Stereospecific Radical Polymerization of α-(Alkoxymethyl)acrylates Controlled by Lewis Acid Catalysts: Mechanistic Study and Effect of Amino Alcohols as Ligand for Zinc Bromide

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ABSTRACT: The stereospecific radical polymerization of methyl and benzyl α-(methoxymethyl)acrylates was performed in the presence of Lewis acids, such as $ZnBr_2$ and $Sc(OTf)_3$. The stereochemistry of the polymerization was significantly affected by the coordination of the Lewis acids to the polar groups of the monomer and polymer. The polymerization systems in the presence of $ZnBr_2$ and $Sc(OTf)_3$ produced syndiotactic- and isotactic-rich polymers, respectively, showing different ESR signals. When amino alcohols were added to the polymerization system with $ZnBr_2$, heterotactic-rich polymers were obtained. Therefore, syndiotactic-, isotactic-, and heterotactic-rich polymers can be synthesized by the radical method in the presence of a catalytic amount of $ZnBr_2$, $Sc(OTf)_3$, and the $ZnBr_2$−amino alcohol complex, respectively, without changing the other polymerization conditions, although an atactic polymer was produced in the absence of a Lewis acid. The detailed tacticity (tetrad) of the obtained polymer was estimated by ^{13}C NMR analysis of the main-chain methylene carbon.

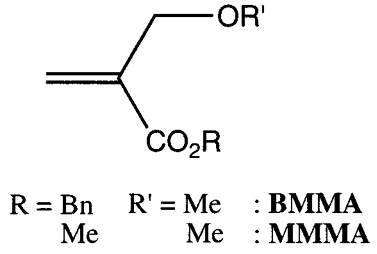
Introduction

The stereocontrol in the radical polymerization of vinyl monomers is an important goal in synthetic polymer chemistry, because many polymers have been produced by radical processes in industry and the properties of the polymeric materials are often significantly affected by the stereoregularity of the main chain. Although several studies on the stereospecific synthesis of vinyl polymers by a radical process have been reported, these methods give only an alternative stereocontrol (isotactic or syndiotactic).[1,2] We recently found that the radical polymerization of benzyl α-(methoxymethyl)acrylate (BMMA) in the presence of a catalytic amount of Lewis acids, such as ZnX_2 (X = Br, Cl) and scandium trifluoromethansulfonate ($Sc(OTf)_3$), afforded syndiotactic-rich (up to $r = 71\%$) and isotactic-rich (up to $m = 69\%$) polymers, respectively,[3,4] whereas the radical polymerization of α-(alkoxymethyl)acrylates without Lewis acids generally affords atactic polymers.[5] The synthesis of stereoregular polymers with the opposite sense was realized to a certain extent by choosing Lewis acid catalysts without changing the other polymerization conditions and the monomer structure. The coordination of the Lewis acids to the polar groups (ester and ether) on the ω-end of the propagating polymer and the monomer should play an important role in this system.

In this paper, the role of the Lewis acid catalysts in the stereocontrol and the effect of amino alcohols as a ligand to $ZnBr_2$ during the radical polymerization of BMMA and methyl α-(methoxymethyl)acrylate (MMMA) were investigated.

Experimental Section

Materials. The solvents, dichloromethane and toluene, used in the polymerization were purchased from Kanto Chemical Co., Inc., as the dehydrate grade. The commercially available



Lewis acids ($ZnBr_2$ and $Sc(OTf)_3$) were dried by heating under reduced pressure. A radical initiator, diisopropyl peroxycarbonate [$(i\text{-PrOCO}_2)_2$], was kindly supplied by the NOF Co. and used as a hexane solution. AIBN was purchased from Kishida Chemical Co., Inc., and purified by recrystallization from methanol. The monomers were synthesized according to a previously reported procedure.[6]

Measurements. ^1H and ^{13}C NMR spectra were measured on a Varian Unity-Inova 500 (500 MHz for ^1H) spectrometer in $CDCl_3$. Chemical shifts were reported in parts per million (ppm) with tetramethylsilane (TMS, 0 ppm) and $CDCl_3$ (77.0 ppm) as the internal standards for ^1H and ^{13}C NMR, respectively. The size exclusion chromatographic (SEC) analyses were performed on a JASCO-BORWIN GPC equipped with JASCO UV-970 and JASCO RI-930 detectors using Tosoh TSKgel G7000HHR and G3000HHR columns connected in series and $CHCl_3$ was used as the eluent. Calibration was performed using standard polystyrenes. The ESR spectra of the polymer radicals were taken by a JEOL JES-TE2000 spectrometer at the X band with a 100 kHz modulation frequency using the TE mode cavity.

Polymerization Procedure. Polymerization was typically carried out using a Lewis acid (0.06 mmol), BMMA (0.6 mmol), a solvent (0.5 mL), and $(i\text{-PrOCO}_2)_2$ (0.02 mmol) with stirring in a Schlenk tube at 30 °C. The reaction products were precipitated into methanol containing ca. 1% HCl, repeatedly washed with methanol, and then dried in vacuo.

Results and Discussion

We previously reported that the stereospecific radical polymerization of BMMA was realized with $(i\text{-PrOCO}_2)_2$ in nonpolar solvents, such as toluene and CH_2Cl_2, at

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Table 1. Radical Polymerization of BMMA in the Presence of Lewis Acids[a]

entry	Lewis acid (equiv)	initiator	temp (°C)	solvent	yield (%)[b]	DP (M_w/M_n)[c]	*rr*/*mr*/*mm*[d]	*r*/*m*[e]
1	none	(*i*-PrOCO$_2$)$_2$	30	CH$_2$Cl$_2$	96[f]	63 (2.5)	22/48/30	46/54
2[g]	ZnBr$_2$ (0.10)	(*i*-PrOCO$_2$)$_2$	30	toluene	90	110 (3.2)	51/40/9	71/29
3	ZnBr$_2$ (0.20)	AIBN + UV	30	toluene	87	44 (3.0)	51/42/7	72/28
4	ZnBr$_2$ (0.10)	AIBN + UV	−20	CH$_2$Cl$_2$	60	149 (2.7)	47/47/6	70.5/29.5
5	ZnBr$_2$ (0.18)	AIBN	60	toluene	84	44 (3.5)	47/38/15	66/34
6	ZnI$_2$ (0.10)	AIBN + UV	30	toluene	62	70 (2.7)	46/44/10	68/32
7	ZnI$_2$ (0.10)	AIBN	60	toluene	75	70 (2.7)	46/41/13	66.5/33.5
8[h]	Sc(OTf)$_3$ (0.09)	(*i*-PrOCO$_2$)$_2$	30	CH$_2$Cl$_2$	77	92 (1.9)	12/38/50	31/69
9[h]	Sc(OTf)$_3$ (0.10)	AIBN + UV	30	CH$_2$Cl$_2$	82	93 (1.7)	17/39/44	36.5/63.5
10	Sc(OTf)$_3$ (0.10)	AIBN + UV	−20	CH$_2$Cl$_2$	42	100 (2.3)	16/45/39	38.5/61.5

[a] Initiator: (*i*PrOCO$_2$)$_2$, [monomer] = 1.0 M, [monomer]/[initiator] = 30, polym time 48 h. [b] MeOH-insoluble part. [c] Determined by SEC (polystyrene standard). [d] Determined by ^{13}C NMR analysis. [e] Calculated from triad tacticity, $r = rr + mr/2$, $m = mm + mr/2$. [f] Hexane-insoluble part. [g] Data from ref 3. [h] Data from ref 4.

Table 2. Solubility of ZnBr$_2$ in Toluene and CH$_2$Cl$_2$ and Their 1.0 M BMMA Solutions[a]

		BMMA solution	
toluene	CH$_2$Cl$_2$	toluene	CH$_2$Cl$_2$
≈0	1.5	66	>100

[a] Solubility: mg/mL of solvent.

Table 3. Triad Tacticity of Poly(BMMA)s Prepared by Radical Polymerization in the Presence of ZnBr$_2$[a]

ZnBr$_2$ equiv to BMMA	*rr*/*mr*/*mm*[b]
0.10	51/40/9
0.20	50/41/9
sat[c]	50/42/8
0.50[d]	50/42/8

[a] Polymerization was carried out in toluene at 30 °C for 48 h with strring. Initiator: (*i*-PrOCO$_2$)$_2$, [BMMA]/[(*i*-PrOCO$_2$)$_2$] = 30. [b] Determined by ^{13}C NMR analysis. [c] Polymerization was carried out after filteration of a heterogeneous mixture. [d] Hetereogeneous.

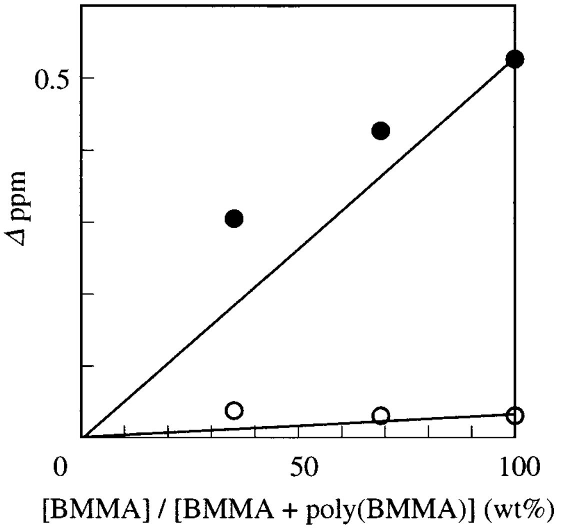


Figure 1. Changes in the chemical shifts of carbonyl (solid circle) and methoxy (open circle) carbons of BMMA in the presence of ZnBr$_2$. Conditions: [BMMA] + [monomer unit of poly(BMMA)] = 1 M, [ZnBr$_2$]/{[BMMA] + [poly(BMMA)]} = 0.1, solvent; CDCl$_3$, temperature 30 °C, value indicates downfield shift.

30 °C in the presence of a zinc halide (syndiotactic, r = 71%)[3] and Sc(OTf)$_3$ (isotactic, m = 69%).[4] To investigate the role of the Lewis acids during the stereospecific radical polymerization of α-(alkoxymethyl)acrylates, the influences of the initiator and polymerization temperature were examined for BMMA. The polymerization with AIBN at 30 °C under UV-light irradiation in the presence of Lewis acids proceeded in good yields to afford the polymers with a stereoregularity comparable to the previous polymer produced with (*i*-PrOCO$_2$)$_2$ (Table 1, entries 3 and 9). Zinc iodide also affected the stereoregularity during the radical polymerization of BMMA (r = 68%) (entry 6). These results demonstrate that the initiator has little effect on the stereocontrol during the polymerization. The polymers obtained at −20 °C had a different tacticity with slightly higher *mr* contents (entries 4 and 10) than those obtained at 30 °C in the presence of ZnBr$_2$ and Sc(OTf)$_3$. These results clearly indicate that the effect of the Lewis acids depends on the polymerization temperature.

The polymerization in the presence of a large amount of Lewis acids, such as zinc salts and Sc(OTf)$_3$, proceeded in a heterogeneous state; that is, part of the Lewis acids was insoluble in this system. Although ZnBr$_2$ is hardly soluble in toluene and CH$_2$Cl$_2$, which are useful solvents for the stereocontrol of the radical polymerization of BMMA,[3] ZnBr$_2$ was dissolved in a 1.0 M monomer solution to a certain extent; 0.29 equiv to the monomer in toluene and >0.49 equiv in CH$_2$Cl$_2$ (Table 2). The solubility of the Lewis acid in a nonpolar solvent significantly increases through the interaction with the monomer. The polymers obtained under the heterogeneous and homogeneous conditions had almost the same stereoregularity[3] (Table 3). Therefore, 0.1 equiv of ZnBr$_2$ is enough to control the stereochemistry during this polymerization, and an excess amount of ZnBr$_2$ did not result in any improvements in the stereospecificity.[3]

The interaction of ZnBr$_2$ with BMMA in the presence of the polymer [poly(BMMA)] was studied by ^{13}C NMR spectroscopy. Figure 1 shows that the chemical shift changes of the carbonyl and methoxy carbons of BMMA in the presence of ZnBr$_2$ at different BMMA and poly(BMMA) compositions. The carbon resonances were downfield shifted due to the ZnBr$_2$ coordination to the carbonyl and methoxy groups. The changes in the chemical shifts are more pronounced at a low monomer content, suggesting that ZnBr$_2$ more preferentially interacts with the monomer than the polymer. The same situation must occur during the radical polymerization in the presence of the Lewis acid.

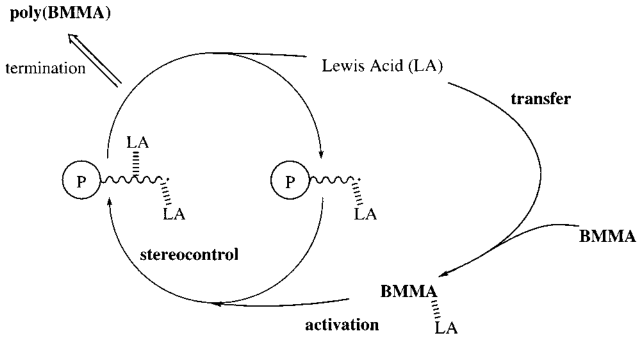
The radical polymerization of BMMA was carried out in the presence and absence of ZnBr$_2$ (0.1 equiv to BMMA) (Table 4). The addition of ZnBr$_2$ accelerated the polymerization rate in a manner similar to the report for the methacrylates.[7] After 4 h, the polymerization with the zinc salt produced a polymer in 63% yield, while that without zinc salt had only a 33% yield. The monomer coordinated by ZnBr$_2$ seems to be more reactive. The triad tacticities determined by ^{13}C NMR

Table 4. Radical Polymerization of BMMA in the Presence and Absence of $ZnBr_2$[a]

additive[b]	time (h)	yield (%)[c]	DP (M_w/M_n)[d]	rr/mr/mm[e]
$ZnBr_2$	0.25	6	104 (1.9)	47/41/12
	0.5	12	114 (1.9)	50/40/10
	1	24	129 (2.0)	48/42/10
	2	40	139 (2.1)	51/40/9
	4	63	143 (2.1)	49/41/10
	48[f]	90	110 (3.2)	51/40/9
none	1	1	114 (2.0)	
	2	9	127 (2.0)	
	4	33	132 (1.9)	
	8	61	110 (2.0)	
	12	74	98 (2.1)	20/47/33
	24	90	76 (2.4)	
	48[f]	96[g]	63 (2.5)	22/48/30

[a] Initiator: $(i\text{-}PrOCO_2)_2$; solvent: CH_2Cl_2; [BMMA]/[initiator] = 30, temperature 30 °C. [b] $[ZnBr_2]/[BMMA] = 0.1$. [c] MeOH-insoluble part. [d] Determined by SEC (polystyrene standard). [e] Determined by ^{13}C NMR analysis. [f] Data from ref 3. [g] Hexane-insoluble part.

analysis[3,4] were almost constant ($rr{:}mr{:}mm \approx 50{:}40{:}10$), regardless of the polymerization yield. $ZnBr_2$ always seems to exist around the ω-end of the propagating polymer and affects the stereochemistry of the polymerization process. Therefore, the catalytic stereocontrol of the polymerization with a Lewis acid may proceed as follows: (1) The monomer is activated by the coordination of a Lewis acid to preferentially polymerize over the noncoordinated monomer. This leads to the selective existence of the Lewis acid around the ω-end of the propagating polymer. (2) The coordination of the Lewis acid to the polar groups near the propagating polymer can control the stereochemistry of the polymerization. (3) The Lewis acid splits off from the polymer chain after adding some monomers to coordinate to the free monomer.



To obtain information on the propagation radical species, the ESR of the BMMA polymerization systems was measured in the presence and absence of the Lewis acids, $ZnBr_2$ and $Sc(OTf)_3$, at room temperature. Under these conditions, syndiotactic ($rr{:}mr{:}mm = 51{:}42{:}7$) and isotactic (17:39:44) polymers have been obtained with $ZnBr_2$ and $Sc(OTf)_3$[3,4] (temperature 30 °C), respectively. The ESR spectra recorded after a 30-scan accumulation are shown in Figure 2. The seven-line spectrum overlapping with an undefined peak appeared without a Lewis acid (Figure 2a). The seven-line spectrum may be based on the four β-hydrogens and the free rotation around the $C_\alpha{-}C_\beta$ axis of the propagation radical.[8] Although the spectrum (b) observed in the presence of $ZnBr_2$ (nine-line or more) was less resolved, it is clearly different from (a). $ZnBr_2$ characteristically affects the stereoregularity during the radical polymerization of α-(alkoxymethyl)acrylates, while only a slight effect was observed for the polymerization of methyl methacrylate (MMA). The polar α-substituent on the acrylates must play an important role in the stereocontrol in this system.[3] In addition to the six-membered chelation to the polar groups at the ω-end of the propagating polymer,[4] $ZnBr_2$ may interact with the penultimate ether group to fix the conformation of the propagating radical; that is, the Lewis acid restricts the free rotation around the $C_\alpha{-}C_\beta$ axis. The ESR spectrum of the BMMA system in the presence of $Sc(OTf)_3$ was quite different from those of the above two, suggesting that the propagating radical coordinated with $Sc(OTf)_3$ may have a different conformation. These ESR signals were repeatedly observed.

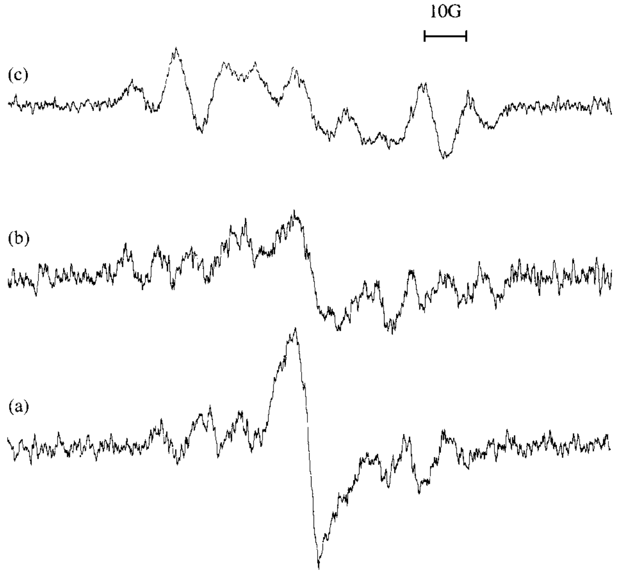
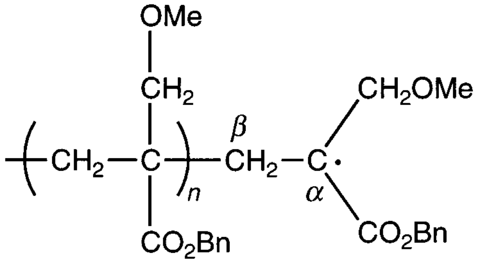


Figure 2. ESR spectra of the radical polymerization of BMMA with AIBN under UV-light irradiation at room temperature. [BMMA] = 1.0 M, [AIBN] = 0.033 M, solvent: toluene, in the absence of Lewis acid (a), in the presence of $ZnBr_2$ (0.1 equiv to BMMA, solvent: toluene) (b), and $Sc(OTf)_3$ (0.1 equiv to BMMA, solvent: CH_2Cl_2) (c).



Assuming that the monomer attacks the propagating radical only from the opposite side of the polymer chain, the tacticity is determined by the competition between the *meso* and *racemo* propagations as illustrated in Figure 3. The ω-end groups rapidly rotate around the $C_\alpha{-}C_\beta$ axis, and exchange between the *meso* and *racemo* propagations frequently occurs under the usual radical polymerization conditions. Therefore, the obtained polymer is almost atactic. In the presence of a Lewis acid, the coordination by the polar substituents of the penultimate unit to the Lewis acid can restrict the rotation around the $C_\alpha{-}C_\beta$ axis and, therefore, can fix the conformation of the propagating polymer radical. In the presence of $ZnBr_2$, the propagating radical may preferentially exist as the transition state **R** (*racemo* propaga-

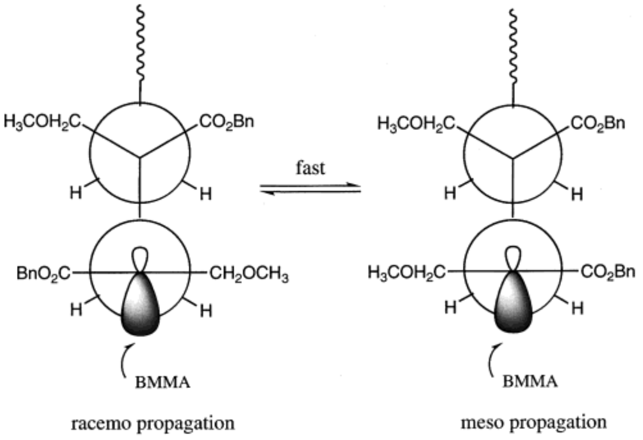


Figure 3. Transition-state models for *racemo* and *meso* propagations in the radical polymerization of BMMA.

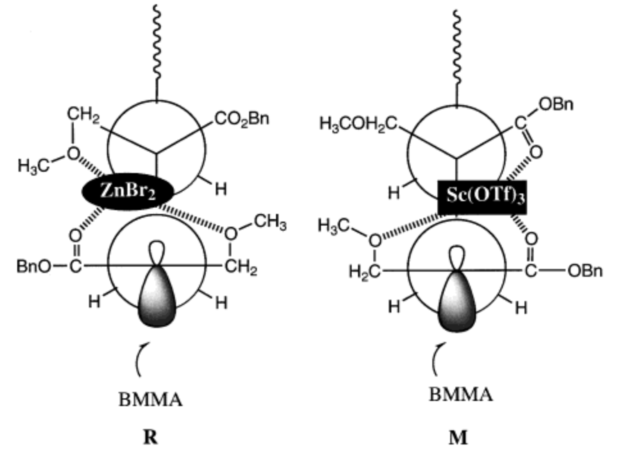


Figure 4. Proposed transition states for propagation in the radical polymerization of BMMA in the presence of Lewis acids.

tion model, Figure 4) due to the coordination by the ether group in the penultimate unit so that the syndiotactic polymer is obtained. On the other hand, $Sc(OTf)_3$ was also effective for stereocontrol during the radical polymerization of MMA, and the isotactic content increased.[9] Therefore, $Sc(OTf)_3$ in the ω-end must preferentially interact with the carbonyl groups in the penultimate unit, and the transition state **M** (*meso* propagation model, Figure 4) seems to be more plausible.

Table 5. Radical Polymerization of BMMA in the Presence of $ZnBr_2$–Amino Alcohol[a]

entry	ligand	yield (%)[b]	DP (M_w/M_n)[c]	rr/mr/mm[d]
1[e]		90	110 (3.2)	51/40/9
2	**1**[f]	74	47 (4.2)	30/51/19
3	**1**	79	73 (2.8)	18/56/27
4[g]	**1**	83	83 (2.4)	21/57/22
5	**1**[h]	34	41 (2.5)	16/54/30
6	**2**	59	113 (2.0)	16/56/28

[a] Initiator: $(i\text{-PrOCO}_2)_2$; solvent: toluene, [BMMA]/[initiator] = 30, $[ZnBr_2]/[BMMA] = 0.05$, $[ligand]/[ZnBr_2] = 1.1$, temperature: 30 °C. [b] MeOH-insoluble part. [c] Determined by SEC (polystyrene standard). [d] Determined by ^{13}C NMR analysis. [e] Data from ref 3. [f] $[ligand]/[ZnBr_2] = 0.5$. [g] $[ZnBr_2]/[BMMA] = 0.1$. [h] $[ligand]/[ZnBr_2] = 2.0$.

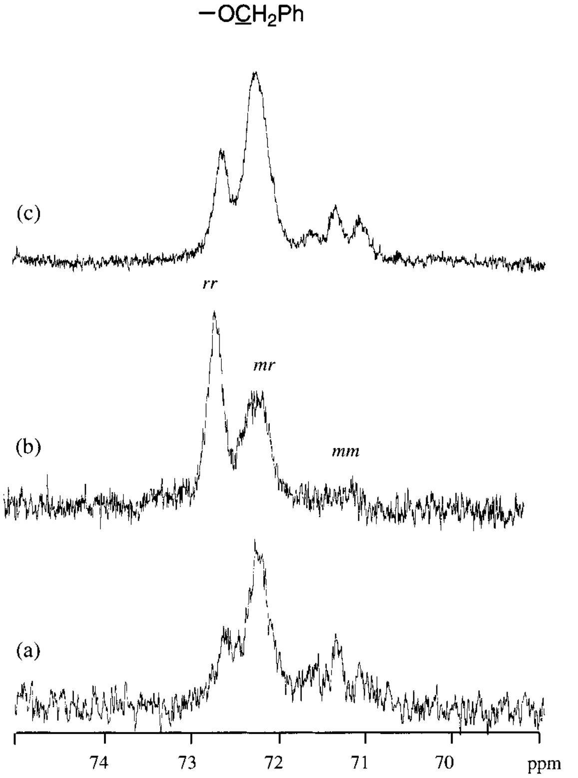
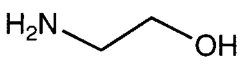


Figure 5. ^{13}C NMR spectra of the methylene carbon in the ester groups of poly(BMMA) obtained by the normal radical method (a),[3] in the presence of $ZnBr_2$ (b),[3] and the $ZnBr_2$–**1** complex (Table 5, entry 4) (c) ($CDCl_3$, 60 °C).

The coordination structure of the Lewis acid to the propagating chain end significantly affects the stereoregularity of the obtained polymer during the radical polymerization of BMMA. The successful design of a Lewis acid is expected to realize a further tacticity control. Therefore, the ligand effect of amino alcohols for $ZnBr_2$ was studied for the radical polymerization of BMMA. These results are summarized in Table 5. The stereoregularity of the polymer obtained using the $ZnBr_2$–2-aminoethanol (**1**) complex was quite different from those of the polymer prepared with $ZnBr_2$ alone, as well as by the normal radical method. Figure 5 shows the ^{13}C NMR spectra of the methylene carbon in the ester group of the poly(BMMA)s prepared by the normal radical method (a), in the presence of a catalytic amount of $ZnBr_2$ (b), and $ZnBr_2$–(**1**) (c). The triad tacticity of poly(BMMA) is assigned as shown in the figure.[3,4] The heterotacticity (*mr* content) increased by adding **1**, and the highest value was obtained for the ratio $[ligand]/[ZnBr_2]$ = ca. 1 (*mr* = 57%, Table 5, entry 4). The $ZnBr_2$ complex with (+)-norephedrine (**2**) also afforded a polymer rich in heterotacticity. The $ZnBr_2$–amino alcohol complexes catalytically affect the stereochemistry during the radical polymerization of BMMA to produce heterotactic-rich polymers (up to *mr* = 57%). Further design of the Lewis acids is now in progress to achieve a higher stereocontrol.



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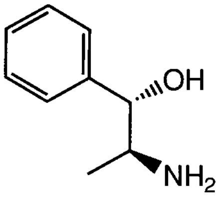

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The catalytic stereocontrol by the Lewis acids was also studied for the radical polymerization of methyl α-(meth-

Table 6. Radical Polymerization of MMMA in the Presence of Lewis Acids[a]

entry	Lewis acid (equiv)	solvent	yield (%)[b]	DP (M_w/M_n)[c]	*rr*/*mr*/*mm*[d]	*r*/*m*[e]
1[f]		CH_2Cl_2	50[g]	61 (2.6)	24/51/25	49.5/50.5
2[f]	$ZnBr_2$ (0.11)	CH_2Cl_2	62	76 (2.1)	42/48/10	66/34
3	$ZnBr_2$ (0.13)	toluene	87	76 (2.0)	43/45/12	65.5/34.5
4	$Sc(OTf)_3$ (0.09)	CH_2Cl_2	80	96 (1.9)	16/36/48	34/66
5	$ZnBr_2$−**1** (0.10)	toluene	39	90 (2.3)	22/55/23	49.5/50.5

[a] Polym temperature: 30 °C; time: 48 h; initiator: (i-$PrOCO_2)_2$; [monomer] = 1.0 M; [monomer]/[(i-$PrOCO_2)_2$] = 30. [b] $MeOH-H_2O$ (4/1, v/v)-insoluble part. [c] Determined by SEC (polystyrene standard). [d] Determined by ^{13}C NMR analysis. [e] Calculated from triad tacticity, $r = rr + mr/2$, $m = mm + mr/2$. [f] Polym time: 24 h. [g] Hexane-insoluble part.

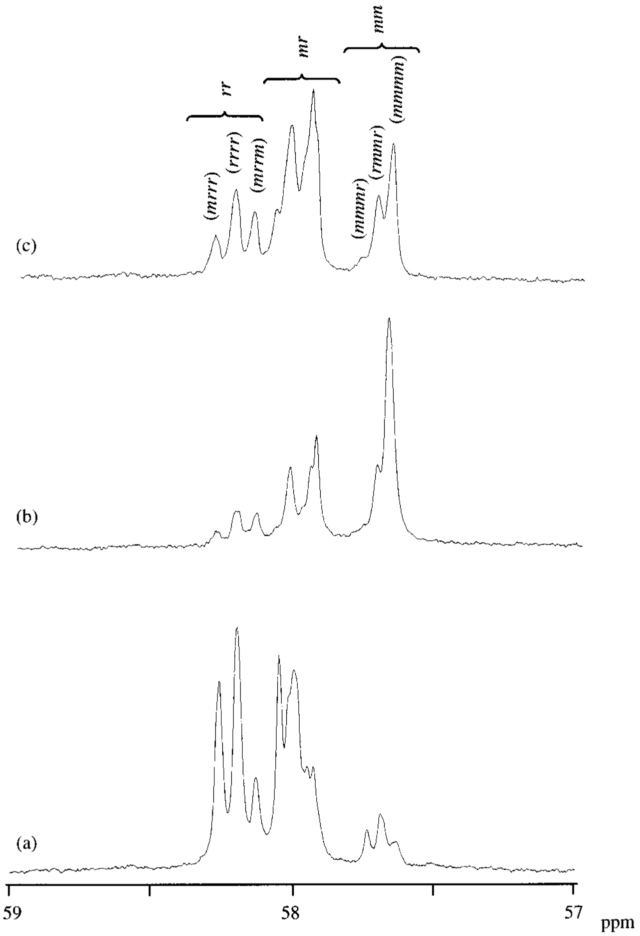

Figure 6. ^{13}C NMR spectra of the methyl carbon in the ether groups of poly(MMMA) obtained by the radical polymerization in the presence of $ZnBr_2$ (Table 6, entry 3) (a), $Sc(OTf)_3$ (Table 6, entry 4) (b), and $ZnBr_2$−**1** complex (Table 6, entry 5) (c) ($CDCl_3$, 60 °C).

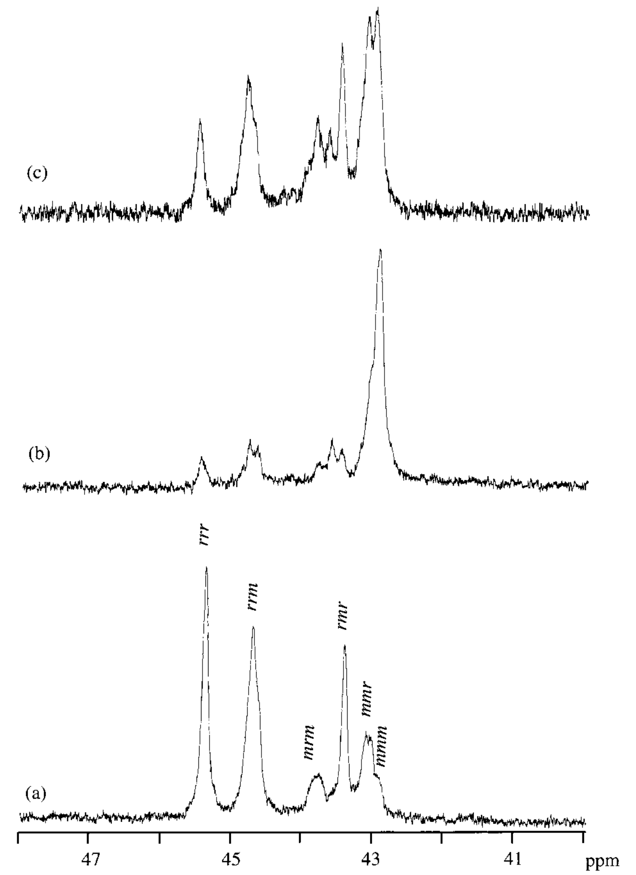

Figure 7. ^{13}C NMR spectra of the main chain methylene carbon of poly(MMMA) obtained by the radical polymerization in the presence of $ZnBr_2$ (Table 6, entry 3) (a), $Sc(OTf)_3$ (Table 6, entry 4) (b), and the $ZnBr_2$−**1** complex (Table 6, entry 5) (c) ($CDCl_3$, 60 °C).

oxymethyl)acrylate, MMMA[10] (Table 6). Although the analysis of the tacticity of the poly[α-(alkoxymethyl)-acrylate] was unsuccessful except for poly(BMMA)[3,4] and poly[methyl α-(phenoxymethyl)acrylate],[5,6] the triad tacticity of poly(MMMA)s could be estimated by ^{13}C NMR analysis. The methyl carbon peaks in the ether group were split by the pentad sequences and assigned to the triad sequences, *mm*, *mr*, and *rr* as shown in Figure 6. The polymer obtained by the normal radical method was evaluated to be atactic (rr:mr:mm = 24:51:25, r:m = 49.5:50.5). Syndiotactic- (r = 66%), isotactic- (m = 66%), and heterotactic-rich (mr = 55%) polymers were obtained in the polymerizations with $ZnBr_2$, $Sc(OTf)_3$, and $ZnBr_2$−**1**, respectively. Lewis acid-catalyzed stereocontrols similar to those for BMMA took place. Moreover, in the ^{13}C NMR analysis, the peaks of the main chain methylene carbon indicated splitting due to the tetrad sequence. By comparison with the triad tacticity, the peaks may be assigned as indicated in Figure 7. The tacticity for poly(MMMA) obtained in the presence of $ZnBr_2$ (Figure 7a) was estimated to be rrr:rrm:mrm:rmr:mmr + mmm = 0.25:0.31:0.09:0.17:0.18, which leads to the calculated triad, $rr = rrr + rrm/2 = 0.405$, $mr = rrm + 2mrm = 0.49$, and diad tacticities, $r = rrr + rrm + mrm = 0.65$. These values are in good agreement with those estimated from the methyl carbon of the ether group ($rr = 0.42$, $mr = 0.48$, and $r = 0.66$). The tetrad tacticity of poly(MMMA)s obtained in the presence of $Sc(OTf)_3$ (Table 6, entry 4), $ZnBr_2$−**1** complex (Table 6, entry 5), and by the normal radical method (Table 6, entry 1) were also estimated as follows: rrr:rrm:mrm:rmr:mmr + mmm = 0.06:0.13:0.09:0.11:0.61 ($rr = 0.125$, $mr = 0.31$, and $r = 0.28$), 0.08:0.21:0.16:0.17:0.38 ($rr = 0.185$, $mr = 0.53$, and $r = 0.45$), and 0.10:0.21:0.14; 0.17:0.38 ($rr = 0.205$, $mr = 0.49$, and $r = 0.45$), respectively, although the r content was slightly smaller than that evaluated from the methyl carbon in the ether group.

In conclusion, the Lewis acid catalysts clearly changed the stereochemistry of the radical polymerization of α-(alkoxymethyl)acrylates. The Lewis acids seem to change the conformations of the propagating radicals through coordination of the polar substituents (ether or ester group) of the monomer and polymer end to the Lewis acid. The ESR measurement supported this. The $ZnBr_2$−amino alcohol system afforded the heterotactic-rich polymers. Therefore, the stereospecific synthesis of the polymers rich in syndiotacticity ($r \approx 72\%$), isotacticity ($m \approx 70\%$), and heterotacticity ($mr \approx 57\%$) by using the Lewis acid was achieved.

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References and Notes

(1) For reviews: (a) Hatada, K.; Kitayama, T.; Ute, K. *Prog. Polym. Sci.* **1988**, *13*, 189. (b) Pino, P.; Suter, U. W. *Polymer* **1976**, *17*, 977. (c) Yuki, H.; Hatada, K. *Adv. Polym. Sci.* **1979**, *31*, 1.

(2) (a) Porter, N. A.; Allen, T. R.; Breyer, R. A. *J. Am. Chem. Soc.* **1992**, *114*, 7676. (b) Wu, W.-X.; McPhail, A. T.; Porter, N. A. *J. Org. Chem.* **1994**, *59*, 1302. (c) Nakano, T.; Mori, M.; Okamoto, Y. *Macromolecules* **1993**, *26*, 867. (d) Nakano, T.; Matuda, A.; Okamoto, Y. *Polym. J.* **1996**, *28*, 556. (e) Yamada, K.; Nakano, T.; Okamoto, Y. *Proc. Jpn. Acad. Ser. B* **1998**, *74*, 46. (f) Yamada, K.; Nakano, T.; Okamoto, Y. *Macromolecules* **1998**, *31*, 7598. (g) Yamada, K.; Nakano, T.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2677.

(3) Habaue, S.; Uno, T.; Okamoto, Y. *Polym. J.* **1999**, *31*, 900. (b) Habaue, S.; Uno, T.; Baraki, H.; Okamoto, Y. *Macromolecules* **2000**, *33*, 820.

(4) Habaue, S.; Baraki, H.; Okamoto, Y. *Polym. J.* **2000**, *32*, 1022.

(5) (a) Lenz, R. W.; Saunders, K.; Balakrishnan, T.; Hatada, K. *Macromolecules* **1979**, *12*, 392. (b) Balakrishnan, T.; Devarajan, R.; Santappa, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 1909.

(6) Habaue, S.; Yamada, H.; Uno, T.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 721.

(7) For example: (a) Mudruga, E. L.; Roman, J. S.; Rodriguez, M. J. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 2749. (b) Malavasic, T.; Vizovisek, I.; Osredkar, U.; Anzur, I. J. *J. Polym. Sci., Polym. Symp.* **1981**, *69*, 73. (c) Mudruga, E. L.; Roman, J. S. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1101. (d) Srivastava, A. K.; Mathur, G. N. *Polymer* **1981**, *22*, 391. (e) Imoto, M.; Otsu, T.; Hatada, Y. *Makromol. Chem.* **1963**, *65*, 180. (f) Imoto, M.; Otsu, T.; Shimizu, S. *Makromol. Chem.* **1963**, *65*, 174.

(8) Yamada, B.; Kobatake, S.; Aoki, S. *Macromol. Chem. Phys.* **1994**, *195*, 933.

(9) Isobe, Y.; Nakano, T.; Yamada, K.; Okamoto, Y. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 1463.

(10) Thompos, R. D.; Barclay, T. B.; Basu, K. R.; Mathias, L. J. *Polym. J.* **1995**, *27*, 325.

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