA	1.0	6.5	9.0	1.76
MBMA	3.0	5.9	3.6	1.48
AB	2.4	6.5	28.0	2.42
AB	4.7	6.4	18.6	2.04
AB	30.6	5.8	3.6	1.53
AB	51.1	5.8	2.7	1.42
BZB	10.3	6.1	104	1.89
BZB	31.0	6.2	75.9	2.26
BZB	51.7	6.8	61.2	2.59

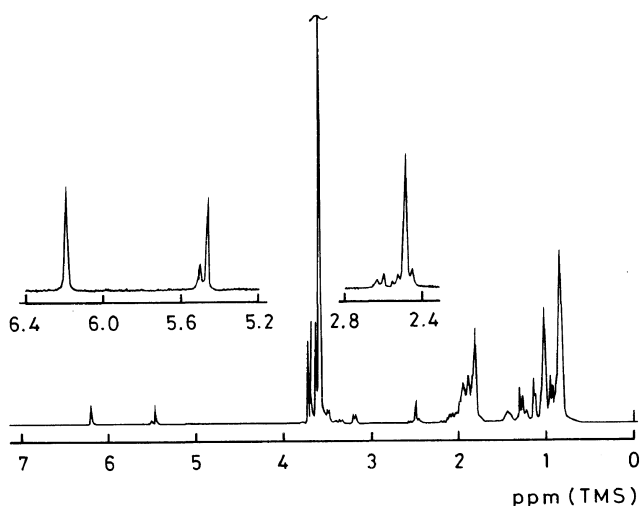


Figure 1. ¹H NMR spectrum of poly(MMA) prepared by polymerization in the presence of MBMA: [MMA] = 6.27 mol l⁻¹, [MBMA]/[MMA] = 0.10 (molar ratio), and [AIBN] = 0.005 mol l⁻¹.

Based on \bar{M}_n of poly(MMA), C_s in the MMA polymerization were evaluated by the Mayo plot to be 0.93 (MBMA), 0.10 (AB), and 0.002 (BZB). The difference in C_s between MBMA and AB seems to be smaller than that expected from the fact that MMA is 56 times more reactive than allyl chloride in their copolymerization.¹⁰ However, we have shown that the reactivity of the α -(halomethyl)-acrylate is significantly lowered by an increase in size of the halogen atom,⁶ and the reactivity of MBMA is expected to be considerably lower than that of MMA toward poly(MMA) radical.

Figure 1 shows the ^1H NMR spectrum of the poly(MMA) ($\bar{M}_n=1200$ and $\bar{M}_w/\bar{M}_n=$

1.59) obtained at $[\text{MBMA}]/[\text{MMA}]=0.10$ (molar ratio). The peaks at 5.48 and 6.20 ppm have been assigned to the olefinic protons of the unsaturated end group.^{5,7} The methylene group bound to the carbon-carbon double bond in the unsaturated end group exhibits a singlet at 2.49 ppm. If the chain length was determined solely by the addition-fragmentation reaction, Br and $\text{CH}_2=\text{C}(\text{COOCH}_3)\text{CH}_2$ should be bound at the α - and ω -ends, respectively.

To assign the signals of the CH_2Br , the spectra of the polymer before and after the reaction with the tin hydride shown in Figures 2A and 2B are compared.

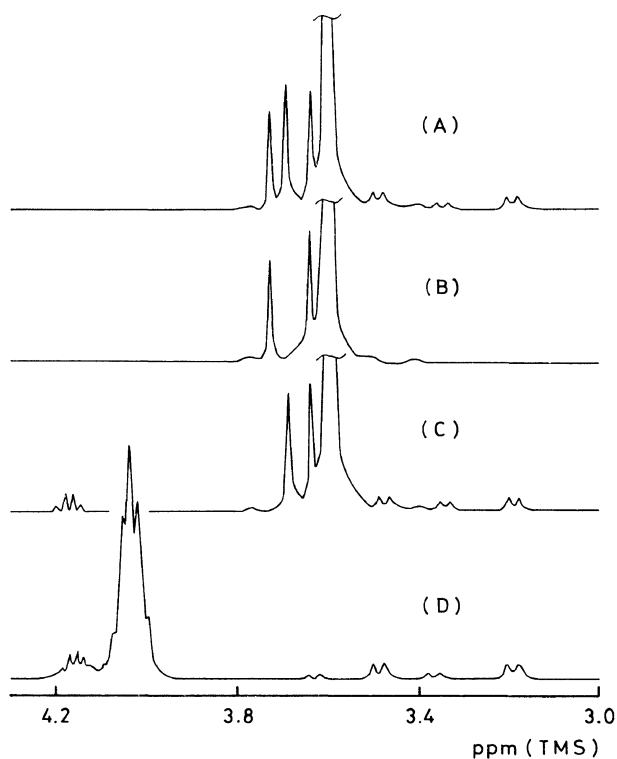
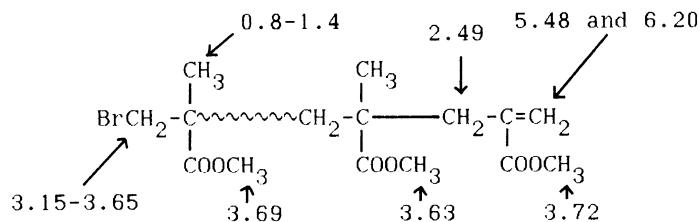


Figure 2. NMR spectra of poly(MMA) obtained by polymerization in the presence of MBMA before (A) and after (B) reduction with tributyltin hydride. C shows the spectrum of poly(MMA) which was prepared under the conditions of $[\text{MMA}]=3.76 \text{ mol l}^{-1}$, $[\text{EBMA}]/[\text{MMA}]=0.10$ (molar ratio), and $[\text{AIBN}]=0.006 \text{ mol l}^{-1}$, and D shows the spectrum of poly(EMA) obtained by polymerization at $[\text{EMA}]=5.59 \text{ mol l}^{-1}$, $[\text{EBMA}]/[\text{EMA}]=0.10$, and $[\text{AIBN}]=0.006 \text{ mol l}^{-1}$.

pairs of the doublet at a lower and higher magnetic fields given in Figure 3 are shown by the dyad tacticity of the consecutive MMA units from the α -end, *meso* and *recom* alignments, respectively, and the configuration of the asymmetric carbon bound to the CH_2Br . Content of the *meso* dyad is estimated to be 31% from the expanded spectrum in



Although the signals of the α - CH_3 of the monomeric units seemed to be changed by the tacticity and the structure of the end group, quantitative interpretation of these signals could not be done.

On the basis of the signals assigned to the end group and the repeating monomeric unit, \bar{M}_n of the polymer was estimated. Table II shows \bar{M}_n determined by GPC, vapor pressure osmometry (VPO), and the NMR spectroscopy. Apparently, the amounts of the end groups agree with the estimates from \bar{M}_n by VPO, and the order of increasing \bar{M}_n determined by GPC is in accordance with those of \bar{M}_n by VPO and the NMR spectroscopy.

The NMR spectrum of the poly(MMA) ($\bar{M}_n=1800$ and $\bar{M}_w/\bar{M}_n=1.30$) obtained by the polymerization at $[\text{AB}]/[\text{MMA}]=0.92$ (molar ratio) is depicted in Figure 4. In addition to the resonances of the repeating

Figure 3. The dyad tacticity of the other end of the polymer can be obtained from the intensity ratio of the peaks at 5.50 and 5.47 ppm¹²; the content of *meso* dyad may be 23%.

Thus the chemical shifts for the terminuses of the poly(MMA) in ppm can be given as follows:

unit of poly(MMA), the peaks due to the allyl group are observed at 5–6 ppm as characteristic multiplets. The signals likely to those in Figures 2A and 2C in the chemical shift range from 3.1 to 3.7 ppm can be assigned to the CH_2Br . The intensity ratio of the resonances of the $\text{CH}_2=\text{CH}$ to those of the CH_2Br is estimated to be 3:2, indicating that the reinitiation occurs quantitatively. These findings evidence that the control of the chain length with AB proceeds through the addition–fragmentation reaction. Abstraction of the allylic hydrogen or bromine could not be a main reaction of the chain transfer, and the polymer structure can be expressed as follow:

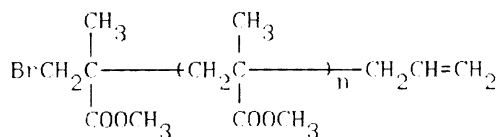


Table II. \bar{M}_n of poly(MMA) determined by different methods

Polymerization condition [MBMA]/[MMA]	\bar{M}_n			\bar{M}_w/\bar{M}_n (GPC)
	GPC	VPO	¹ H NMR	
0.05	3200	3800	3800	1.38
0.10	1200	1540	1700	1.59
0.15	900	1140	1100	1.54

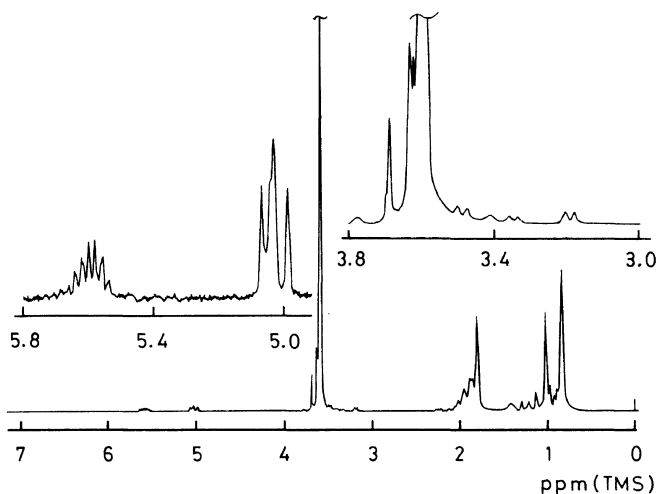


Figure 4. NMR spectrum of poly(MMA) prepared by polymerization in the presence of AB: $[\text{MMA}] = 3.76 \text{ mol l}^{-1}$, $[\text{AB}]/[\text{MMA}] = 0.92$ (molar ratio), and $[\text{AIBN}] = 0.005 \text{ mol l}^{-1}$.

Table III. Polymerization of MA in the presence of MBMA or AB at 60°C :
 $[\text{MA}] = 4.43 \text{ mol l}^{-1}$, $[\text{AIBN}] = 0.005 \text{ mol l}^{-1}$

Bromide	$\frac{[\text{Bromide}]}{[\text{MA}]} \times 10^2$	Time	Conv.	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n
		h	%		
None	0	0.5	50.7	733	1.63
MBMA	0.40	0.5	23.7	6.1	2.03
MBMA	1.06	1.0	25.9	2.7	1.75
MBMA	2.13	1.0	17.3	1.6	1.47
AB	0.52	0.5	34.8	35.1	2.66
AB	1.04	0.5	34.5	15.9	2.55
AB	2.09	0.5	24.7	8.9	2.10

Since one of the initiations of thermal degradation has been known to be scission of the labile carbon-carbon bond between poly(MMA) chain and the end group, $\text{CH}_2 = \text{C}(\text{COOCH}_3)\text{CH}_2$, introduced by disproportionation,¹³ the poly(MMA) bearing the same end group was considered to show lower thermal stability than that terminated with the $\text{CH}_2 = \text{CHCH}_2$. Consistently, TGA of the poly(MMA) controlled with MBMA showed T_{init} and T_{max} to be 290 and 321°C , respectively, and $T_{\text{init}} = 280$ and $T_{\text{max}} = 350^\circ\text{C}$ were determined for the poly(MMA) terminated with AB. Apparently the $\text{CH}_2 = \text{C}(\text{COOCH}_3)-$

CH_2 facilitated the thermal degradation more than $\text{CH}_2 = \text{CHCH}_2$ did.

Polymerization of MA

MA which polymerizes faster to higher molecular weight than MMA was allowed to polymerize in the presence of a small amount of MBMA or AB. Although as shown in Table III, MBMA and AB effectively reduced the chain length of poly(MA), the polymerization rate was also significantly lowered. In these cases, reinitiation with bromine could not be sufficiently fast. The values of C_s for MBMA and AB were evaluated to be 2.93

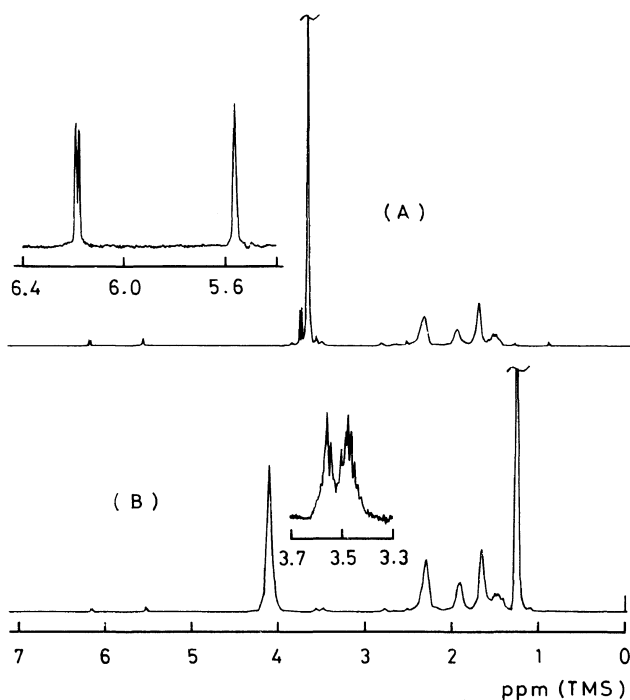
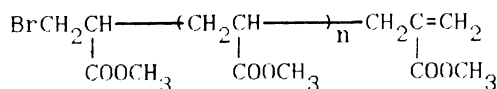


Figure 5. NMR spectra of poly(MA) (A) and poly(EA) (B) prepared by polymerization in the presence of MBMA and EBMA ($[MA]=4.43 \text{ mol l}^{-1}$, $[MBMA]/[MA]=0.021$ (molar ratio), $[AIBN]=0.005 \text{ mol l}^{-1}$, $[EA]=3.69 \text{ mol l}^{-1}$ and $[EBMA]/[EA]=0.023$ (molar ratio), and $[AIBN] 0.006 \text{ mol l}^{-1}$), respectively.

and 0.46, respectively.

The polymerization of MA terminated with MBMA gave the polymer of which ^1H NMR



spectrum is shown in Figure 5A: The observed signals from 1.0 to 2.5 ppm are due to the main chain of the poly(MA) ($\bar{M}_n=1600$ and $\bar{M}_w/\bar{M}_n=1.47$). Among the signals of the methoxy groups, that due to the unsaturated terminal group appears at 3.7–3.8 ppm. Figure 5B shows the spectrum of poly(EA) terminated with EBMA. The peaks assignable to the CH_2Br are observed at 3.4 to 3.6 ppm. A difference in chemical shift between the two peaks, which is too large to be split by coupling of geminal hydrogens, seems to be caused by the asymmetric carbon bound to the CH_2Br or different tacticities.

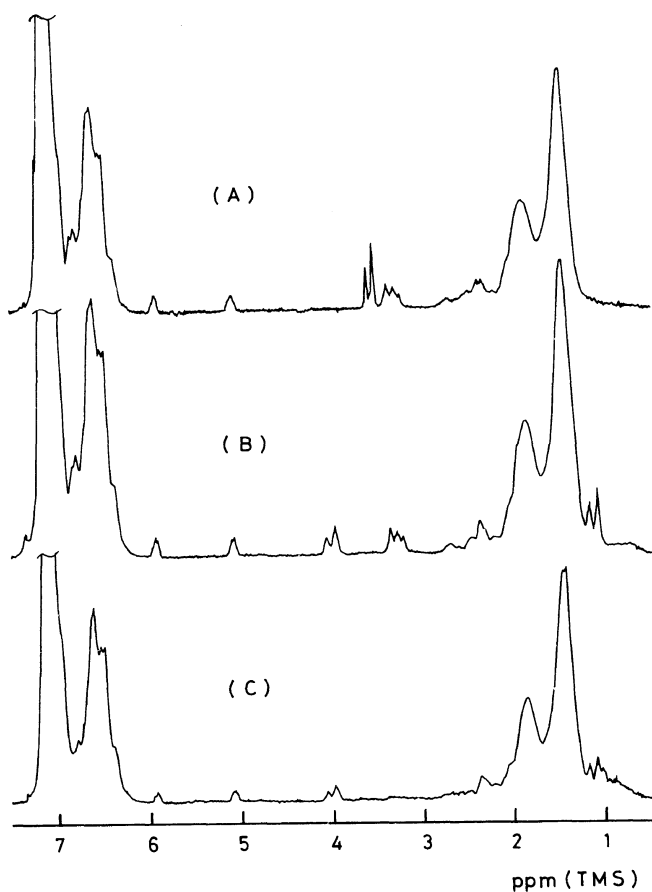
Polymerization of St

Results of the St polymerization in the presence of MBMA, AB, and BZB are summarized in Table IV. While an increase in MBMA concentration substantially reduced \bar{M}_n of the resulting poly(St), AB exerted only a limited effect of \bar{M}_n . The C_s 's were evaluated to be 2.34 (MBMA), 0.06 (AB), and 0.02 (BZB). This tendency could be accounted for by fast addition of electron donating poly(St) radical to MBMA bearing an electron attracting group. Contrarily, the addition to AB seems to be unfavorable by polar factor. Decreases in \bar{M}_n of poly(St) caused by AB and BZB could be ascribed to hydrogen or bromine abstraction.

If the decrease in \bar{M}_n was induced by the addition–fragmentation reaction, the polymer should bear the Br and $\text{CH}_2=\text{C}(\text{COOR})\text{CH}_2$ at the α - and ω -ends, respectively:

Table IV. Polymerization of St in the presence of MBMA, AB, or BZB in benzene at 60°C:
[St] = 3.48 mol l⁻¹, [AIBN] = 0.005 mol l⁻¹

Bromide	$\frac{[\text{Bromide}]}{[\text{St}]} \times 10^2$	$R_p/\% \text{ h}^{-1}$	$\bar{M}_n \times 10^{-3}$	\bar{M}_w/\bar{M}_n
None	0	1.50	59.0	1.69
MBMA	1.25	0.85	3.6	1.86
MBMA	2.23	0.40	2.8	1.31
AB	2.27	1.45	27.9	1.89
AB	5.00	1.40	20.6	1.79
BZB	2.53	1.47	35.8	2.03
BZB	5.07	1.45	32.9	2.10

**Figure 6.** NMR spectra of poly(St) prepared by polymerization in the presence of MBMA ([St] = 6.96 mol l⁻¹, [MBMA]/[St] = 0.02 (molar ratio), and [AIBN] = 0.005 mol l⁻¹) (A) and EBMA ([St] = 6.96 mol l⁻¹, [EBMA]/[St] = 0.02 (molar ratio), and [AIBN] = 0.005 mol l⁻¹) (B), and of the polymer (B) after reduction with tributyltin hydride (C).

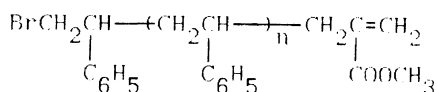
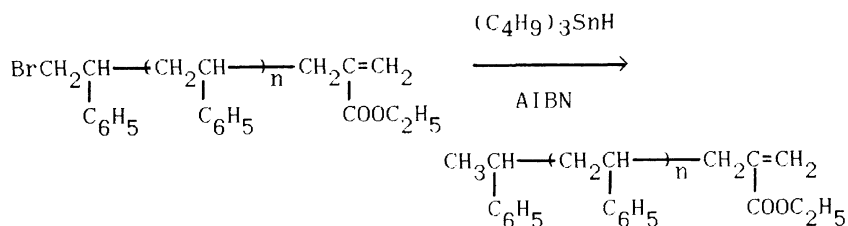


Figure 6A shows the ^1H NMR spectrum of the poly(St) ($\bar{M}_n=2200$ and $\bar{M}_w/\bar{M}_n=1.38$) obtained at $[\text{MBMA}]/[\text{St}]=0.02$ (molar ratio), which is quite similar to those of the poly(St) end-functionalized with α -((hydroxy-

ethyl)thiomethyl)vinyl monomers reported by Meijs and coworkers,³ except for the signals due to the α -end group. The spectra of the poly(St) (prepared at $[\text{EBMA}]/[\text{St}]=0.02$ (molar ratio), $\bar{M}_n=2000$, and $\bar{M}_w/\bar{M}_n=1.34$) before and after the reduction with tributyltin hydride are also given in Figures 6B and 6C, respectively.



Comparison of these spectra reveals that signals at 3.2—3.4, 3.5—3.6 or *ca.* 4, and 5.09 and 5.92 ppm are due to the CH_2Br , CH_3O or CH_2O , and $\text{CH}_2=\text{C}$, respectively. Split of the signals of the CH_2Br , CH_3O , and CH_2O could be caused by the magnetic anisotropy of the phenyl group depending on the dyad tacticities at the both chain ends.

CONCLUSION

MBMA and EBMA effectively shortened poly(MMA), poly(St), and poly(MA) chains and the end groups of the polymers relating to the reaction mechanism are unambiguously determined. Chain transfer of poly(MMA) and poly(MA) radical to AB was found to proceed through the addition-fragmentation mechanism, since the Br and $\text{CH}_2=\text{CHCH}_2$ were quantitatively introduced to the α - and ω -ends, respectively. The higher reactivities of AB toward poly(MMA) and poly(MA) radicals than poly(St) radical are ascribable to the nucleophilic character of AB in the addition reaction.

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