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Synthesis of Controlled Block and Graft Copolymers. II. Block and Graft Polymerization Initiated by Monohalo-Containing Polymer/Manganese Carbonyl Systems

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SYNTHESIS OF CONTROLLED BLOCK AND GRAFT COPOLYMERS. II. BLOCK AND GRAFT POLYMERIZATION INITIATED BY MONOHALO-CONTAINING POLYMER/MANGANESE CARBONYL SYSTEMS

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ABSTRACT

Block polymerization of methyl methacrylate initiated with monohalo-terminated polystyrene/manganese carbonyl systems were investigated. The rate of polymerization was lower than that of the trihalo-terminated polystyrene/manganese carbonyl system. The molecular weight of the block copolymers obtained was independent of the conversion. To define the polymerization mechanism, 1-bromobutane was employed as a model compound for monohalo-terminated polystyrene. Polymerization kinetics followed a modified rate equation based on the Michaelis-Menten mechanism. The molecular weight of the block copolymer could be regulated by varying the ratio of monohalo-terminated polymer to methyl methacrylate. Graft polymerization of methyl methacrylate initiated with chloromethylstyrene-styrene copolymer/manganese carbonyl was also carried out. The polymerization behavior was strongly affected by the concentration of manganese carbonyl. Characterization of graft copolymers by GPC and halogen analysis showed that the number of grafting points per backbone polymer molecule increased when the concentration of manganese carbonyl was raised, but that the branches became shorter.

INTRODUCTION

In an earlier article [1] it was shown that the molecular weight of the poly-(second monomer) block-polymerized from telechelic bromo-terminated backbone polymer as polymeric initiator can be controlled by adjusting the amount of the second monomer, the concentration of the polymeric initiator, and that of manganese carbonyl. The present investigation was undertaken to study the polymerization of methyl methacrylate (MMA) initiated by systems consisting of manganese carbonyl, $\text{Mn}_2(\text{CO})_{10}$ (MnC), and polymers having a monohalo group at the polymer terminal or along the main polymer chain. Comparison of the present results with polymerization initiated by MnC and model compounds or those initiated with MnC and telechelic bromo-terminated polymer can help in the design of block and graft copolymers.

EXPERIMENTAL


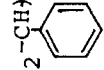
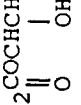


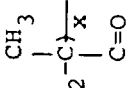

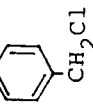
The materials, monobromo-terminated polymers, and procedures have been described previously [1]. Polymeric initiators having monohalo groups along the main chain were prepared by the copolymerization of chloromethylstyrene with styrene and of 2-bromoethyl methacrylate with styrene [2]. The halogen contents of the polymers were estimated by the micro-Carius method [3]. The polymeric initiators used in the study are listed in Table 1, together with the abbreviations used for them.

RESULTS AND DISCUSSION

Block Polymerization of MMA Initiated by the Monohalo-Terminated Polymer/ $\text{Mn}_2(\text{CO})_{10}$ System

Polymerization of MMA was initiated by manganese carbonyl in combination with two types of halo-terminated polymer, monobromo-terminated polystyrene (MBS) and telechelic ($-\text{Br}$ and $-\text{CBr}_3$) bromo-terminated polystyrene (TBS), in benzene at 80°C under identical conditions. Figure 1 shows the time/conversion curves and number-average molecular weights (\bar{M}_n) for these polymerizations. For the TBS/MnC system (Fig. 1, B), polymerization proceeded smoothly, and polymer molecular weights increased with conversion. This indicates that the polymers thus obtained contain an initiating group at the end of the polymer chain, arising by chain transfer and/

TABLE 1. List of Polymeric Initiators Used

Polymeric initiators		$\bar{M}_n \times 10^{-3}$	Halogen, mmol/g	N_{Br}^a
Abbreviation	Structure			
MBS	$C_4H_9-(CH_2-CH)_n$ 	15.5	0.058	0.9
EBSI	$H-(CH_2-CH)_n-SCH_2COCHCH_2Br$  	3.38	0.237	0.8
TBS	$Br_3C-(CH_2-CH)_n$ 	3.34	1.20	4.0
CBS	$(CH_2-CH)_y$  $(CH_2-C)_x$  OCH_2CH_2Br	34.4	2.08	—
CCS	$(CH_2-CH)_y$  $(CH_2-CH)_x$ 	47.1	1.61	—

^aNumber of terminal halogen atoms per polymer molecule.

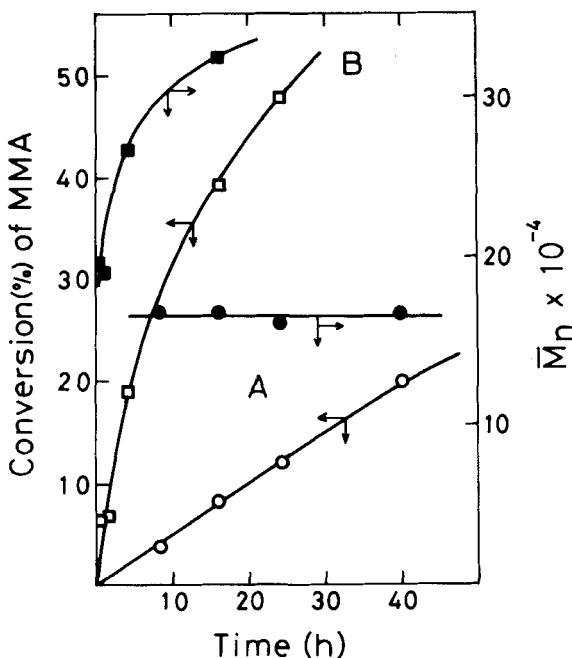


FIG. 1. Effect of polymeric initiator type on time-conversion and time-molecular weight relations for the block polymerization of MMA with the MBS/MnC system (A) and with the TBS/MnC system (B) at 80°C. $[M] = 3.0$ mol/L, $[Br]$ in polymeric initiator = 12.0 mmol/L, and $[MnC] = 3.0$ mmol/L.

or primary radical termination. On the other hand, in the MBS/MnC system (Fig. 1, A), the polymerization rate was lower than that for TBS/MnC and \bar{M}_n remained constant, independent of conversion.

Therefore, the polymerization mechanism for monohalo-terminated polymer/MnC was studied with 1-bromobutane (BB) as the model compound for MBS.

The linear relationships for both plots in Fig. 2 indicate that the polymerization rate, R_p , is proportional to $[MnC]$ and $[M]$. We propose a modified rate equation for polymerization with the carbon tetrabromide (CTB)/MnC system based on the Michaelis-Menten mechanism as shown in

$$\frac{[MnC][M]^2}{\delta^2} \frac{1}{R_p^2} = \frac{1}{\alpha\beta} \frac{1}{[RX]} + \frac{1}{\alpha}, \quad (1)$$

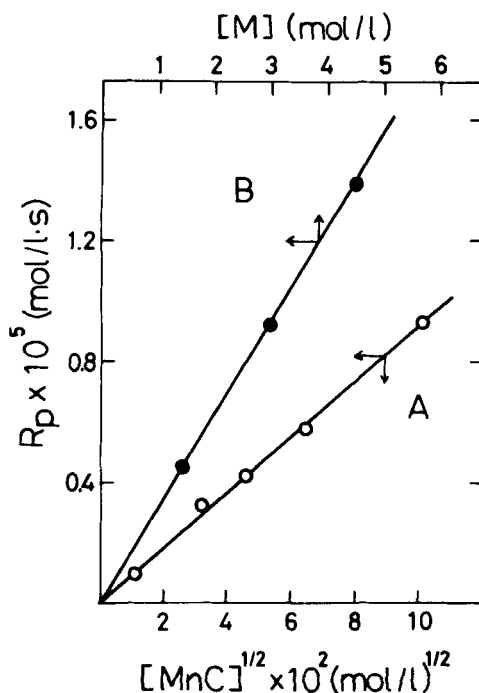


FIG. 2. Effect of manganese carbonyl (A) and monomer (B) concentrations on the rate of polymerization for the polymerization of MMA initiated by the system 1-bromobutane (BB)/MnC at 80°C: A, [MMA] = 3.0 mol/L and [BB] = 150 mmol/L; B, [MnC] = 10 mmol/L and [BB] = 50 mmol/l.

where [MnC], [M], and [RX] are the concentrations of manganese carbonyl, monomer, and alkyl halide, respectively, while δ is given by $\delta = k_t^{1/2}/k_p$, where k_t and k_p are the rate constants for termination and propagation, respectively.

The plot of Eq. (1) for polymerization with BB, Fig. 3, is a good straight line, and thus the polymerization of MMA with BB/MnC obeys Eq. (1), similarly to that with CTB/MnC. The kinetic parameters α and β , determined from the intercept and slope in Fig. 3 by linear regression, are in excellent agreement with those resulting from Fig. 2. The mean values of the kinetic parameters estimated from the two treatments are summarized in Table 2, together with those for CTB/MnC. Both α and β for the former system are much

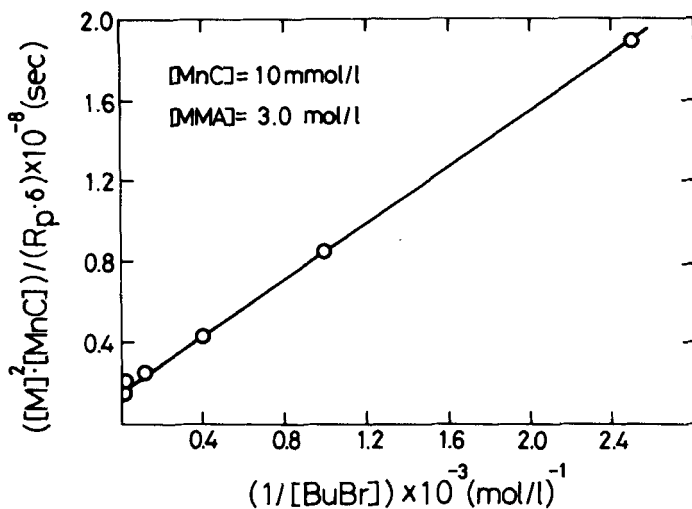


FIG. 3. Effect of 1-bromobutane (BB) concentrations on the rate of polymerization for the polymerization of MMA with BB/MnC.

smaller than those for the latter, especially α , the rate constant of transformation from the complex to the free radical, as described before [1], probably due to a difference in the stability of the free radical.

The polymer molecular weight did not change with conversion (Fig. 4), similarly to the case of the monohalo-containing polymeric initiator (Fig. 1), but it increased with 1-bromobutane concentration ([BB]). This means that

TABLE 2. Kinetic Parameters for the Polymerization of MMA with the BB^a/MnC^b or the CTB^c/MnC Initiator System at 80°C

Initiator system	α , s ⁻¹	β , L/mol	Remarks
BB/MnC	5.1×10^{-8}	290	This work
CTB/MnC	1.5×10^{-5}	1400	Ref. 1

^a 1-Bromobutane.

^b Manganese carbonyl, Mn₂CO₁₀.

^c Carbon tetrabromide.

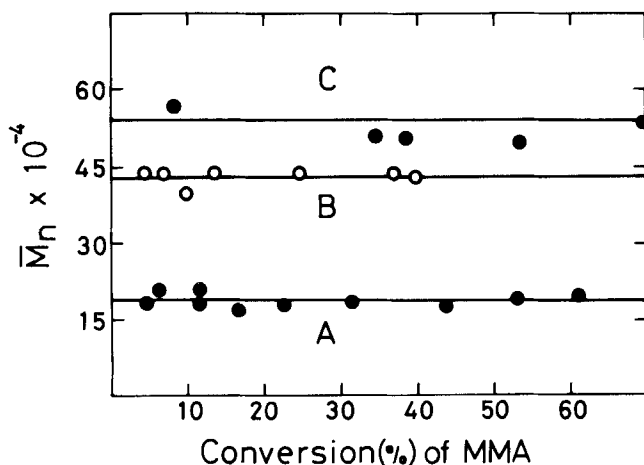


FIG. 4. Dependence of molecular weight on conversion at various BB concentrations: A, 10.0; B, 400; C, 800 mmol/L. [MMA] = 3.0 mol/L, [MnC] = 10.0 mmol/L.

it is impossible to control the molecular weight by varying the conversion. Therefore, we examined the effect on \bar{M}_n of the ratio C of the concentration of monobromo-terminated polymeric initiator, EBSI, to that of monomer while keeping the ratio of [EBSI] and [MnC] (r) constant at 4. It was found that the molecular weight decreased with increasing C , as shown in Table 3.

Graft Polymerization of MMA Initiated by 2-Bromoethyl Methacrylate-Styrene Copolymer and Chloromethylstyrene-Styrene Copolymer

Graft polymerizations of MMA initiated with CBS/MnC and CCS/MnC were carried out in benzene at 100°C. The ratio (r) of the concentration of halogen, [Br] or [Cl], in the copolymeric initiator to that of MnC was kept constant at 4 or 100. Figure 5 shows the results. The rate of polymerization at $r = 4$ is much larger than that at $r = 100$. The extent of halogen consumed was estimated from the Cl contents of the graft copolymer and CCS. The conversion of halogen in CCS decreased with the conversion of MMA, and the conversion of halogen was relatively higher at $r = 4$ than at $r = 100$, as shown in Fig. 6. Table 4 shows the results.

Conversion of MMA (X_M) for [MnC] = 3.0 mmol/L ($r = 4$) was higher

TABLE 3. Block Polymerization^a of MMA with EBSI^b-MnC at Different Concentrations of the Initiator System

[EBSI], mmol/L	[MnC], mmol/L	$C,^c$ %	Conversion, % at 8 h	$\bar{M}_n \times 10^{-4}$
24	6.0	0.80	44.2	10.0
12	3.0	0.40	28.1	14.8
6.0	1.5	0.20	19.4	23.3
1.2	0.30	0.04	9.62	42.2

^aPolymerization was carried out in benzene, with $[M] = 3.0$ mol/L at 100°C . Feed ratio, $r = ([\text{EBSI}]/[\text{MnC}])$, was kept constant at 4.0.

^bMonobromo-terminated polymer was prepared by the reaction of carboxy-terminated polymer with epibromohydrine, $\text{H}(\text{St})_n\text{-SCH}_2\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Br}$.

^cFeed ratio of $[\text{EBSI}]$ to $[\text{MMA}]$.

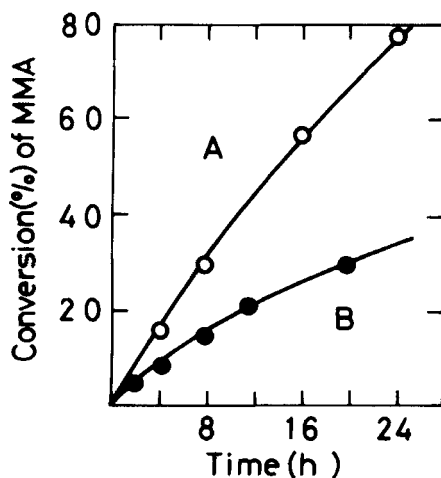


FIG. 5. Time-conversion curves for the graft polymerization of MMA initiated by CCS/MnC in benzene at 100°C . $r = [\text{Cl}]/[\text{MnC}]$: A, 4.0; B, 100.

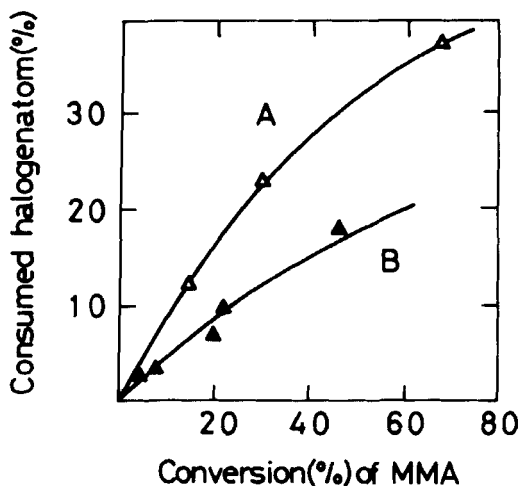


FIG. 6. Relationship between the consumed halogen in the CCS-backbone and the conversion of MMA for the graft polymerization of MMA with CCS/MnC at 100°C: A, $r = 4$; B, $r = 100$.

TABLE 4. Effect of Polymerization Conditions on the Number and Length of the Graft Chains for the Polymerization of MMA with CCS/MnC^a

Run	[MnC], mmol/L	Temperature, °C	X_M , ^b %	X_{Cl} , ^c	\overline{DP}_g ^d	\overline{N}_g ^e
96	0.12	100	20.9	7.03	746	5.0
84	3.0	100	51.7	24.3	532	17.4
73	3.0	80	13.6	11.6	293	8.3

^aCCS: Copolymer of chloromethylstyrene and styrene, $\overline{DP}_n = 297$, Cl = 2.08 mmol/g. [M] = 3.0 mol/L, [Cl] = 12 mmol/L, polymerization time = 16 h.

^bConversion of MMA.

^cConversion of halogen.

^dLength of graft chains per halogen atom, estimated from conversion of MMA and Cl.

^eNumber of grafts per backbone polymer molecule.

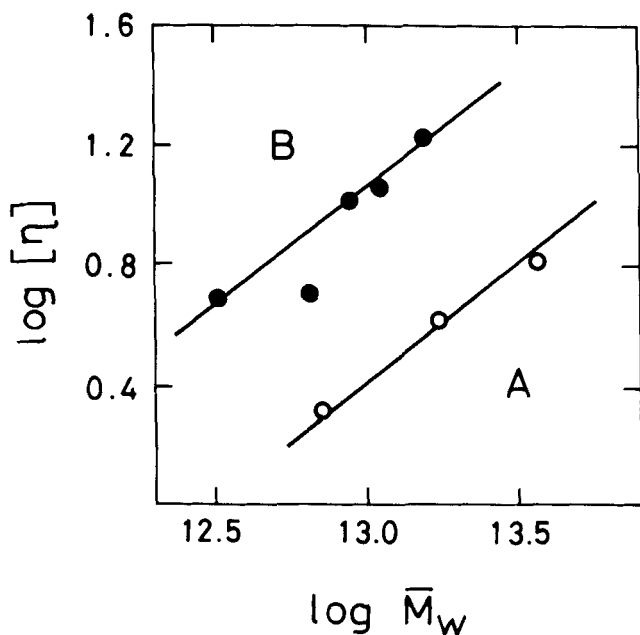
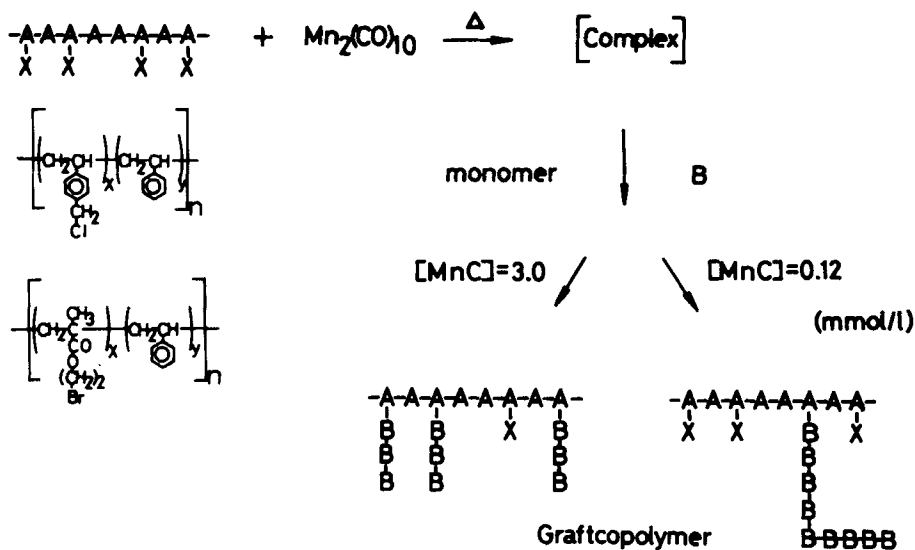


FIG. 7. Plots of $\log [\eta]$ vs $\log \bar{M}_w$ for CCS-MMA graft copolymers: A, $r = 4$; B, $r = 100$.

than for $[\text{MnC}] = 0.12 \text{ mmol/L}$ ($r = 100$) because of the higher extent of halogen consumed (X_X). However, the MMA polymerized per consumed halogen atom on the backbone polymer was significantly higher at the lower $[\text{MnC}]$. Therefore, the number of grafting points per backbone polymer at higher $[\text{MnC}]$ was higher than that at the lower value and was accompanied by longer grafted chains.

Plots of $\log [\eta]$ vs $\log \bar{M}_w$ for the graft copolymers obtained (Fig. 7) show linear relationships for $r = 4$ and $r = 100$, but on different lines. This suggests that at lower $[\text{MnC}]$, longer chains grafted on PMMA for $r = 100$ lead to larger molecular coils in solution than the greater number of shorter grafted chains for $r = 4$ at the same molecular weight.

Graft polymerization of MMA with CBS/MnC proceeded more rapidly than with CCS/MnC. However, gelation was observed during the polymerization. In conclusion, the above system might be useful for synthesis of a well-defined graft copolymer. Under appropriate polymerization conditions



SCHEME 1.

(halogen concentration in backbone polymer, $[\text{MnC}]$, and $[\text{M}]$, and/or conversion of monomer), the number of graft points on the backbone polymer and the length of the grafts could be readily regulated as shown in Scheme 1.

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