

Radical Polymerization of Methyl Methacrylate in the Presence of Magnesium Bromide as the Lewis Acid

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ABSTRACT: We carried out the radical polymerization of methyl methacrylate (MMA) at 0–80°C in the presence of magnesium bromide. The polymerization rate and the molecular weight of the resulting polymers increased according to the amount of the added magnesium bromide as the Lewis acid. It was revealed that the microtacticity of the polymer depended on the amount of magnesium bromide. The effects of the solid surface of magnesium bromide, which is partly soluble in the polymerization systems, were also investigated. The results obtained in this work were compared with the results reported for the polymerization systems in the presence of the other Lewis acids.
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Key words: radical polymerization; methyl methacrylate; Lewis acid; magnesium bromide; tacticity; poly(methyl methacrylate); chelation; conformation

INTRODUCTION

In recent years, the control of polymer structures has intensively been developed through radical polymerization process, which is the most important method for the production of high polymers in the industrial and academic fields because of a large number of merits of the process, for example, high polymerization and copolymerization reactivities, many kinds of polymerizable monomers with polar and functional groups, no necessity of any protecting of the groups, simple procedure for polymerization, excellent reproducibility, tolerance to impurities, facile prediction of the polymerization reactions, use of water as the reaction medium, and so on.^{1,2} The molecular weight and molecular weight distribution are precisely controlled by a living radical polymerization technique. The branched structure is designed using macromonomers. In contrast with

these, the control of the stereoregularity of polymers is difficult through a free radical polymerization mechanism. It is well known that the tacticity of the polymers produced in radical polymerization depends on the polymerization temperature for several monomers such as methyl methacrylate (MMA) and acrylonitrile, but is less sensitive for the other monomers including acrylates and vinyl chloride.^{3,4} Stereoregular polymers were uniquely synthesized during the radical polymerizations of specially designed monomers^{5,6} or in the crystalline state.^{7,8}

The complex formation of monomers with Lewis acid often leads to the alteration of the polymerization reactivity and monomer reactivity in copolymerization.^{9,10} In 1957, Bamford et al.¹¹ first reported the increase in the polymerization rate as well as degree of polymerization of the resulting polymer during the polymerization of acrylonitrile in the presence of the lithium chloride as the Lewis acid. They revealed that the increase in the polymerization reactivity resulted from the increase in the propagation rate coefficient due to the interaction of the lithium cation

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with the nitrile group. Similarly, the accelerated propagation of MMA in the presence of ZnCl_2 was also reported,¹² as well as the effect on the stereoregularity^{13,14} in the 1960s.

Recent extensive studies on the reactions of the ester-substituted radicals of small molecules have clarified an effect of Lewis acids on the stereoselectivity.¹⁵ The inversion of the stereoselectivity was observed during the reduction and the allylation in the absence and in the presence of magnesium iodide.¹⁶ When the uncomplexed radical favors the allylic strain conformer, it is attacked from one side, because another face is shielded by the phenyl group. In the presence of magnesium iodide, the radical would have a different conformation, of which the opposite face is shielded. Therefore, the stereoselectivities of the uncomplexed and the complexed radicals are supplementary to each other. The control of the stereoselectivity was also reported for the allylation in the presence and absence of $\text{Eu}(\text{fod})_3$ and other Lewis acids.¹⁷⁻¹⁹ A similar effect is expected to change the propagation manner during radical polymerization in the presence of Lewis acid.

In this work, therefore, we carried out the radical polymerization of MMA in benzene at 0–80°C in the presence of magnesium bromide, MgBr_2 . The polymerization rate and the molecular weight of the resulting polymers as well as the microtacticity of the polymer were investigated.

EXPERIMENTAL

Materials

MMA and solvents were distilled before use. Magnesium bromide diethyl etherate was used as received without further purification (99%, Aldrich). Commercially available ZnCl_2 was used (1.0 mol/L solution in diethyl ether, Aldrich). 2,2'-Azobis(isobutyronitrile) (AIBN) and 1,1'-azobis(cyclohexanecarbonitrile) (ACN) were recrystallized from methanol and ethanol, respectively.

Polymerization

MMA, an initiator, solvent, and Lewis acid were placed in a glass ampoule. The mixture was degassed by the freeze-thaw technique, and then the ampoule was sealed *in vacuo*. After thermal polymerization at 60–80°C or photopolymerization at 0–40°C under UV irradiation, the polymerization mixture was poured into a large

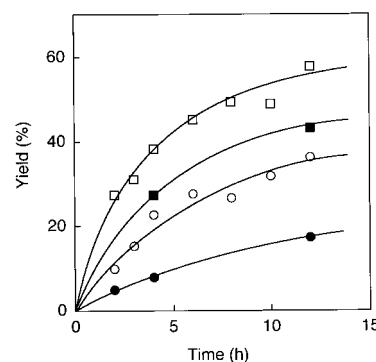


Figure 1 Time-yield relationships for radical polymerization of MMA with AIBN as the photoinitiator in the presence or in the absence of MgBr_2 under UV irradiation. Polymerization conditions: MMA 2 mL, benzene 8 mL, $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ 0.240 g, AIBN 15.3 mg. (○) in the presence of MgBr_2 at 0°C, (●) in the absence of MgBr_2 at 0°C, (□) in the presence of MgBr_2 at 30°C, (■) in the absence of MgBr_2 at 30°C.

amount of methanol to precipitate the resulting poly(MMA). The yield of the polymer was determined gravimetrically. The polymer was purified by reprecipitation.

Measurements

Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by gel permeation chromatography (GPC) calibrated with standard polystyrenes (Tosoh). GPC was carried out with a Tosoh GPC-8000 series system equipped with TSK-gel columns using THF as the eluent at 38°C. NMR spectra were recorded on a JEOL JNM-A400 spectrometer in deuterated chloroform at ambient temperature.

RESULTS AND DISCUSSION

Radical polymerization of MMA was carried out in benzene with AIBN as a typical initiator in the presence or in the absence of MgBr_2 at 0 and 30°C under UV irradiation. The time-yield relationships are shown in Figure 1. The addition of MgBr_2 increased the polymerization rate, despite a very small amount of the MgBr_2 added (0.05 equimolar to MMA). The time-yield curves suggest that MgBr_2 functioned as the activator of the monomer or the propagating radical and resulted in the enhancement of the polymerization rate, because the photodecomposition rate of AIBN is

Table I Results of Radical Polymerization of MMA in the Presence of MgBr_2 ^a

Temp. (°C)	Lewis Acid	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Triad Fraction			P_r ^b	$P_{m/r} + P_{r/m}$ ^c
					<i>mm</i>	<i>mr</i>	<i>rr</i>		
0	None	7.7	2.1	1.32	1.8	25.0	73.2	0.857	1.02
0	MgBr_2	21.2	3.0	1.52	4.8	34.7	60.5	0.779	1.01
0	ZnCl_2	5.2 ^d	2.0	1.28	1.9	26.0	72.1	0.851	1.03
30	None	27.4	1.9	1.42	2.8	29.9	67.3	0.823	1.02
30	MgBr_2	40.1	3.7	1.79	4.4	35.4	60.2	0.779	1.03
40	None	31.8	2.4	1.78	3.0	30.4	66.6	0.818	1.02
40	MgBr_2	48.0	2.5	1.74	5.7	35.9	58.4	0.764	0.994
60	None	31.0	6.6	1.74	3.1	33.6	63.3	0.801	1.06
60	MgBr_2	46.7	8.2	1.96	7.2	39.1	53.7	0.733	0.998
80	None	42.5 ^e	15.6	1.52	3.6	35.9	60.5	0.785	1.06
80	MgBr_2	55.0 ^e	16.0	1.65	8.3	40.8	50.9	0.713	0.997

^a MMA 2 mL, benzene 8 mL, $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ 0.240 g (0.93 mmol), AIBN 15.3 mg, polymerization time 4 h. The polymerization at 0–40°C was carried out under photoirradiation with a high-pressure Hg lamp.

^b $P_r = [rr] + [mr]/2$.

^c $P_{m/r} = [mr]/(2[mm] + [mr])$; $P_{r/m} = [mr]/(2[rr] + [mr])$.

^d With ZnCl_2 150 mg (1.1 mmol). Polymerization time 2 h.

^e ACN (22.8 mg) was used as the initiator.

less sensitive to the medium and additives. The interaction between Lewis acid and the monomer or the propagating radical has been reported in the literature. For example, Bamford et al.¹¹ first reported the increase in the propagation rate coefficient of acrylonitrile, $k_p = 3680 \text{ L/mol}\cdot\text{s}$ in *N,N*-dimethylformamide in the presence of lithium chloride ($[\text{monomer}] = 2.53 \text{ mol/L}$ at 60°C in the presence of 0.1 equimolar of lithium chloride), which was twice of the value in the absence of the salt (1960 $\text{L/mol}\cdot\text{s}$). Similarly, the propagation rate coefficient of MMA increased twice in the presence of the ZnCl_2 ; $k_p = 610$ and $250 \text{ L/mol}\cdot\text{s}$ in the presence and absence of the ZnCl_2 at 25°C.¹² The polymerization reactivity enhanced by the addition of MgBr_2 in this work would be due to the increase in the propagation rate.

Table I summarizes the results of the polymerization of MMA in the presence or in the absence of MgBr_2 at various polymerization temperatures. The polymerizations at 0–40°C were carried out under photoirradiation. For the polymerization at 80°C, ACN was used as the initiator. The M_n and M_w/M_n values of the resulting polymers were $2\text{--}16 \times 10^4$ and 1.3–2.0, respectively. The addition of the Lewis acid resulted in the increase in the yield and the molecular weight of the resulting polymer at each temperature, compared with those for the polymer produced in the absence of the Lewis acid. The interaction of the Lewis acid was observed even at a high temperature such as 80°C.

The triad tacticity of the polymers was determined by $^1\text{H-NMR}$ spectroscopy to compare the stereochemical structure of the polymers produced in the presence and in the absence of the Lewis acid. A typical spectrum is illustrated in Figure 2. As shown in Table I, the fractions of *mm* and *mr* triads increased and the *rr* triad fraction decreased when MgBr_2 was added. The possibility of racemo addition (P_r) was calculated according to eq. (1).

$$P_r = [rr] + [mr]/2 \quad (1)$$

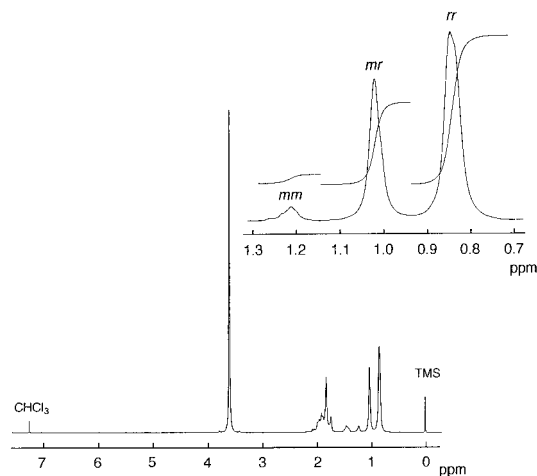


Figure 2 $^1\text{H-NMR}$ spectrum of poly(MMA) obtained for radical polymerization of MMA in the presence of MgBr_2 in benzene at 30°C.

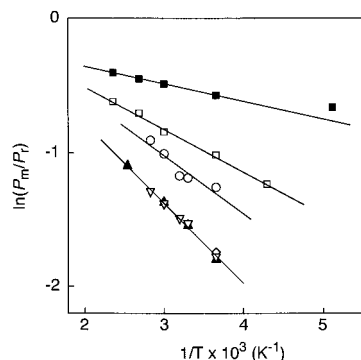


Figure 3 Arrhenius plot of P_m/P_r value for radical polymerization of MMA in the presence or absence of MgBr_2 . (○) in benzene in the presence of MgBr_2 (0.05 eq.) (this work), (▽) in benzene in the absence of MgBr_2 (this work), (▲) in benzene in the absence of MgBr_2 (ref. 20), (◇) in benzene in the presence of ZnCl_2 (0.05 eq.) (this work), (□) in bulk in the presence of ZnCl_2 (0.4 eq.) (ref. 13), and (■) in bulk in the presence of ZnCl_2 (1.0 eq.) (ref. 13).

If the propagation obeys the Bernoullian statistics, the summation of $P_{m/r}$ and $P_{r/m}$ should be equal to unity. Here, $P_{m/r}$ means the probability of the racemo addition to the meso chain end. Similarly, $P_{r/m}$ represents an opposite relation.

$$P_{m/r} = [mr]/(2[mm] + [mr]) \quad (2)$$

$$P_{r/m} = [mr]/(2[rr] + [mr]) \quad (3)$$

All the $P_{m/r}$ plus $P_{r/m}$ values indicated in Table I were approximately unity, irrespective to the presence or absence of Lewis acid and to the polymerization temperature. This means that the propagation seems to proceed independently of the stereochemistry of the chain end. It is expected that an interaction of bidentate Lewis acid with the propagating chain end might induce only a small deviation from the Bernoullian statistics, because the degree of the interaction would be weak. Therefore, we should check the $P_{m/r} + P_{r/m}$ value carefully. When the MgBr_2 was present in the polymerization system, the $P_{m/r} + P_{r/m}$ values tended to decrease slightly than those for the polymerization in the absence of the Lewis acid.

In contrast with the addition effect of MgBr_2 , ZnCl_2 was valid for the increase in the yield and molecular weight, but the microtacticity of the polymer was similar to that obtained without any Lewis acid, under the polymerization conditions used in this work. This indicates that ZnCl_2 acts

only as the activation of the monomer during the polymerization in benzene in the presence of 0.04 eq. of ZnCl_2 to MMA. This was different from the results reported for the bulk polymerization of MMA in the presence of ZnCl_2 in the literature.^{13,14}

The Arrhenius plot of the P_m/P_r value is shown in Figure 3. The slope of the line for the polymerization with MgBr_2 was greater than that without MgBr_2 . The differences in the activation enthalpies for the meso and racemo propagations ($\Delta H_m^\ddagger - \Delta H_r^\ddagger$) and those in the activation entropies ($\Delta S_m^\ddagger - \Delta S_r^\ddagger$) were calculated and listed in Table II. An apparent value of $\Delta H_m^\ddagger - \Delta H_r^\ddagger$ was estimated to be 2.9 kJ/mol for the polymerization in the presence of MgBr_2 , being smaller than that for the polymerization in the absence of the Lewis acid in this work (5.0 kJ/mol) or in the literature (4.8 kJ/mol, 4.0 kJ/mol).^{3,13} This value is similar to the value for the polymerization in bulk with 0.04 eq. ZnCl_2 (2.6 kJ/mol), but much larger than that with 1.0 eq. of ZnCl_2 (1.1 kJ/mol).

Subsequently, we investigated the effect of the amount of MgBr_2 on the polymerization reactivity and the structure of the resulting polymer. The results are shown in Table III.

The polymerization system in this work was not homogeneous; that is, when 0.024 g of MgBr_2 was added to the polymerization system, a part of MgBr_2 was insoluble, indicating the low solubility of MgBr_2 in this system. However, as the amount of the MgBr_2 added increased, the polymer yield and molecular weight of the polymer increased, being different from our expectation. The M_w/M_n value increased from 1.4 to 2.2. The triad fraction was also found to significantly depend on the amount of the Lewis acid. The probability of the racemo addition decreased from 0.823 in the absence of MgBr_2 to 0.736 in the presence of MgBr_2

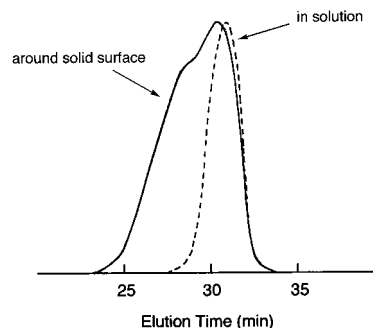


Figure 4 GPC elution curves of poly(MMA). Polymerization conditions are shown in Table IV.

Table II Arrhenius Parameter for Meso and Racemo Propagation for Radical Polymerization of MMA

Lewis Acid	Solvent	$\Delta H_m^\ddagger - \Delta H_r^\ddagger$ (kJ/mol)	$\Delta S_m^\ddagger - \Delta S_r^\ddagger$ (J/mol · K)
None	Benzene	4.97	3.71
MgBr ₂	Benzene	2.88	0.04
ZnCl ₂ (0.04 eq) ^a	None	2.59	1.06
ZnCl ₂ (1 eq) ^a	None	1.07	-0.79

^a Recalculated from data in literature (ref. 13).

(0.960 g, 0.2 eq. to MMA). These results are interesting, because the amount of the MgBr₂ existing in the solution are constant, irrespective to the total amount of the MgBr₂ added. This finding suggests that the surface of MgBr₂, which partly exists as the solid in the polymerization system, influences the polymerization behavior. The effect of the solid surface may be greater than that of a small amount of MgBr₂ in the solution. In fact, when the large amount of MgBr₂ was added, the $P_{m/r} + P_{r/m}$ value deviated from the unity. When methanol was added to the polymerization system to carry out the polymerization in a homogeneous polymerization system, the polymerization reactivity was enhanced by the addition of MgBr₂, similar to the polymerization in benzene. However, the tacticity of the produced polymer was very similar to that of the polymer prepared for the polymerization in the absence of MgBr₂. This supports the important role of the solid surface of the insoluble MgBr₂ as the strong Lewis acid to affect the propagating fashion of MMA. There-

fore, the enthalpy and entropy parameters shown in Table II should be considered as the apparent values involving both the effects of in the solution and on the surface of the Lewis acid.

After the polymerization in benzene in the presence of MgBr₂, the reaction mixture was poured into a large amount of methanol to precipitate the polymer. When this procedure was carried out carefully, we could obtain two kind forms of the polymer; one was powdery and another was isolated as the replica of a lump of the insoluble MgBr₂. We examined the molecular weight and its distribution as well as the tacticity of both the polymers. The GPC elution curves are shown in Figure 4. The results of the characterization are summarized in Table IV.

It has been revealed that the polymer produced around surface of the solid MgBr₂ has a higher molecular weight and *mm* value. Because of the difficulty of complete separation of the two kinds of polymers, a peak with a shoulder was observed in the GPC chromatogram. It is supposed that the

Table III Results of Radical Polymerization of MMA in the Presence of MgBr₂^a

MgBr ₂ · Et ₂ O (g)	Yield (%)	$M_n \times 10^{-4}$	M_w/M_n	Triad Fraction			P_r^b	$P_{m/r} + P_{r/m}^c$
				<i>mm</i>	<i>mr</i>	<i>rr</i>		
0	27.4	2.2	1.36	2.8	29.9	67.3	0.823	1.02
0.024	32.2	3.5	1.45	3.4	31.7	64.9	0.808	1.02
0.048	35.4	3.6	1.47	4.0	33.5	62.5	0.793	1.02
0.096	34.4	3.7	1.46	4.2	34.1	61.7	0.788	1.02
0.240	40.1	3.7	1.79	5.4	35.8	58.8	0.767	1.00
0.480	39.0	3.8	1.96	6.0	36.7	57.3	0.757	0.996
0.960	n.d.	4.4	2.17	7.5	37.9	54.6	0.736	0.974
0.240 ^d	33.7	2.6	1.29	3.0	30.4	66.6	0.818	1.02

^a MMA 2 mL, benzene 8 mL, AIBN 15.3 mg, polymerization time 4 h, temperature 30°C, under UV irradiation.^b $P_r = [rr] + [mr]/2$.^c $P_{m/r} = [mr]/([2mm] + [mr])$; $P_{r/m} = [mr]/([2rr] + [mr])$.^d Solvent: benzene 4 mL, methanol 4 mL.

Table IV Effect of Reaction Loci on Molecular Weight and Tacticity of the Poly(MMA) Produced during Radical Polymerization of MMA in the Presence of MgBr_2 ^a

Reaction Loci	$M_n \times 10^{-4}$	M_w/M_n	Triad Fraction			P_r ^b	$P_{m/r} + P_{r/m}$ ^c
			<i>mm</i>	<i>mr</i>	<i>rr</i>		
In solution	2.2	1.48	4.2	34.0	61.8	0.788	1.02
Around surface	4.3	3.56	7.9	38.8	53.3	0.727	0.977

^a MMA 2 mL, benzene 8 mL, $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ 0.240 g, AIBN 15.3 mg, polymerization time 4 h.^b $P_r = [rr] + [mr]/2$.^c $P_{m/r} = [mr]/(2[mm] + [mr])$; $P_{r/m} = [mr]/(2[rr] + [mr])$.

polymer produced at the solid surface has a higher molecular weight and is eluted out at 28 min in the chromatogram. The observed P_r value was very low as 0.727. A proposed interaction of the polymer chain end and the Lewis acid during polymerization is illustrated in Figure 5.

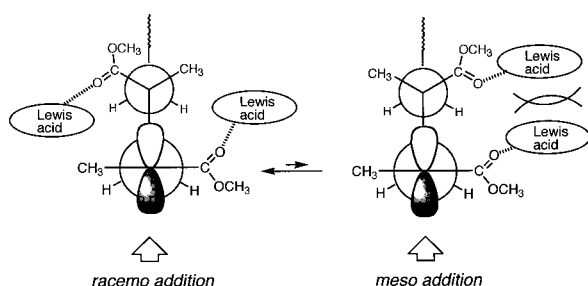
When the Lewis acid interacts with the carbonyl groups as the monodentate ligand, racemo addition would be preferred because of the steric repulsion between the chain end and the penultimate unit group. On the other hand, if the Lewis acid acts as the bidentate ligand, meso propaga-

tion occurs more frequently. Probably, the latter type of interaction is important at the surface of MgBr_2 as the solid Lewis acid in this work.

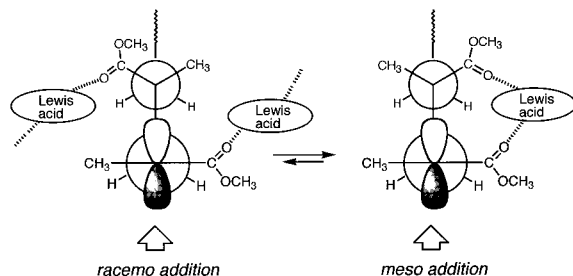
CONCLUSION

We have demonstrated that the addition of magnesium bromide as the Lewis acid to the polymerization system of MMA increases the polymerization reactivity deduced from the yield and molecular weight of the resulting polymer. From the comparison of the microtacticity of the poly(MMA)s produced from the polymerization in the presence and in the absence of magnesium bromide, it has been revealed that the probability of racemo addition decreases by the addition of the Lewis acid. Furthermore, greater effects of the Lewis acid on the polymerization rate and the fashion of the propagation were observed at the solid surface of the magnesium bromide, which was partly soluble in the polymerization system, because the significant interaction between the Lewis acid and the MMA monomer and the propagating chain end.

In the presence of monodentate Lewis acid



In the presence of bidentate Lewis acid

**Figure 5** Schematic models of propagation during polymerization of MMA in the presence of monodentate and bidentate Lewis acid.

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