Synthesis of Controlled Block and Graft Copolymers. I. Block-Polymerizations Initiated Asymmetric Telechelic Bromo-Terminated Polymer Together with Manganese Carbonyl

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SYNTHESIS OF CONTROLLED BLOCK AND GRAFT COPOLYMERS. I. BLOCK–POLYMERIZATIONS INITIATED ASYMMETRIC TELECHELIC BROMO–TERMINATED POLYMER TOGETHER WITH MANGANESE CARBONYL

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ABSTRACT

Various types of halogen-terminated polymers having different backbones were synthesized and used as polymeric initiators together with manganese carbonyl for block polymerizations. The number of end groups and the molecular weights of the polymeric initiators could be varied by adjusting the feed composition and the transfer agent. Block polymerizations of methyl methacrylate and styrene with these telechelic bromo-terminated polymers-manganese carbonyl initiator systems were carried out photochemically at 30°C and in the dark at 80°C. It was found that the dark polymerization with the initiator system at 80°C provided excellent conditions to control the length of the blocks. Polymerization of methyl methacrylate initiated by manganese carbonyl together with carbon tetrabromide as a model compound of the polymeric initiator was also investigated. Block-forming efficiencies of these block polymerizations were estimated to range from 96 to 99%. The number-average degree of polymerization of blocks of the second monomer obtained by use of the telechelic bromo-terminated backbone polymer as polymeric initiator could be controlled by adjusting the amount of the second monomers and the polymeric initiator/manganese carbonyl ratio.

INTRODUCTION

Recently, macromonomers, macroinitiators, and macroinifers have been investigated with the objective of designing polymers [1-5]. Bamford and coworkers [6] were the first to show that the polymerization of methyl methacrylate is initiated by manganese carbonyl in the presence of carbon tetrachloride as a result of the formation of trichloromethyl radical. This method has been successfully applied to the synthesis of block copolymers starting with poly(methyl acrylate-*alt*-butadiene) having tribromomethyl end groups [7].

We have been studying the possibility of designing block and graft co-polymers by free-radical polymerization using macrophotoiniferter [4, 8] and macromonomers [2]. The present paper deals with the preparation of some halogen-terminated polymers and the polymerization of vinyl mono-mers by manganese carbonyl and halogen-terminated polymers as polymeric initiators, together with a kinetic study of the polymerization of methyl methacrylate with the carbon tetrabromide-manganese carbonyl initiator system.

EXPERIMENTAL

Materials

Manganese carbonyl (MnC) (Strem Chemicals, U.S.A.) was purified at room temperature by sublimation in vacuum. Styrene (St), methyl meth-acrylate (MMA), ethyl acrylate (EA), carbon tetrabromide (CTB), 1-bromo-butane, thioglycolic acid, epibromohydrin, and solvents were purified by the usual methods. Azobisisocyanovaleric acid (ACVA) and azobisisobutyro-nitrile (AIBN) (Aldrich Chemical, U.S.A.) were used without further purifica-tion.

Preparation of Halogen-Terminated Polymers

For the design of the halo-terminated polymers as polymeric initiators, we utilized the method described in a previous paper [2]. Polymerizations were carried out by the conventional method [2]. The polymer was purified by reprecipitation from benzene or acetone into methanol (poly-St backbone) or petroleum ether (poly-MMA and poly-EA backbones). The carboxyl-ter-minated prepolymers were purified by reprecipitation with acetone-petro-leum ether and then with acetone-distilled water to remove unreacted thio-

glycolic acid. The monofunctional polymeric initiator with a bromomethyl end group was prepared by the reaction of the prepolymer obtained with 50 mol% excess of epibromohydrin at 140°C according to the method reported previously [9].

Polymerization Procedure

In a nitrogen-filled dry box, MnC was weighed into a volumetric flask which was than capped. MnC-benzene solution, polymeric initiator, monomer, and benzene were introduced by pipetting required volumes into a hard-glass tube. The tube was degassed under vacuum by the usual freezing-and-thawing technique and then sealed.

The tube was placed in a thermostated bath for the desired time. Free-radical polymerization was carried out in the dark at 80°C and photopolymerization by a low-pressure mercury lamp (150 W, Riko Co.) at a constant distance of 50 mm at 30°C. The ampule was then removed from the bath, and the polymerization was stopped by cooling to -20°C. Then the ampule was cautiously opened, and the mixture was poured into a large amount of precipitant. The polymer was purified by reprecipitation cycles and then dried in vacuum to constant weight.

Measurements

Number-average molecular weights were measured with a Knauer vapor-pressure osmometer and a Knauer membrane osmometer.

Measurements of ultraviolet and visible spectra were made with a Model 120 Shimadzu spectrophotometer in a quartz cell of 10 mm optical length at constant temperature.

Molecular weight distributions (MWD) were measured with a Shimadzu high-performance liquid chromatograph, Model LC-3A, equipped with three columns (HSG-15, HSG-30, and HSG-50) and Model LC-5A, equipped with two columns (HSG-40 and HSG-60). The products were detected with a dual differential refractometer and an ultraviolet spectrophotometer. The flow of tetrahydrofuran was maintained at 1.0 mL/min. A molecular weight calibration curve was obtained on the basis of universal calibration with 12 standard narrow-MWD polystyrene samples of molecular weights 800-860 000. From the results of gel-permeation chromatography (GPC), the number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were obtained by conventional procedures.

Carboxyl and halogen end groups of the polymers were estimated by potentiometric titration with a Hiranuma reporting titrator (Model Comtite-7) and by the micro-Carius method [10].

Proton NMR spectra were recorded on a 400 MHz instrument, Joel JNM-GX400 FT NMR spectrometer, with deuterochloroform as solvent.

RESULTS AND DISCUSSION

Preparation of Halogen-Terminated Polymers

Table 1 shows the structural formulas of halogen-containing polymers used as polymeric initiators for block polymerization. The synthesis conditions and the characteristics of polymeric initiator are summarized in Table 2. The experimentally observed and calculated number-average molecular weights were in agreement with only a small deviation. The polymeric initiator with ester spacers, EBS1 and EBS2, were obtained by the reaction of the carboxyl-terminated polystyrene with epibromohydrin. The number of terminal bromine atoms per polymer molecule was estimated to be 4.0-4.2 (telechelic type) and 0.8-1.0 (monofunctional type) by the use of the molecular weight and the bromine content data. The results indicate that polymeric initiators of the desired functionality and molecular weights are obtained. In this study we employed telechelic polymeric initiators.

### Photo and Dark Polymerization of MMA Initiated by Asymmetric Telechelic Bromo-Terminated Poly-St, TBS, and MnC

Block polymerization of MMA with the TBS initiator system was carried out in benzene ([MMA] = 3.0 mol/L) at 80°C in the dark and at 30°C irradiated by UV. The time/conversion curves are shown in Fig. 1. Both polymerizations proceeded smoothly and homogeneously. It is clear that the photopolymerization of MMA with TBS proceeded even in the absence of MnC (Fig. 1, Line C), although it was slower than the polymerization in the presence of MnC.

In the polymerization of St with the same initiator system, the chain-extended poly-St was obtained as shown by Scheme 1. It was found that the polymerization by UV irradiation is faster than that in the dark at 80°C for both St and MMA polymerizations with the TBS-MnC initiator system.

Typical GPC chromatograms of the block copolymer products under various polymerization conditions are compared in Fig. 2. There is a significant difference between the photopolymerization and dark polymerization. For the polymerization with TBS-MnC in the dark, the GPC curve showed the presence of two species (Fig. 2, A). The area of the low molecular weight

TABLE 1. Structural Formula of Halogen-Terminated Polymers Synthesized as Polymeric Initiators for Block Polymerization

$$FG_1 \left(CH_2 - \underset{\underset{R_2}{|}}{\overset{\overset{R_1}{|}}{C}} \right)_n FG_2$$

Polymer	FG$_1$	FG$_2$	R$_1$	R$_2$	n
TBM1	$-CBr_3$	$-Br$	$-CH_3$	$-\overset{\overset{O}{\|\|}}{C}OCH_3$	35
TBM2					312
TBS	$-CBr_3$	$-Br$	$-H$	phenyl	29
TBE	$-CBr_3$	$-Br$	$-H$	$-\overset{\overset{O}{\|\|}}{C}OCH_3$	283
MBS	$-C_4H_9$	$-Br$	$-H$	phenyl	148
EBS1	$-SCH_2\overset{\overset{O}{\|\|}}{C}OCH_2\overset{\overset{OH}{\|}}{C}HCH_2Br$	$-H$	$-H$	phenyl	4
EBS2					30

peak, which is in agreement with the peak position of the TBS, decreased with increasing polymerization time. From the difference between the refractive index and UV responses, it is obvious that the higher peak corresponds to the main block copolymer derived from TBS. The intensity of the peaks increased with the polymerization time, and the peak position gradually shifted to a higher molecular weights.

TABLE 2. Results of the Synthesis and Characterization of Halogen-Terminated Polymers[a]

Polymer	Transfer agent[b]	f_0[c]	Yield, %	$\bar{M}_n \times 10^{-3}$[d]	Br, mmol/g	N_{Br}[e]
TBS	CTB[e]	50	25.2	3.34	1.198	4.0
TBM1	CTB	10	27.4	3.81	1.060	4.0
TBM2	CTB	75	28.8	31.6	0.128	4.0
TBE	CTB	200	44.5	24.7	0.169	4.2
MBS	BB	5	35.2	15.5	0.058	0.9
EBS1	TGA	40	17.8	3.38	0.237	0.8
EBS2	TGA	20	30.3	0.60	1.667	1.0

[a]The polymers are used as a polymeric initiator with manganese carbonyl.
[b]CTB = carbon tetrabromide, BB = 1-bromobutane, TGA = thioglycolic acid. Monobromo-terminated polymer is prepared by the reaction of carboxyl-terminated prepolymer with epibromohydrine.
[c]Concentration ratio of monomer per transfer agent in feed.
[d]By vapor-pressure and membrane osmometry.
[e]Number of bromine atoms per polymer molecule.

On the other hand, the GPC chromatograms of the polymer produced from the photopolymerization with the TBS-MnC system had a broad molecular weight distribution (Fig. 2, B). The position of the peak maximum lies between the position of block copolymer and that of TBS starting material. The results of the photopolymerization of MMA with TBS-MnC were markedly different from those of the thermal polymerization with the same initiator system, evidently because of the difference in the initiation ability of TBS in the absence of MnC.

The GPC chromatograms of the polymers from the photopolymerization with TBS in the absence of MnC again showed two peaks (Fig. 2, C). The changes in the GPC pattern and the relation between time and conversion are generally similar to those of the dark polymerization with the TBS-MnC system, but the peak position of the corresponding block copolymer is shifted slightly to lower molecular weights with conversion.

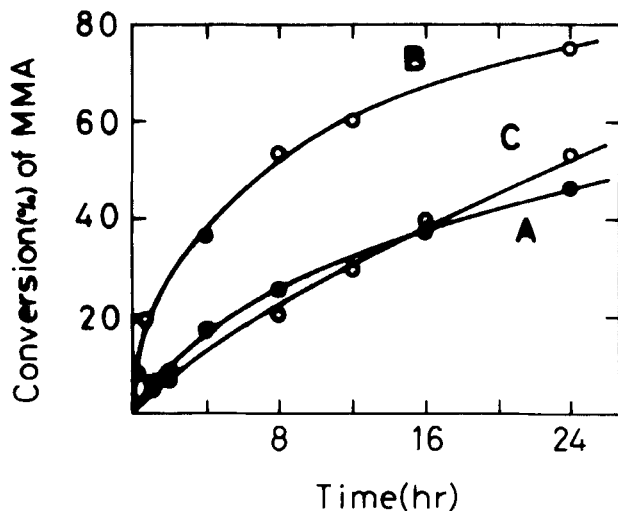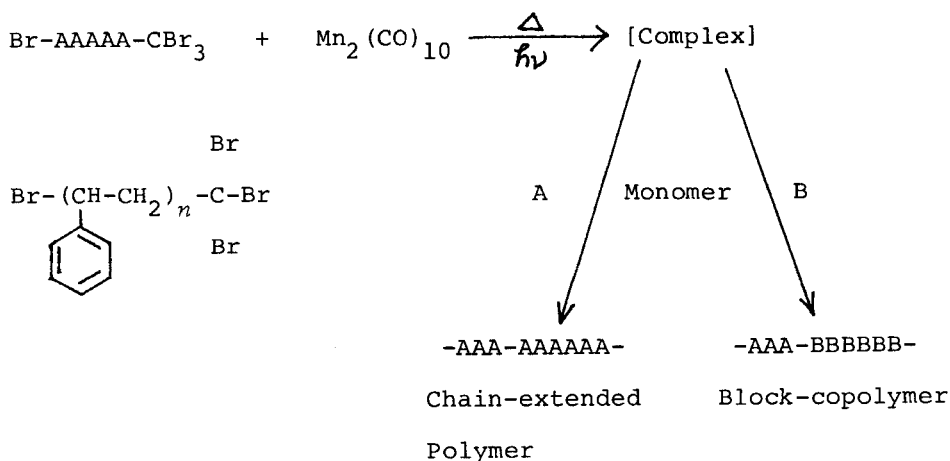These results suggest that photopolymerizations with TBS-MnC and TBS

FIG. 1. Time/conversion curves of the block polymerization of MMA (3.0 mol/L) initiated by the telechelic bromo-terminated polystyrene (TBS) with manganese carbonyl (MnC) in benzene ([TBS] = [MnC] = 3.0 mmol/L): A, 80°C in the dark; B, 30°C by UV irradiation; C, 30°C by UV irradiation in the absence of MnC.
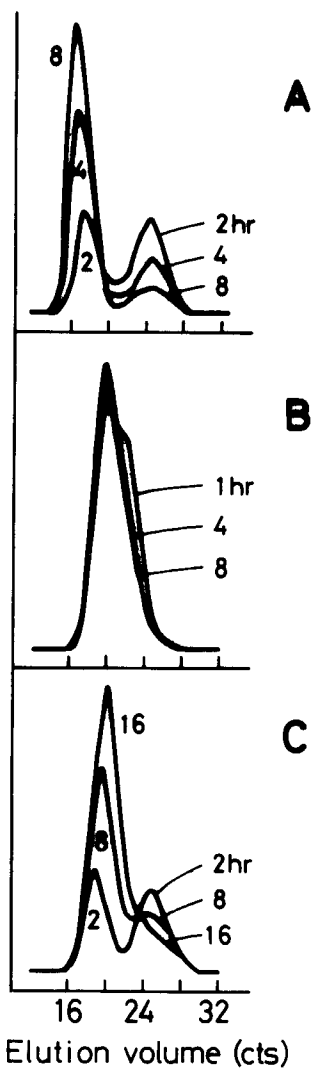

SCHEME 1.

FIG. 2. GPC chromatograms of block copolymeric products: A, TBS-MnC system in the dark; B, TBS-MnC system by UV irradiation; C, TBS only by UV irradiation.
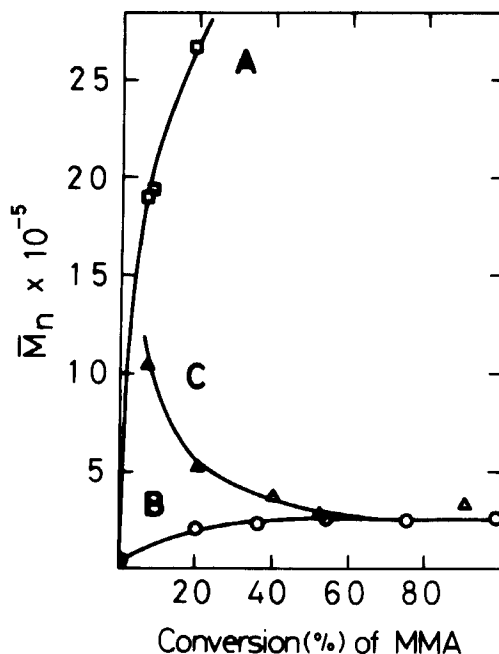
FIG. 3. Relationship between the molecular weight of the block copoly-
mer and the conversion. A, TBS-MnC system in the dark; B, TBS-MnC system
by UV irradiation; C, TBS only by UV irradiation.

alone are not really excellent for designing block copolymers, although TBS
is most likely consumed by photochemical reaction.

   Figure 3 shows the relationship between block-copolymer molecular weight
and conversion for the polymerization of MMA. The molecular weight in-
creases with conversion up to 30-40% in both thermal and photopolymeriza-
tion with TBS-MnC. The increase of molecular weight with conversion is much
sharper in thermal polymerization than in photopolymerization. For photo-
polymerization with TBS alone, the molecular weight of the block copolymer
decreased with increasing conversion up to ~40% and leveled off at ~50%. The
molecular weight was similar to that of polymer derived from photopolymeri-
zation with TBS-MnC.

   These results indicate that the dark polymerization with TBS-MnC is pre-
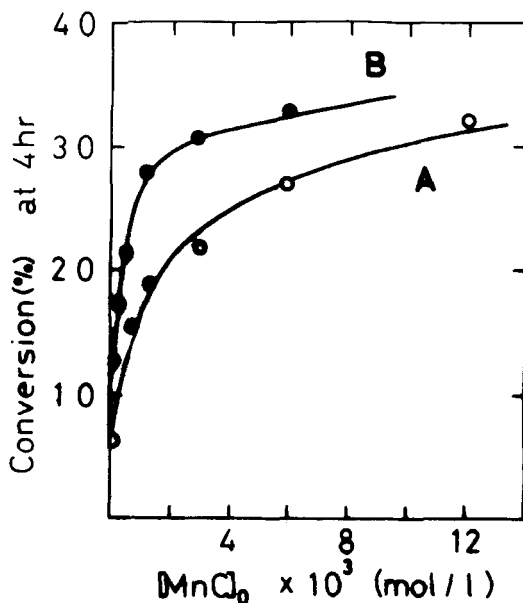ferable for molecular weight control of block copolymer.

FIG. 4. Plots of the conversion after 4 h vs the concentration of MnC for MMA polymerization. Concentration of TBS, 3.0 mmol/L. A, at 80°C in the dark; B, at 30°C by UV irradiation.

Effect of MnC Concentrations on the Rate of Polymerization and the Molecular Weight

The concentration of MnC was varied in the range of 0.12-12.0 mmol/L by keeping the concentration of TBS (3.0 mmol/L) and MMA (3.0 mol/L) constant. Figure 4 shows the relationship between the conversion at 4.0 h and the MnC concentration for the polymerization of MMA with the TBS-MnC system. The conversion increases markedly with MnC concentration up to 1.2 mmol/L and then gradually increases up to 12.0 mmol/L. This may indicate that the rate of polymerization tends toward a steady value above 12.0 mmol/L MnC. The dependence of the rate of polymerization on MnC concentrations for thermal and photopolymerizations are similar.

The dependence of the rate of polymerization on the MnC concentrations in the range from 0.12 to 1.20 mmol/L was determined by the gravimetric method. Conversion were kept below 10% (Fig. 5). In the range of the concentrations studied, the plots gave a square-root relationship with a slope of
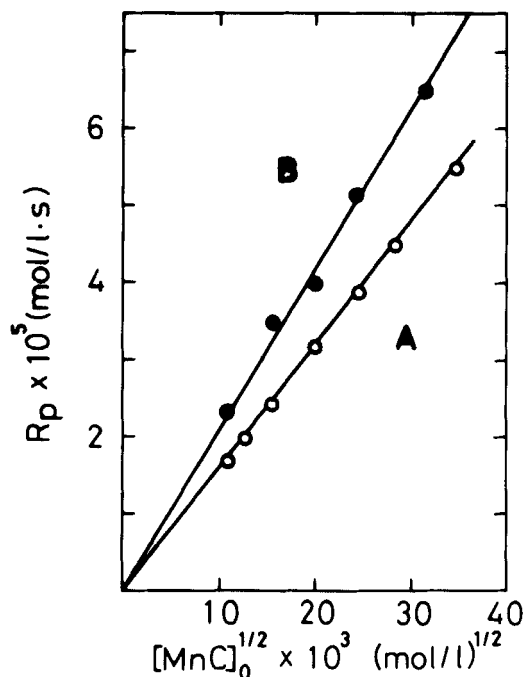
FIG. 5. Effect of MnC concentrations on the rate of polymerization of MMA with the TBS-MnC initiator system. ([TBS] = 30 mmol/L and [MMA] = 3.0 mol/L): A, at 80°C in the dark; B, at 30°C by UV irradiation.

1.59 and of 2.07 for the thermal and photopolymerizations, respectively. As is shown later, the rate of polymerization for CTB-MnC, as a low molecular weight model of TBS, was found to be first order in the monomer concentration. Therefore, the rate of polymerization, R_p, of MMA initiated by the TBS-MnC system with a constant TBS concentration is given by the following equation, where $\delta = k_t^{1/2}/k_p$ [(mol·s)/L]$^{1/2}$.

$$R_p = (\delta^{-1})\theta^{1/2} [MnC]^{1/2} [M].\tag{1}$$

Values of θ for both polymerizations were calculated by using $\delta = 6.90$ at 80°C and $\delta = 21.3$ [(mol·s)/L)]$^{1/2}$ at 30°C [11]. The values of θ at constant TBS (3.0 mmol/L) for dark polymerization at 80°C and photopolymerization at 30°C were determined to be 1.34×10^{-5} and 21.6×10^{-5} s^{-1},
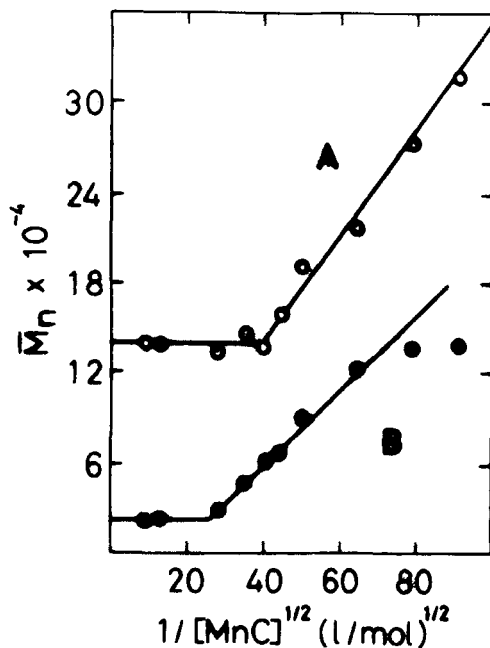
FIG. 6. Plots of molecular weight of the block copolymer vs the reciprocal square root of the MnC concentration: A, at 80°C in the dark; B, at 30°C by UV irradiation.

respectively, i.e., the θ value for photopolymerization at 30°C was about 16 times as high as that for dark polymerization at 80°C.

Molecular weights of block copolymer obtained with various MnC concentrations and constant TBS concentration were calculated from GPC chromatograms (Fig. 6). The molecular weight of the block copolymers increased linearly with the reciprocal square root of the MnC concentration decreased at MnC < 1.0 mmol/L. At higher MnC concentration, the plots were flat in both polymerizations; however, the molecular weight for dark polymerization was considerably greater than that for photopolymerization. Dark polymerization is excellent for designing block copolymers because the molecular weight is controllable over a wide range.
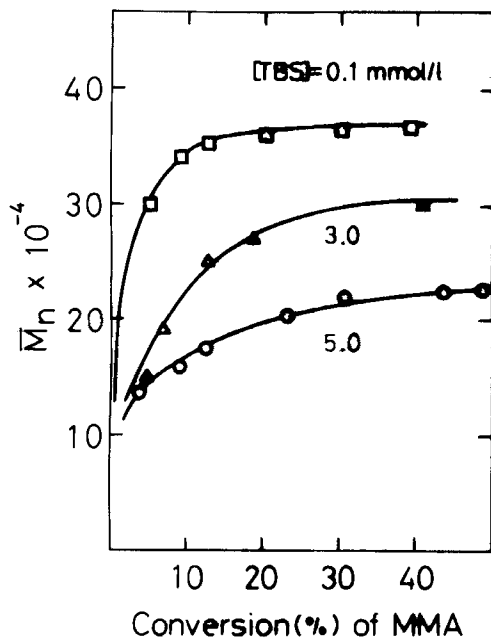
FIG. 7. Dependence of molecular weight of the block copolymer on the TBS concentration.

Effect of TBS Concentrations on Molecular Weight of Block Copolymer

Polymerization of MMA with the TBS-MnC system was carried out in benzene at 80°C. The concentration of MnC was kept at 3.0 mmol/L. The relationship between the molecular weight of block copolymer and the conversion of MMA is shown in Fig. 7. The molecular weight of the block copolymer increased and as the TBS concentration decreased. It seems that the ratio of TBS to MnC concentrations is important for designing well-defined block copolymers. Since a more detailed study of the effect of polymeric initiator concentration on the molecular weight and the rate of polymerization is difficult, we employed a model compound of polymeric initiator.

Polymerization of MMA Initiated by the CTB-MnC System

Figure 8, Line A, shows the relationship between the rate of polymerization and the concentration of MMA in benzene for CTB, a model compound
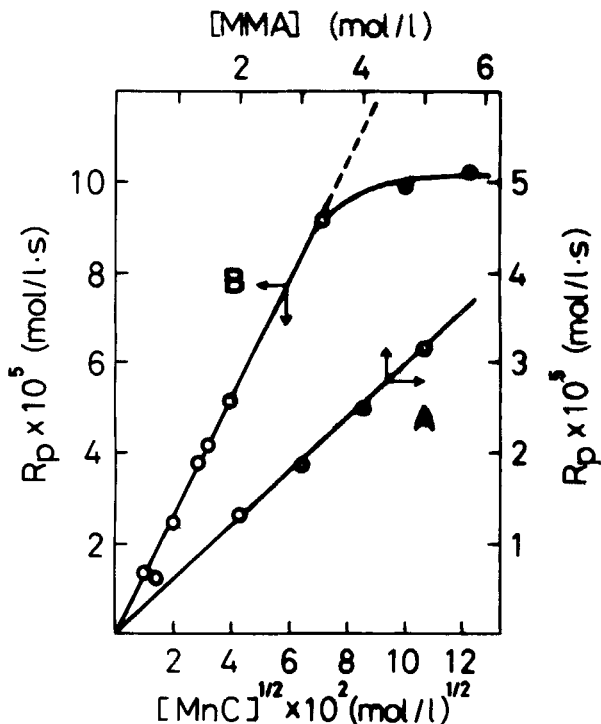
FIG. 8. Dependence of the rate of polymerization on monomer concentration ([CTB] = 0.1 mmol/L, [MnC] = 1.0 mmol/L, 80°C) (A) and MnC concentration ([CTB] = 1.0 mmol/L, [MMA] = 3.0 mol/L) (B) for the polymerization of MMA with CTB-MnC.

for the polymeric initiator. A linear plot was obtained for R_p vs monomer concentration, [M], with a slope of 6.34×10^{-6} (s^{-1}). The rate of polymerization is first order in monomer. A plot of the rate of polymerization vs the square root of MnC concentration from 0 to 1.6 mmol/L gave a straight line with a slope of 1.31×10^{-3} $(mol/L)^{1/2}/s$ as shown in Fig. 8, Line B. At higher concentrations of MnC, it seems that the primary radicals are wasted by coupling in the solvent cage or by termination with fragments outside the cage before they can initiate polymerization.

The relationship between the rate of polymerization of MMA and CTB concentration is shown in Fig. 9 at several levels of MnC. In all cases, the re-
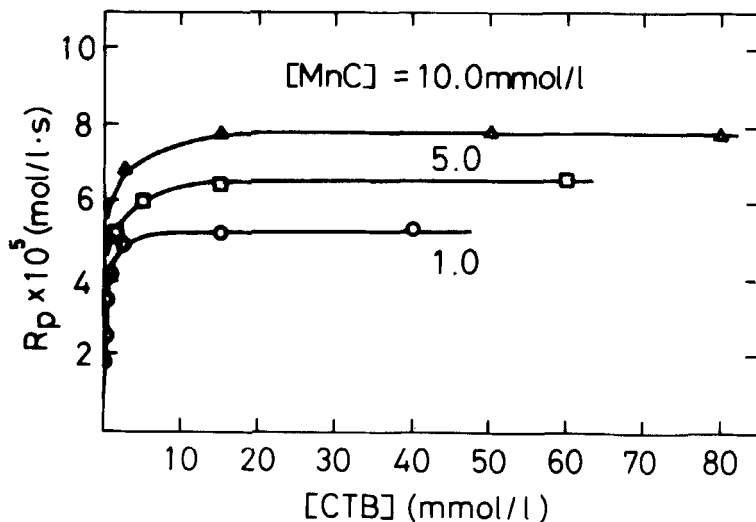
FIG. 9. Effect of CTB concentrations on the rate of polymerization for the polymerization of MMA with CTB-MnC ([MMA] = 3.0 mol/L).

lation of R_p and [CTB] had a similar form, R_p increasing rapidly with increasing CTB concentration up to 2.5 mmol/L and then leveling out.

If a Michaelis-Menten type rate equation can be applied to the initiation of this system, the rate of initiation is given by

$$MnC + CTB \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [complex] \xrightarrow{k_3} R^* + Mn_2(CO)_9,$$
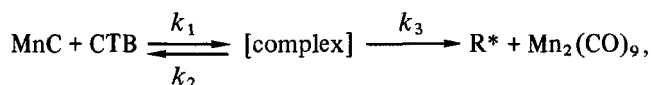
$$R_i = f\alpha[MnC] \ \frac{\beta[CTB]}{1 + \beta[CTB]}, \tag{2}$$

where $\alpha = k_3$ (s^{-1}) and $\beta = k_1/(k_2 + k_3)$ (L/mol). The rate of polymerization, R_p, is given by

$$R_p = \delta^{-1}f^{1/2} \left[\frac{\alpha\beta[CTB]}{1 + \beta[CTB]} \right]^{1/2} [MnC]_0^{1/2} [M], \tag{3}$$

where $\delta = k_t^{1/2}/k_p$; k_t and k_p are the termination and propagation rate constants, respectively; and f is the initiator efficiency. The rate of polymerization can also be expressed as Eq. (4) when $f = 1$:

$$\frac{1}{R_p^2} = \frac{\delta^2}{\alpha\beta[MnC]_0[M]^2} \frac{1}{[CTB]} + \frac{\delta^2}{\alpha[MnC]_0[M]^2}. \tag{4}$$

For the polymerization at a constant concentration of MnC and monomer, a plot of $(1/R_p^2)$ vs $1/[CTB]$ should yield a straight line. The linear relationship observed in Fig. 10 supports the mechanism as postulated. The values of α and β are determined as 15.1×10^{-6} s^{-1} and 1.4×10^3 L/mol, respectively, from the slope and intercept of the straight line for the polymerization.

On the other hand, from the slopes of the straight lines in Fig. 8, the values of θ in Eq. (1) were estimated to be 1.92×10^{-6} s^{-1} for CTB = 0.1 mmol/L and 9.07×10^{-6} s^{-1} for CTB = 1.0 mmol/L. Comparison of Eqs. (1) and (3) indicates that θ is equivalent to $\alpha\beta[CTB]/(1 + \beta[CTB])$. Then the values of α and β were estimated as 15.5×10^6 s^{-1} and 1.41×10^3 L/mol, respectively,

FIG. 10. Plot of Eq. (4) for dependence of polymerization rate on the concentration of CTB ([MnC] = 1.0 mmol/L).

FIG. 11. Plot of the reciprocal of the number-average degree of polymeri-zation as a function of the [CTB]/[MMA] ratio.
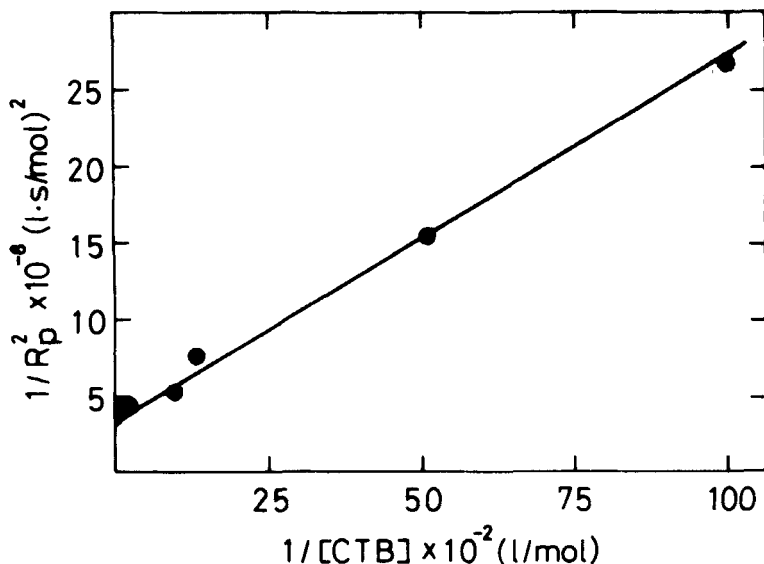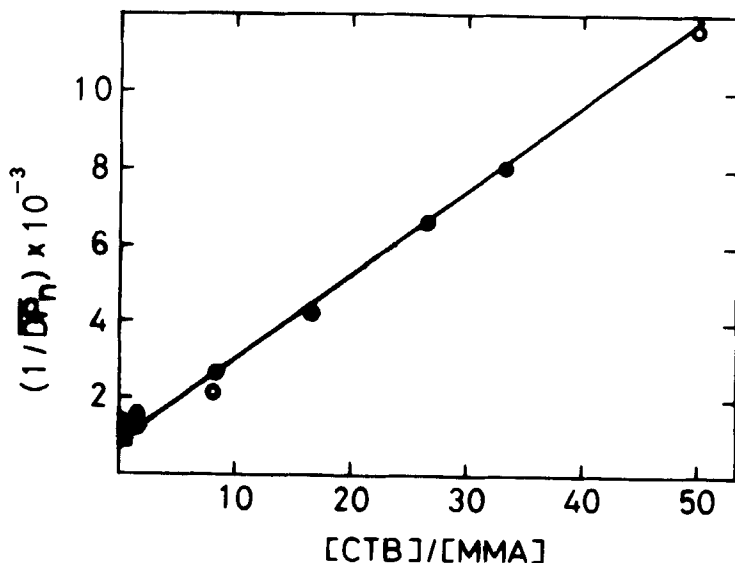
in good agreement with the values obtained from the data on the effect of CTB concentration on the rate of polymerization. The theoretical relation of R_p and [CTB] was calculated by Eq. (3) with the use of the estimated values, and the results for the case [MnC] = 1.0 mmol/L is illustrated in Fig. 9 with a solid line. In this case, all experimental points showed good fits to the calculated line. However, for [MnC] 5.0 and 10.0 mmol/L, all experi-mental points were lower than the theoretical lines. This is attributed to low efficiency.

To examine the effect of CTB concentrations on the molecular weight, number-average molecular weights of the instantaneous polymers were de-termined. For free-radical polymerization, the number-average degree of polymerization, $\overline{DP}_n$, is related to CTB concentration by Mayo's equation. In order to evaluate the chain-transfer constant C_f, that equation was used, and $1/\overline{DP}_n$ plotted against [CTB]/[M] is represented in Fig. 11. A good straight line is obtained independent of MnC concentrations. From the slope, a C_f value of 0.25 was obtained. This almost agrees with the value obtained in the polymerization of MMA with AIBN in the presence of CTB [9].

TABLE 3. Characterization of Polymer Formed in the Polymerization of MMA Initiated by the MnC-CTB System in Benzene at $80°C^a$

Time, h	Conversion, %	$\bar{M}_n \times 10^{-3}$	Br content, mmol/g	$N_{Br}{}^b$
0.33	5.6	40.2	1.00	4.0
3.0	22.0	40.0	0.95	3.8
6.0	41.9	38.0	1.05	4.0
9.0	50.1	40.4	1.01	4.1
18.0	70.9	39.2	1.02	4.0
21.0	82.6	36.7	0.98	3.6

^{a}[MnC] = 7.0 mmol/L, [CTB] = 15.0 mmol/L, and [MMA] = 3.0 mol/L.
^{b}Number of bromine atom end groups per polymer molecule.

Table 3 shows the characterization of some typical polymers. Under these conditions, the molecular weight was unaffected by conversion, and the number of terminal bromine atoms per polymer molecule, N_{Br}, was found to be ~4.0, independent of conversion. This result indicates that polymerization with this initiator system is also an effective and useful method for the synthesis of telechelic polymers, and that $\bar{M}_n$ can be regulated by adjusting the concentrations of CTB and MnC.

These model studies show the polymerization at higher concentrations of MnC-polymeric initiator to be more favorable for controlling the block length, whereas the initiator efficiencies become lower.

Block Polymerization of St Initiated by the TBM2-MnC System

To synthesize block copolymers having various length of St blocks, polymerization of St with TBM2-MnC was carried out at 80°C in benzene (see Table 4). GPC chromatograms of the polymers showed only one peak, as shown in Fig. 12. The peak position gradually shifts to higher molecular weights with increasing monomer conversion, owing to block copolymerization. Molecular weights, M_g, estimated from the peak maxima of GPC chromatograms, were almost in agreement with the values calculated from monomer conversion. Under these conditions, it is easy to control the molecular weight and composition of the block copolymer by adjusting the conversion of the second monomer.

TABLE 4. Results of Block Polymerization of Styrene with TBM2-MnC or TBE-MnC Initiator Systems in Benzene at 80°C[a]

Run	Polymeric initiator[b]	Yield, %	$MW^c \times 10^{-3}$	$M_g{}^d \times 10^{-3}$	Blocking efficiency	Degree of polymerization	
						Backbone	St blocks[e]
106	TBE	2.8	29.5	30.0	99.0	242	47
109	TBE	9.8	40.0	41.2	98.7	242	148
112	TBM2	9.4	41.3	41.7	98.9	312	97
114	TBM2	14.8	46.2	44.2	98.2	312	154
115	TBM2	22.0	53.9	56.1	95.9	312	220
134	TBM2	26.5	72.1	73.8	98.1	312	406
132	TBM2	45.4	101.1	99.8	97.1	312	668

[a][TBM2] = [MnC] = 5.0 mmol/L.
[b]TBE = poly(ethyl acrylate) backbone, TBM2 = poly(methyl methacrylate) backbone.
[c]Calculated from the conversion of St and the polymeric initiator concentration.
[d]Molecular weight estimated from peak maximum of GPC chromatograms.
[e]Determined by intensity ratio of benzene ring proton peaks of St unit to methoxy proton peak of polymeric initiator unit.
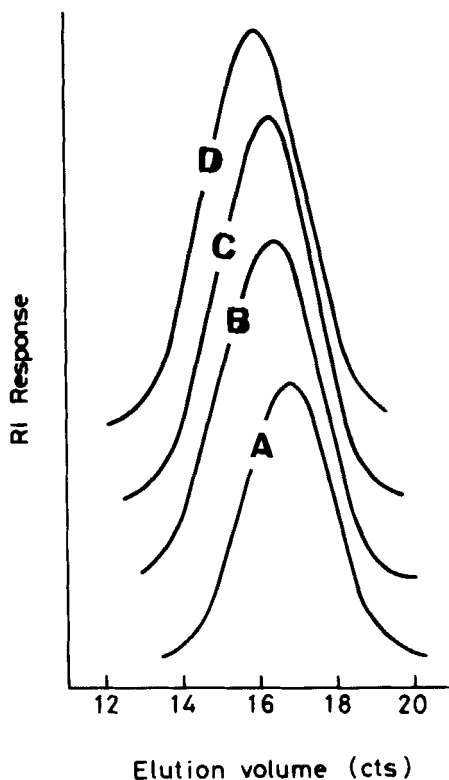
FIG. 12. GPC chromatograms of TBM2-block-St copolymers and TBM2
(A). Conversion of St: B, 9.4%; C, 14.8%; D, 22.0%.

Soxhlet extraction with cyclohexane for 16 h of block copolymer products
removed part of the homopoly-St. Homopolymer contents in the copolymer
samples were below 4%.

A typical proton NMR spectrum of the block copolymer is shown in Fig.
13. The spectrum shows a sharp singlet signal at δ = 3.6 ppm for methoxy
protons. The figure shows that St and MMA units are incorporated into the
block polymer chain as blocks because, as in the random copolymer, any ap-
preciable existence of SMS unit should give a multiplet methoxy proton
resonance due to shielding of neighboring St units.

The degree of polymerization of the poly-St blocks from TBM was deter-
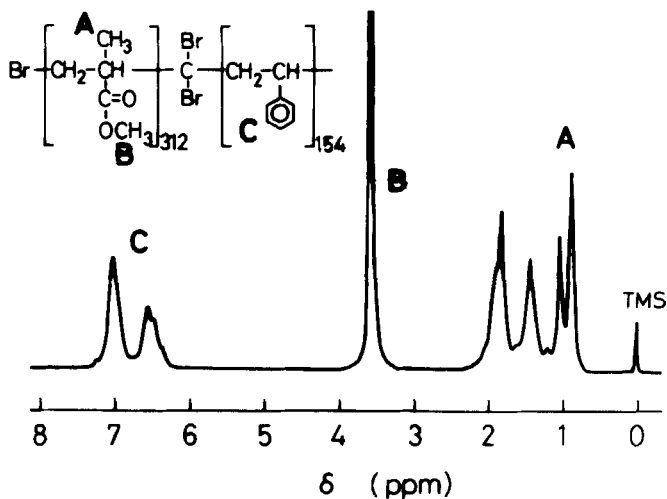mined by the intensity ratio of phenyl proton peaks of St units to the

FIG. 13. 400 MHz proton NMR spectrum of the TBM2-block-St copolymer (Run 114) in deuterochloroform.

methoxy proton peak of TBM units. As shown in Table 4, these are in excellent agreement with the values calculated from conversion and TBM input concentration. The agreement between stoichiometric and experimental values of poly-St blocks proves that nearly all polymerized St monomer has been incorporated into block copolymers. The $\overline{DP}_n$ of poly-St blocks and the composition of the block copolymer are controlled by the addition of St to TBM in the original charge.

Results of block and graft copolymerizations using monohalo functional polymers as polymeric initiators will be described in a future publication.

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