

Polymerization of Methyl Methacrylate with $\text{Mn}(\text{acac})_3$ in the Presence of Organic Halides. Possibility of Molecular Weight Control of Polymer

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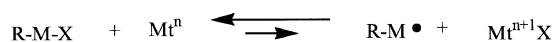
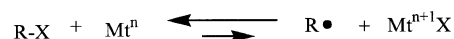
ABSTRACT: Molecular weight control of the polymers in the polymerization of methyl methacrylate (MMA) by $\text{Mn}(\text{acac})_3$ in the presence of organic halide (RX) was investigated. In the polymerization of MMA with $\text{Mn}(\text{acac})_3$ and in the presence of methyl 2-bromopropionate (MBP), the relationship between the polymer yields and molecular weights of the polymers gave a straight line, and the line passed through the origin. The M_w/M_n was not so narrow, but the values of the M_w/M_n kept almost constant around 2.0–3.0 during the reaction, indicating that the molecular weight control of polymer was achieved in the polymerization of MMA with $\text{Mn}(\text{acac})_3/\text{MBP}$. When methyl bromoacetate (MBA) was used, some polymerization behavior was different from that of MBP. It was demonstrated that the structure of RX played an important role to control the molecular weight of the polymer in the polymerization of MMA with $\text{Mn}(\text{acac})_3/\text{RX}$. The effects of MMA concentration and reaction temperatures were observed. The poly(St-*b*-MMA) was synthesized by the polymerization of MMA using poly(St) obtained from the polymerization with $\text{Mn}(\text{acac})_3/\text{MBP}$.

KEY WORDS Methyl Methacrylate / $\text{Mn}(\text{acac})_3$ / Methyl 2-Bromopropionate / Methyl Bromoacetate / Radical Polymerization / Molecular Weight Control /

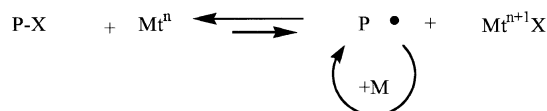
Living radical polymerization of vinyl monomers is important from the viewpoints of synthesizing well-defined polymers.¹ This polymerization has been achieved by several methods as follows; the polymerization by nitroxides such as 2,2,6,6-tetramethyl-4-piperidionoxy,² atom transfer radical polymerization (ATRP),³ transition metals mediated radical polymerization,⁴ a reversible addition fragmentation chain transfer (RAFT) process,⁵ iniferter polymerization,⁶ and cyclic disulfides mediated radical polymerization.⁷ Among them, the method by a transition metal compound (Mt) in combination with an organic halide (RX) has some advantages that can be applied to many monomers at relative low reaction temperature. The mechanism for the living radical polymerization with Mt/RX system proposed is shown in Scheme 1. For this mechanism, Ru,⁴ Fe,⁴ Ni,⁴ Rh,⁸ and Pd⁹ complexes besides Cu complex/RX/2,2'-bipyridine system³ have been used as an effective transition metal. However, a middle transition metals such as manganese complexes has paid less attention to the living radical polymerization.

$\text{Mn}(\text{acac})_3$ in combination with RX seems to be an effective catalyst for the controlled polymerization of various vinyl monomers.^{10,11} Nevertheless, polymerization of MMA with $\text{Mn}(\text{acac})_3$ in the presence of RX has not been studied from the point of molecular weight control of polymers. If the polymerization

Initiation:



Propagation:

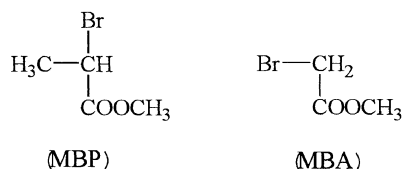


Scheme 1. Polymerization mechanism (Mt: transition metal, M: monomer).

of MMA with $\text{Mn}(\text{acac})_3/\text{RX}$ proceeds with a similar mechanism proposed to the transition metals mediated radical polymerizations, it will be able to control the molecular weight of the polymers.

Previously, we reported the polymerization of St with $\text{Mn}(\text{acac})_3$ in the presence of benzyl bromide.¹² Taking the radical structure generated from RX into consideration, the control of molecular weight of the polymer may be possible by selecting adequate organic halides. In this article, we report the polymerization of MMA with the $\text{Mn}(\text{acac})_3$ in the presence of methyl 2-bromopropionate (MBP) and methyl bromoacetate (MBA), which are similar to the structure of acrylic monomer.

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EXPERIMENTAL

Materials

Commercially available $Mn(acac)_3$ (Dojin Chem. Co.) and bpy (Wako Pure Chem.) were used without further purification. MMA, St, MBP, and MBA were purified by distillation over a calcium hydride before use. Solvents and other reagents were purified by conventional methods.

Polymerization Procedure

Polymerization was carried out in a sealed glass tube in a thermostat at a constant temperature for a given time. The required amounts of reagents were introduced successfully $Mn(acac)_3$ diluted with polymerization solvent, RX, MMA, and other reagents if necessary into the tube. The tube was degassed several times, and then sealed under high vacuum. After the polymerization the tube was opened, and contents of the tube were poured into a large amount of methanol to precipitate the polymer formed. The resulting polymers were washed well with an excess of methanol, and dried in high vacuum at room temperature. The polymer yield was determined by gravimetry.

Characterization

The number-average (M_n) and weight-average (M_w) molecular weight of the polymers were determined by GPC using a Tosoh GPC-8800 at 38°C in THF as calibrated with poly(St) standards. The 1H and ^{13}C NMR spectra for the polymers were recorded on JEOL A-400 spectrometer in $CDCl_3$ at 50°C.

RESULTS AND DISCUSSION

Polymerization of MMA with $Mn(acac)_3/RX$

Since the structure of the initiation chain end plays a role in the controlled polymerization of vinyl monomers with Mt/RX system, we selected MBP and MBA as a RX in the polymerization of MMA, which is resemble the propagating radical of MMA. The results for the polymerization of MMA with $Mn(acac)_3$ in the presence of MBP or MBA performed in toluene at 80°C are listed in Table I. The polymerization of MMA proceeded with $Mn(acac)_3$ in the presence of MBP and MBA, although some difference in poly-

Table I. Polymerization of MMA with $Mn(acac)_3/RX$ in toluene at 80°C

R-X	Time/h	Yield/%	$M_n \times 10^{-4}$	M_w/M_n
MBA	3	7.9	14.2	2.22
	5	15.3	27.2	1.88
	8	27.8	30.0	1.96
MBP	3	22.1	10.1	2.16
	5	25.0	14.6	2.49
	8	29.8	20.6	2.27

$[Mn(acac)_3] = 8.0 \times 10^{-4} \text{ mol L}^{-1}$, $[RX] = [bpy] = 2.0 \times 10^{-3} \text{ mol L}^{-1}$, $[MMA] = 2.8 \text{ mol L}^{-1}$.

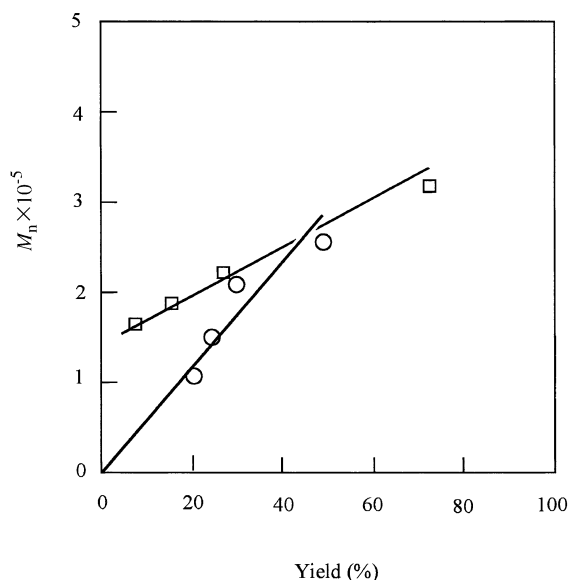


Figure 1. Polymerization of MMA with $Mn(acac)_3/MBP$ (○), $Mn(acac)_3/MBA$ (□); $[Mn(acac)_3] = 2.0 \times 10^{-3} \text{ mol L}^{-1}$, $[RX] = 4.0 \times 10^{-3} \text{ mol L}^{-1}$, $[MMA] = 2.7 \text{ mol L}^{-1}$.

merization behavior between MBP and MBA was observed. The polymer yields and the molecular weights of the polymers increased as a function of reaction time in the polymerization of MMA with $Mn(acac)_3/RX$ (RX:MBP, MBA). Such polymerization behavior was not observed in the polymerization of MMA with $Mn(acac)_3$ alone.^{10,11} This suggests that the mechanism for the transition metal mediated living radical polymerization proposed by Sawamoto⁴ and Matyjaszewski³ will be applicable to this polymerization.

To elucidate the possibility of the molecular weight control of the polymer in the polymerization of MMA with $Mn(acac)_3/MBP$, the polymer yields were plotted against the molecular weights of the polymers. The results are shown in Figure 1. The relationship gave a straight line, and the line passed through the origin. The M_w/M_n of the polymer was not narrow, but the values of the M_w/M_n did not change significantly during the reaction. Moreover, the GPC elution curves for the polymers obtained with $Mn(acac)_3/MBP$ moved to the higher molecular weight side as a function of reac-

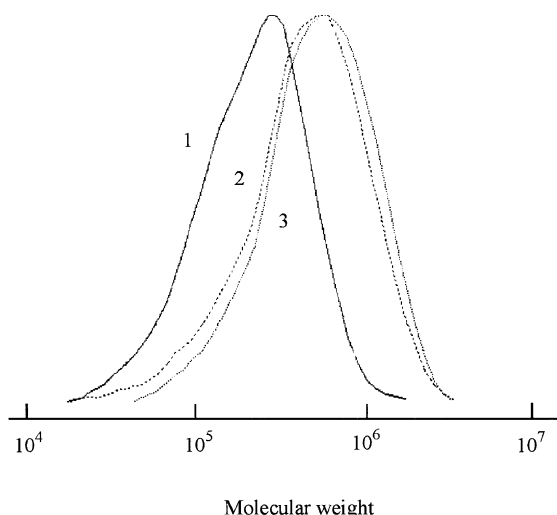


Figure 2. GPC elution curves of poly(MMA) with Mn(acac)₃/MBP (1) 10.1×10^4 , $M_w/M_n = 2.16$, (2) 14.6×10^4 , $M_w/M_n = 2.49$, (3) 20.6×10^4 , $M_w/M_n = 2.27$.

tion time as shown in Figure 2. Since a fast initiation and an fast equilibrium between active species and dormant ones are essential conditions to obtain polymers having a narrow M_w/M_n ,⁴ our results may be attributed to a slow initiation of the polymerization of MMA with Mn(acac)₃/MBP. Thus, the feasibility of fast initiation is an essential factor to control exactly the molecular weight of the polymer in this radical polymerization.

On the other hand, in the polymerization of MMA with Mn(acac)₃/MBA, similar the straight line to that obtained with Mn(acac)₃/MBP was not obtained, although the M_n of the polymer increased with reaction time. The results obtained in this study indicate that the structure of R of the RX plays an important role to control the molecular weight of the polymer, which may be related to the rate of initiation reaction.

Effect of MMA Concentration

Since the molecular weight control of polymer was found to be possible in the polymerization of MMA with Mn(acac)₃/MBP, the effect of MMA concentration on polymerization of MMA with Mn(acac)₃/MBP was examined. The results are shown in Figure 3. The polymerization rate increased with an increase of MMA concentration in the feed. Moreover, the molecular weight of the polymer increased with an increase of the polymer yields as shown in Figure 4. The relation between the polymer yields and the M_n of the polymers gave the straight lines, and the lines passed through the origin regardless of MMA concentration examined. The M_w/M_n of the polymers kept almost constant during the reaction, but was not narrow at any MMA concentration examined. Moreover, the M_n of the polymer increased with an increase of MMA con-

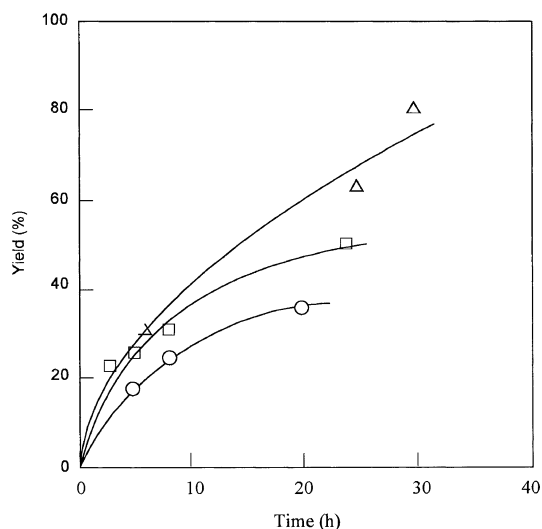


Figure 3. Polymerization of MMA with Mn(acac)₃/MBP; [Mn(acac)₃] = 2.0×10^{-3} mol L⁻¹, [MBP] = 4.0×10^{-4} mol L⁻¹, [MMA] = 0.9 mol L⁻¹ (○), 2.8 mol L⁻¹ (□), 5.6 mol L⁻¹ (△).

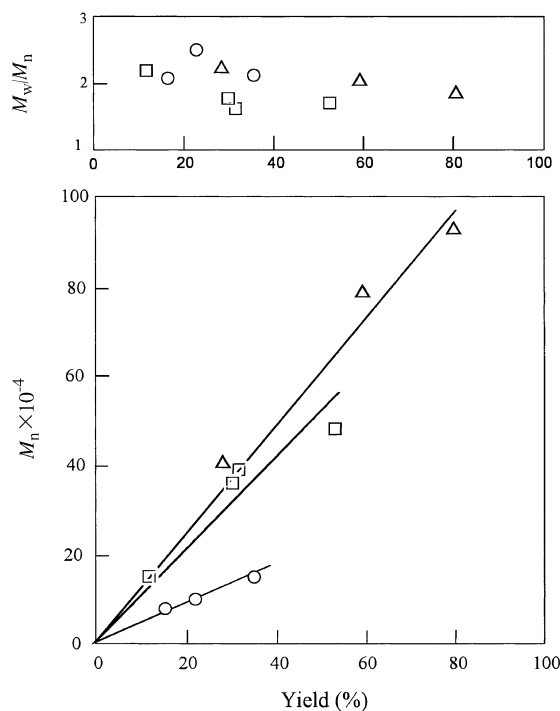


Figure 4. Effect of MMA concentration on polymerization of MMA with Mn(acac)₃/MBP/bpy; [Mn(acac)₃] = 2.0×10^{-3} mol L⁻¹, [MBP] = [bpy] = 4.0×10^{-3} mol L⁻¹, [MMA] = 0.9 (○), 2.8 (□), 5.6 (△) mol L⁻¹.

centration at the same polymer yield. Accordingly, the molecular weight of polymer may be controlled in the polymerization of MMA at various monomer concentration.

Effect of Reaction Temperature

The effect of reaction temperature on the polymerization of MMA with Mn(acac)₃/MBP was examined. The polymer yields obtained at various reaction tem-

Table II. Synthesis of poly(St-*b*-MMA) in toluene^a

Monomer	Catalyst	Temp. °C	Time h	Yield %	$M_n \times 10^{-4}$	M_w/M_n
St	Mn(acac) ₃ -MBP	110	8	50.0	2.5	2.32
MMA	Mn(acac) ₃ -PSt-Br ^b	80	8	32.1	10.4	2.46
					(9.8) ^c	(2.27) ^c

^a[Mn(acac)₃] = 2.0 × 10⁻³ mol L⁻¹, [MBP] = 4.0 × 10⁻³ mol L⁻¹, [St] = 1.8 mol L⁻¹, [MMA] = 2.8 mol L⁻¹. ^bPoly(St)-Br = 2.5 g L⁻¹. ^cAfter Soxhlet extraction with cyclohexane and acetonitrile.

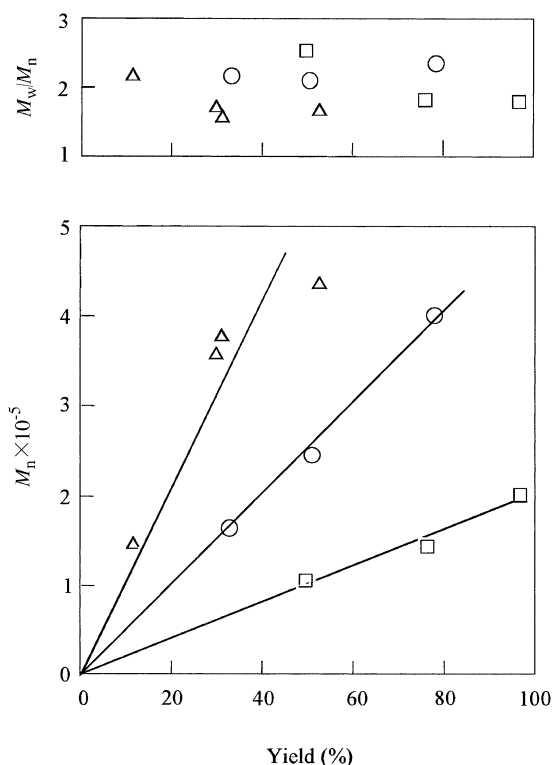


Figure 5. Effect of reaction temperature on polymerization of MMA with Mn(acac)₃/MBP in toluene at 60°C (□), 70°C (○), 80°C (△); [Mn(acac)₃] = 2.0 × 10⁻³ mol L⁻¹, [MBP] = 4.0 × 10⁻³ mol L⁻¹, [MMA] = 2.8 mol L⁻¹.

peratures were plotted against M_n of the resulting polymers, and the results are shown in Figure 5. The relationships between the polymer yields and M_n of the polymers gave straight lines regardless of reaction temperatures examined. The control of M_n of the polymer was found to be more easily at lower reaction temperature. This may be explained by that the decrease of the propagating species with decreasing reaction temperature suppresses the undesirable reactions such as disproportionation and recombination of propagating radicals, leading to improvement of the molecular weight control of the polymers.

As mentioned above, it is difficult to control the M_w/M_n of the polymer in the polymerization of MMA with Mn(acac)₃/RX even at low temperature. This may be due to a slow initiation by the Mn(acac)₃/RX system and formation of a small amount of active species pro-

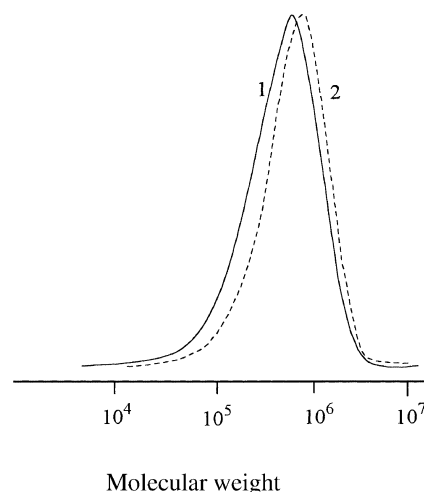


Figure 6. GPC elution curves of poly(St-*b*-MMA) from polymerization of MMA with poly(St) obtained with Mn(acac)₃/MBP; (1) Poly(St)-Br and (2) Poly(St-*b*-MMA).

duced from Mn(acac)₃ alone.^{10,11} Because the radical derived from Mn(acac)₃ alone is unfavorable to control the M_w/M_n of the polymer, although the amount of the radical is low.

Synthesis of Poly(St-*b*-MMA)

The polymer obtained from the polymerization with the Mn(acac)₃/MBP has the C-Br bond at the chain end, that is regarded as a dormant species. Since such polymer may be used as a macroinitiator for synthesizing a block copolymer, block copolymerization of St and MMA was examined using poly(St)-Br obtained from the polymerization of St with the Mn(acac)₃/MBP in toluene at 110°C for 8 h (polymer yield; 50%). We used the parent poly(St)-Br after the treatment by washing well with an excess of methanol and dried *in vacuo* at room temperature. The results are shown in Table II.

The GPC elution curves of poly(St-*b*-MMA) after Soxhlet extraction to remove the homopolymer with cyclohexane for poly(St)-Br and acetonitrile for poly(MMA) are shown in Figure 6. After the block polymerization with MMA, the molecular weight of the product increased as compared with that of the parent poly(St)-Br. Thus, it is clear that the block copolymer consisting of St and MMA segment was synthesized

by this method. The block copolymerization of MMA with the Mn(acac)₃/MBP proceeded by a similar mechanism to Mt/RX system.^{3,4}

CONCLUSION

The molecular weight control of polymer was achieved in the polymerization of MMA with Mn(acac)₃/MBP. The structure of RX gave an influence to the molecular weight control of the polymer in the polymerization of MMA with Mn(acac)₃/RX. However, the narrow molecular weight distribution of the polymer was not obtained even when the polymerization of MMA with Mn(acac)₃/MBP was carried out at low reaction temperature. This may be attributed to a slow initiation of the polymerization, which is related to the structure of RX.

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