Asymmetric Anionic Polymerization of Chiral (R)-(+)-N-α-Methylbenzylmaleimide with Chiral Ligand/Organometal Complex

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ABSTRACT: Asymmetric anionic polymerizations of chiral (R)-(+)-N-α-methylbenzylmaleimide (MBZMI) were performed with (−)-sparteine (Sp) or (S, S)-(1-ethylpropylidene)bis(4-benzyl-2-oxazoline) (Bnbox)/organometal complexes in toluene or tetrahydrofuran (THF). All polymers obtained were optically active. Specific optical rotations ($[\alpha]_{435}^{25}$) of the polymers initiated by Et$_2$Zn/Sp and Et$_2$Zn/Bnbox were $-113.5°$ to $-195.7°$ and $+56.0°$ to $+170.2°$, respectively. Number-average molecular weights ($\overline{M}_n$) of the polymers were from 7.2×10^3 to 2.9×10^4. Chirality of the polymers was attributed not only to chirality of optically active MBZMI units but also to stereogenic centers (S, S) and (R, R), in the main chain induced by the polymerization, judging from the results of circular dichroism (CD), ^{1}H and ^{13}C NMR spectra, and GPC curves obtained with polarimetric and UV detectors. Anionic polymerizability of MBZMI using organometal with and without chiral ligand, and chiroptical properties of the polymers are discussed.
KEY WORDS Chiral N-Substituted Maleimide / Chiral Ligand / Asymmetric Polymerization / Optically Active Polymer /

There are a number of papers on synthesis of chiral polymers and their applications.[1,2] Okamoto and coworkers investigated asymmetric polymerizations with chiral ligand–organometal complex to form optically active polymers with one handed-helical conformation from bulky methacrylate, isocyanide and acetylene derivatives.[1–3] The authors reported radical polymerizations of chiral N-substituted maleimides (RMI's).[4–9] In these polymerizations, chirality was introduced on the main chain of poly(RMI), but specific optical rotation was very small. Asymmetric anionic polymerizations of

achiral RMI with chiral ligands have been investigated.[10,11] More recently we studied asymmetric polymerizations of achiral RMI using chiral ligand–organometal complexes.[12–17] In these papers, optically active poly(RMI)s exhibited relatively high specific optical rotations. Chirality of the polymers was attributed to excess chiral stereogenic centers, (S, S) and (R, R), in the polymer main chain based on threo-diisotactic structures formed from the asymmetric polymerizations, as shown in Scheme 1. (R)-(+)-N-α-Methylbenzylmaleimide (MBZMI) was polymerized with radical and anionic initiators by the authors.[18] However, there are no studies on asymmetric anionic polymerizations of chiral MBZMI using organometal chiral ligand complexes.

A cyclic olefin monomer with a C$_2$ axis of symmetry such as RMI is polymerized to afford a polymer, in which all asymmetric centers in the main chain are not always true chiral ones. The polymerization of RMI proceeds through trans and cis additions to give four types of structures for poly(RMI). The cis-addition offers two erythro-diisotactic and erythro-disyndiotactic, not optically active because the monomeric units have mirror images plane. Cubbon reported that the polymerization of RMI proceeds through trans-addition because of steric hindrance.[19] The trans-addition gives threo-diisotactic and threo-disyndiotactic structures. Only threo-diisotactic structures show optical activity and threo-disyndiotactic ones show no optical activity because of the same ratio of (S, S) and (R, R). If the polymerization of RMI proceeds through trans-addition, the polymers can have (S, S) and/or (R, R) configurations. If the polymerization of RMI afford a polymer with excess (S, S) or (R, R) configuration, the polymer can be optically active. If the polymer contains only either (S, S) or (R, R) configurations, the poly(RMI) has completely helical structures. Since MBZMI is a chiral RMI monomer, combination of chiral ligand and chiral N-substituent can efficiently in-
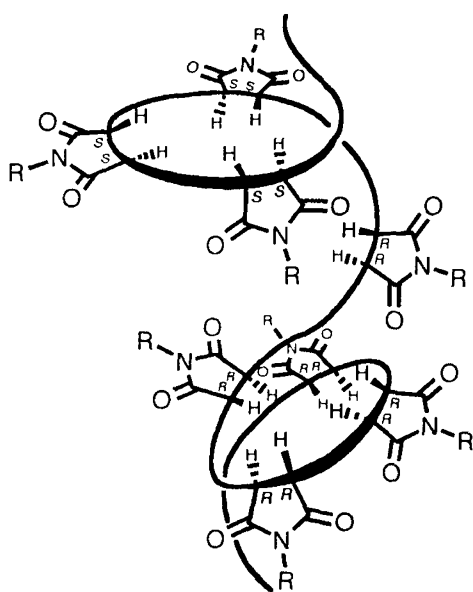
Scheme 1.

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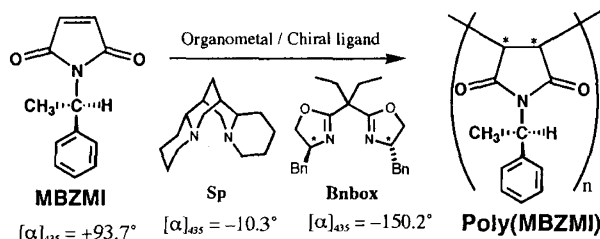
Scheme 2.

fluence stereoregularity of the main chain. Consequently, poly(RMI) with higher specific optical rotation can be obtained and applied to chiral stationary phase in high performance liquid chromatography.

This paper describes asymmetric anionic polymerizations of chiral MBZMI (Scheme 2) with Et_2Zn/Sp or $Et_2Zn/Bnbox$ complex as initiator in toluene or THF. In the polymerization of MBZMI with Et_2Zn/Sp, the obtained polymers showed higher absolute specific rotations in both solvents. In this study, the effects of polymerization solvent, temperature, time and initiator concentration on the asymmetric anionic polymerization of MBZMI are investigated in detail. The polymerizations of chiral MBZMI and chiroptical properties of the formed polymers are discussed on the basis of circular dichroism (CD), GPC, and ^{13}C NMR spectra.

EXPERIMENTAL

Materials

MBZMI was synthesized by the published procedure.[20] MBZMI: bp 177—178°C/6 mmHg; $[\alpha]_{435}^{25} = +93.7°$ ($c = 1.0$ g dL^{-1}, THF, $l = 10$ cm), lit.[18] $[\alpha]_D^{25} = 57.9°$ ($c = 1.0$ g dL^{-1}, THF, $l = 10$ cm). ^1H NMR spectrum: chemical shift, δ in ppm from $Si(CH_3)_4$ in $CDCl_3$: 7.45—7.15 (m, 5 H, aromatic proton), 6.65 (s, 2H, CH=CH), 5.35 (q, 1H, $J = 7.6$ Hz, CH), 1.85 (d, 3H, $J = 7.6$ H, CH_3), ^{13}C NMR: δ in ppm from $Si(CH_3)_4$ in $CDCl_3$: 170.53 (C=O), 140.30, 128.44, 127.62, 127.11 (phenyl), 133.92 (CH=CH), 49.49 (CH), 17.9 (CH_3).

A model compound, (R)-(+)-N-α-Methylbenzylsuccinimide (MBZSI): bp 163—165°C/5 mmHg; mp 59—61°C; $[\alpha]_{435}^{25} = +138.8°$ ($c = 1.0$ g dL^{-1}, tetrahydrofuran(THF), $l = 10$ cm), ^1H NMR spectrum: chemical shift, δ in ppm from $Si(CH_3)_4$ in $CDCl_3$: 7.50—7.20 (m, 5H, aromatic proton), 5.43 (q, 1H, $J = 7.6$ Hz, CH), 2.65 (m, 4H, CH_2–CH_2), 1.85 (d, 3H, $J = 7.6$ H, CH_3), ^{13}C NMR: δ in ppm from $Si(CH_3)_4$ in $CDCl_3$: 176.73 (C=O), 139.39, 128.00, 127.33, 127.19 (phenyl), 49.78 (CH), 27.68 (CH_2–CH_2), 16.18 (CH_3).

Solvents used in the reaction and polymerization were purified according to usual methods.[21] A commercially available n-butyllithium (n-BuLi) hexane solution (1.53 mol L^{-1}) and diethylzinc hexane solution (1.02 mol L^{-1}) were used without further purification. The concentration of n-BuLi solution was determined from titration with standard HCl solution. Fluorenyllithium (FlLi) and N, N'-diphenylethylenediamine monolithium amide (DPEDA-Li) were synthesized from fluorene and N, N'-diphenylethylenediamine, respectively, with an equimo-

lar amount of n-BuLi in toluene or THF.[22]

Bnbox was prepared according to the method reported previously.[23] $[\alpha]_{435}^{25} = -150.2°$ ($c = 1.0$ g dL^{-1}, THF, $l = 10$ cm); $[\alpha]_D^{25} = -22.0°$ ($c = 1.0$ g dL^{-1}, $CHCl_3$, $l = 10$ cm); lit.[23] $[\alpha]_D^{24} = -21.8°$ ($c = 2.55$ g dL^{-1}, $CHCl_3$). Commercially available (−)-sparteine (Sp) was purified by distillation under reduced pressure: bp 93—94°C/5×10^{-2} mmHg; $[\alpha]_{435}^{25} = -10.3°$ ($c = 1.0$ g dL^{-1}, THF, $l = 10$ cm); lit.[24] $[\alpha]_D^{21} = -16.4°$ ($c = 10$ g dL^{-1}, EtOH).

Anionic Polymerizations

MBZMI was placed in a Schlenk reaction tube and toluene or THF was added to dissolve it. The procedure was performed under nitrogen atmosphere. The monomer solution was cooled to the polymerization temperature, and a catalyst solution was added using a cannula. Polymerization was completed by addition of methanol solution containing a small amount of hydrochloric acid. Polymerization solution was poured into excess methanol to precipitate polymers. The polymers were purified three times by precipitation from a small amount of THF solution to excess methanol. The obtained pure polymers were dried at r.t. for 2 days.

Radical Polymerization

Radical polymerizations were performed with 2,2'-azobis(isobutyronitrile) (AIBN) as initiator in toluene in a sealed tube at 60°C. After polymerization, the polymer solution was poured into a large amount of methanol to precipitate the polymer. The resulting polymer was purified by reprecipitation, pouring THF solution two times into excess methanol. The system was filtered and dried in vacuo at r.t. for 2 days.

Measurements

Specific rotation was measured in THF at 25°C using a quartz cell (5 and 10 cm) with a JASCO DIP-140(JASCO Co. Ltd.). CD spectra were measured in THF at 25°C using a quartz cell of 0.1 mm with a JASCO J 20 C (JASCO Co. Ltd.). UV spectra were obtained by measurements at 25°C in THF using a quartz cell of 1 mm. $\overline{M}_n$ of the polymers was measured with gel permeation chromatography (GPC) using THF as eluent and polystyrene as standard at 50°C with a Shimadzu LC-10 A instrument equipped with a UV-Vis photospectrometer SPD-10 A, a polarimetric detector (JASCO OR-990), and a data processor. ^1H and ^{13}C NMR spectra were obtained on a JEOL-EX 270 (Nippon Electric Co., Ltd.).

RESULTS AND DISCUSSION

Anionic Polymerization of MBZMI

Anionic polymerizations of MBZMI shown in Scheme 2 were performed using only organometals without chiral ligand in THF or toluene.

Table I summarizes the results of the polymerization of MBZMI initiated only by n-BuLi, Et_2Zn, or AIBN. Specific optical rotations of the polymers were significantly influenced by the organometal initiator. All polymers initiated with n-BuLi had positive optical rotations. In the case of Et_2Zn as initiator, the polymers showed negative specific rotations. The specific rotations of the polymers initiated by the same organometal in-

Table I. Anionic and radical polymerizations of MBZMI with organometal or AIBN

Run	MBZMI mol L^{-1}	Initiator mol%	Polym. solvent mL	Polym. temp ℃	Polym. time h	Yield [a] %	$\overline{M}_n$ [b] ×10^{-3}	$\overline{M}_w/\overline{M}_n$ [b]	$[\alpha]_{435}^{25}$ [c] deg.
1	0.5	n-BuLi(10)	Tol.(5)	0	72	54.2	3.4	1.7	+85.0
2	0.5	n-BuLi(10)	THF(5)	0	24	16.2	3.8	1.7	+4.3
3	0.5	n-BuLi(10)	Tol.(5)	r.t.	72	46.0	2.5	2.0	+113.2
4	0.5	n-BuLi(10)	THF(5)	r.t.	24	19.5	3.1	1.4	+91.0
5	0.5	Et$_2$Zn(10)	Tol.(5)	0	120	45.6	17.7	2.2	-5.4
6	0.5	Et$_2$Zn(10)	THF(5)	0	120	72.7	13.9	1.4	-70.0
7	0.5	AIBN(5)	Tol.(5)	60	24	77.6	4.3	2.1	+33.3

[a] MeOH-insoluble. [b] By GPC. [c] $c = 1.0$ g dL^{-1}, $l = 10$ cm, THF.

Table II. Anionic polymerizations of MBZMI with Sp as ligand

Run	MBZMI mol L^{-1}	Initiator [a] mol%	Polym. solvent mL	Polym. temp ℃	Polym. time h	Yield [b] %	$\overline{M}_n$ [c] ×10^{-3}	$\overline{M}_w/\overline{M}_n$ [c]	$[\alpha]_{435}^{25}$ [d] deg.
1	0.5	FlLi/Sp(10)	Tol.(5)	0	24	81.7	3.1	2.1	+86.2
2	0.5	FlLi/Sp(10)	THF(5)	0	24	96.6	4.3	2.2	+12.7
3	0.5	DPEDALi/Sp(10)	Tol.5)	0	24	82.1	4.0	2.1	+118.6
4	0.5	DPEDALi/Sp(10)	THF(5)	0	24	96.1	6.4	2.2	+34.3
5	0.5	n-BuLi/Sp(10)	Tol.(5)	0	24	53.9	4.0	1.7	+78.4
6	0.5	n-BuLi/Sp(10)	THF(5)	0	24	76.2	4.0	2.1	+22.8
7	0.5	n-BuLi/Sp(10)	Tol.5)	r.t	24	75.0	3.8	1.4	+106.1
8	0.5	n-BuLi/Sp(10)	THF(5)	r.t	24	80.9	5.0	1.4	+56.4
9	0.5	Et$_2$Zn/Sp(10)	Tol.(5)	-35	72	51.4	28.9	6.9	-195.7
10	0.5	Et$_2$Zn/Sp(10)	Tol.(5)	0	72	91.8	11.2	1.9	-164.3
11	0.5	Et$_2$Zn/Sp(10)	Tol.(5)	r.t.	72	64.1	7.2	2.5	-43.6
12	0.5	Et$_2$Zn/Sp(10)	THF(5)	-35	72	40.5	13.6	3.0	-113.5
13	0.5	Et$_2$Zn/Sp(10)	THF(5)	0	72	51.8	15.6	2.5	-164.9
14	0.5	Et$_2$Zn/Sp(10)	THF(5)	r.t.	72	48.8	8.6	2.8	-151.3

[a] Initiator/Sp = 1.0/1.2. [b] MeOH-insoluble. [c] By GPC. [d] $c = 1.0$ g dL^{-1}, $l = 10$ cm, THF.

itiators were strongly influenced by solvent. The polymer obtained with Et$_2$Zn in THF showed larger absolute specific rotation than in toluene.

Poly(MBZMI) obtained with AIBN in toluene at 60℃ had specific rotation of +33.3° (run 7 in Table I) and $\overline{M}_n$ of 4.3×10^3. These values are in fair agreement with results reported previously.[18]

The specific rotations of the polymers were quite different from those of the starting monomer of MBZMI ($[\alpha]_{435}^{25} = +93.7°$), poly(MBZMI) obtained with AIBN ($[\alpha]_{435}^{25} = +33.3°$), and the model compound MBZSI ($[\alpha]_{435}^{25} = +138.8°$). This suggests that chirality of the polymer is introduced onto the polymer main chain by optically active groups in MBZMI during polymerization. Similar phenomena were observed in the radical polymerizations of RMI reported by the authors.[4-9,18] (+)-Poly(RMI) with dextro specific rotation contains (S, S) more than (R, R) configuration in the main chain and (−)-poly(RMI) with levo specific rotation contains more (R, R) than (S, S).[15,25] Thus, the (−)-poly(MBZMI) obtained with Et$_2$Zn seems to contain more (R, R) than (S, S) configuration of the main chain formed by asymmetric induction because the polymer had negative (levo) specific rotation. The polymerization initiated by Et$_2$Zn proceeded at lower rate and poly(MBZMI)s formed had levo specific rotations, and much higher $\overline{M}_n$ when polymerization time was prolonged, compared to polymers obtained with n-BuLi.

### Asymmetric Anionic Polymerization of MBZMI

Asymmetric anionic polymerizations of MBZMI were performed with the chiral ligand/organometal complex in THF or toluene, as shown in Scheme 2.

Table II summarizes the results of homopolymerization of chiral MBZMI with Sp/organometal complexes in toluene or THF at several temperatures.

Poly(MBZMI) initiated by n-BuLi/Sp, FlLi/Sp, and DPEDALi/Sp showed positive specific rotations ($[\alpha]_{435}^{25}$ +12.7° to +118.6°). $\overline{M}_n$s of the polymers were between 3.1×10^3 and 6.4×10^3. Generally, yields and $\overline{M}_n$ of the polymers obtained in THF were higher than those obtained in toluene under similar conditions because the formed polymers were soluble in THF during polymerization. The polymer obtained with DPEDALi/Sp in toluene showed the highest positive specific rotation ($[\alpha]_{435}^{25}$ +118.6°, run 3 in Table II). Poly(MBZMI) obtained in toluene exhibited larger absolute specific rotation than in THF, compared to the same ligands and temperatures. The specific rotations($[\alpha]_{435}^{25}$) of the polymers obtained with Et$_2$Zn/Sp were −43.6° to −195.7°, which were levo-rotation and opposite to that of polymers obtained with other initiators. $\overline{M}_n$s for the polymers obtained with Et$_2$Zn/Sp were between 7.2×10^3 and 2.9 ×10^4, which were much larger than those with other initiating systems. This agrees with results without chiral ligands. The poly(MBZMI)(run 9 in Table II) initiated by Et$_2$Zn/Sp in toluene at −35℃ showed the highest negative specific rotation ($[\alpha]_{435}^{25} = -195.7°$) and highest $\overline{M}_n$ of 2.9×10^4. These specific rotations of polymers were
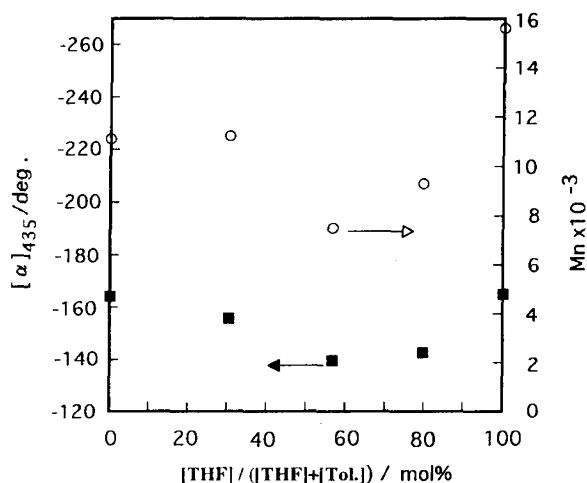
Figure 1. Effects of polymerization solvents (mixture of THF and toluene) on specific rotation (■) and $\overline{M}_n$ (○) of poly(MBZMI) obtained with Et_2Zn/Sp at 0℃.
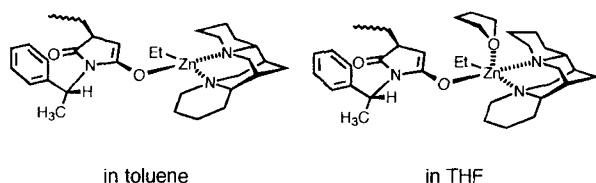
Scheme 3.

quite different from those of the chiral monomer (MBZMI) ($[\alpha]_{435}^{25}=+93.7°$), model compound (MBZSI) ($[\alpha]_{435}^{25}=+138.8°$) and poly(MBZMI)($[\alpha]_{435}^{25}=-5.4°$ to $-70.0°$) obtained with Et_2Zn alone. Chirality of the polymers may thus result from asymmetric induction by the chiral ligand/organometal complex into the polymer main chain.

To clarify the effects of polymerization solvent on specific rotation of poly(MBZMI), polymerizations of MBZMI were performed with Et_2Zn/Sp in a mixture of toluene and THF at 0℃ for 72 h. The results are shown in Figure 1. When the concentration of THF (or toluene) was 50 mol%, specific rotations and $\overline{M}_n$ of the poly-(MBZMI) were smallest. The polymer showed the largest specific rotation and $\overline{M}_n$ when the concentration of THF (or toluene) was 100 mol%, this is quite different from that obtained with n-BuLi/Sp complex reported by the present authors previously.[10] The poly(RMI)s obtained with n-BuLi/Sp in THF and in toluene exhibited almost zero and relatively high specific rotation, respectively. The authors speculate that, using Et_2Zn/Sp as a ligand in THF, the oxygen of THF coordinates with Et_2Zn to form a complex $EtZn/THF/Sp$, as shown in Scheme 3. The chiral space built up in the growing chain end with $EtZn/THF/Sp$ complex is more suitable for the asymmetric polymerization than only with the $EtZn/Sp$ complex.

To observe directly change in optical rotation and conversion in toluene or THF during asymmetric polymerization, polymerization was performed with Et_2Zn/Sp in a 1.0 cm quartz cell in toluene or THF at 25℃. Figure 2 shows change in conversion and optical rotation of the

polymer in toluene (A) and THF (B) during polymerization at [initiator]/[MBZMI] = 10 mol%, $Et_2Zn/Sp=1.0/1.2$ (mol/mol), and 0.5 mol L^{-1} in toluene or THF. When toluene was used as solvent, the initial optical rotation of the monomeric MBZMI was ($\alpha_{435}^{25}+0.94°$), and decreased in a negative direction as polymerization proceeded. The optical rotation of the solution became negative after 30 min. The conversion became 100% after 40 min and optical rotation was almost constant after that. It was difficult to measure the optical rotation of the solution after ca. 100 min from the start of polymerization because of the dark red color of the polymerization solution. For THF, similar results were obtained, as shown in Figure 2 (B). The optical rotation of the initial MBZMI solution was $+0.93°$, the optical rotation of the solution became negative after ca. 200 min, and the optical rotation reached a constant value ($\alpha_{435}^{25}-0.57°$) at ca. 10 h. However, the conversion was 90% after about 20 min, and 100% after 120 min. The optical rotation still gradually increased after the conversion reached 100%. The reason is not clear at present.

Figure 3 depicts the effects of polymerization temperature on specific rotation of poly(MBZMI) formed with Et_2Zn/Sp in toluene or THF. The polymer obtained in toluene at $-35℃$ showed the highest negative specific rotation of $[\alpha]_{435}^{25}=-195.7°$. At 0℃, the polymer obtained in THF showed the highest specific rotation ($[\alpha]_{435}^{25}=-164.9°$). This suggests that the polymerization temperature has an important role in asymmetric anionic polymerization. Using toluene as solvent at lower temperature, the growing chain-end could selectively attack the monomer because of steric hindrance due to ethyl groups of the $EtZn/Sp$ complex. Thus, the obtained polymer showed higher stereoregularity, judging from specific rotation ($[\alpha]_{435}^{25}=-195.7°$). In THF, the polymerization is likely to have appropriate polymerization temperature for effective formation of stereo regular polymers. A suitable temperature seems to depend on solvation of THF. At higher temperature, the growing chain end reacts with the monomer with less stereo selectivity because of high reactivity in THF and in toluene. Consequently, the obtained polymers showed lower specific rotations, stereoregularity and smaller specific optical rotation and $\overline{M}_n$s.

Structure of the Polymers

Figure 4 shows the partly expanded ^{13}C NMR spectra of the main chain carbons of poly(MBZMI) obtained with Et_2Zn/Sp (1), n-BuLi (2) and AIBN (3). The peak in the main chain of poly(MBZMI) initiated by anionic polymerization (1, 2) were sharper than that of radical initiator AIBN (3). This suggests that the polymers obtained with anionic initiators shows higher stereoregularity than with the radical initiator. The polymer obtained with Et_2Zn/Sp may have more stereoregularity (much more (R, R)-configurations) than only with organometal because the peak in the main chain of the polymer was sharpest in the polymers.

To clarify the effects of temperature on the specific rotation of poly(MBZMI), the specific rotations of poly-(MBZMI)($[\alpha]_{435}^{25}-195.7°$, run 9 in Table II) obtained with Et_2Zn/Sp were measured in THF at several temperatures. Figure 5 shows the results of change of spe-
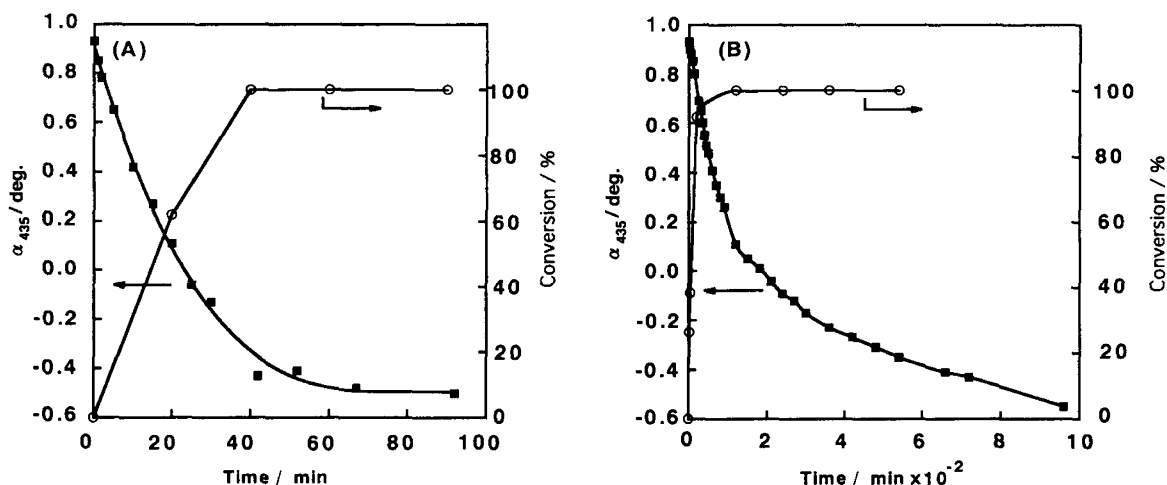
Figure 2. Change in conversion and optical rotations for polymerization systems of MBZMI with Et₂Zn/Sp in (A) toluene and (B) THF at 25°C in a quartz cell.
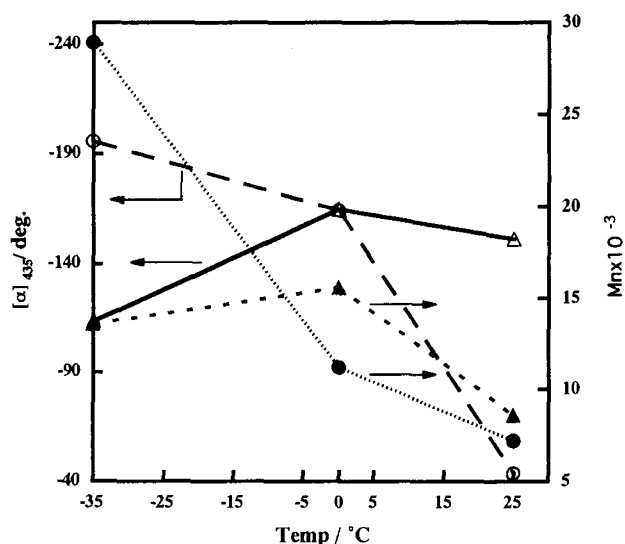
Figure 3. Effects of polymerization temperature on specific rotation (△, ○) and $\overline{M}_n$ (▲,●) of poly(MBZMI) in solvents: THF:△, ▲ : toluene:○, ●.

Figure 4. Expanded ¹³C NMR spectra for poly(MBZMI) obtained with (1) Et₂Zn/Sp (run 9, Table II), (2) AIBN, and (3) n-BuLi (run 1 in Table I).

cific rotations at various temperatures. The magnitude of specific rotation slightly decreased with increase of temperature. The temperature coefficient ($\Delta[\alpha]/\Delta T$) was relatively small (-0.46), suggesting that the poly-(MBZMI) scarcely contains helical conformations.[16]

The dependence of the concentration of Et₂Zn/Sp on the specific rotations of poly(MBZMI) is summarized in Table III. The obtained polymers in toluene exhibited the largest specific rotations $[\alpha]_{435}^{25}$ of $-183.0°$, $\overline{M}_n$ and yield (run 1 in Table III) when initiator concentration was 5 mol%. At greater initiator concentration, the specific rotation of the polymer was smaller in the toluene and THF systems.

Table IV summarizes the results of the asymmetric anionic polymerization of MBZMI with Et₂Zn/Bnbox complex as initiator in toluene or THF. All polymers showed positive (dextro) specific rotation ($+56.0°$ to $+170.2°$). At room temperature, the polymer obtained in

THF showed the highest specific rotation (run 4 in Table IV). The polymer obtained at 0°C in toluene showed higher $\overline{M}_n$ of 2.0×10^4 (run 1 in Table IV).

Using the same organometal Et₂Zn, specific rotations of the polymers were influenced by structures of ligands of Bnbox and Sp. This may be explained by different chiral spaces of the ligands. That is, Sp builds more suitable asymmetric fields at the polymer growth end than Bnbox. Chirality may be induced into the main chain of the poly(MBZMI) when polymerization is initiated by an ethyl group on Et₂Zn, and another ethyl group acts as a shielding group in ZnEt/Sp at the growing chain end of

Table III. Anionic polymerizations of MBZMI with diethylzinc/sparteine in toluene or THF using different initiator concentration

Run	MBZMI mol L^{-1}	Initiator [a] mol%	Polym. solvent mL	Polym. temp °C	Polym. time h	Yield [b] %	$\overline{M}_n$ [c] $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$ [c]	$[\alpha]_{435}^{25}$ [d] deg.
1	0.5	Et$_2$Zn/Sp(5)	Tol.(5)	0	72	100	24.6	5.2	−183.0
2	0.5	Et$_2$Zn/Sp(5)	THF(5)	0	72	48.9	18.1	4.4	−154.5
3	0.5	Et$_2$Zn/Sp(10)	Tol.(5)	0	72	91.8	11.2	1.9	−164.3
4	0.5	Et$_2$Zn/Sp(10)	THF(5)	0	72	51.8	15.6	3.3	−164.9
5	0.5	Et$_2$Zn/Sp(20)	Tol.(5)	0	72	99.8	17.0	4.9	−127.2
6	0.5	Et$_2$Zn/Sp(20)	THF(5)	0	72	98.4	19.0	2.8	−148.6

[a] Et$_2$Zn/Sp = 1.0/1.2. [b] MeOH-insoluble. [c] By GPC. [d] $c = 1.0$ g dL^{-1}, $l = 10$ cm, THF.

Table IV. Anionic polymerizations of MBZMI with diethylzinc/Bnbox complex in toluene or THF

Run	MBZMI mol L^{-1}	Initiator [a] mol%	Polym. solvent mL	Polym. temp °C	Polym. time h	Yield [b] %	$\overline{M}_n$ [c] $\times 10^{-3}$	$\overline{M}_w/\overline{M}_n$ [c]	$[\alpha]_{435}^{25}$ [d] deg.
1	0.5	Et$_2$Zn/Bnbox(10)	Tol.(5)	0	72	59.0	20.0	2.4	+138.3[e]
2	0.5	Et$_2$Zn/Bnbox(10)	Tol.(5)	r.t.	72	89.4	5.2	3.7	+139.5[e]
3	0.5	Et$_2$Zn/Bnbox(10)	THF(5)	0	72	59.3	8.7	2.8	+56.0
4	0.5	Et$_2$Zn/Bnbox(10)	THF(5)	r.t.	72	95.8	8.6	2.1	+170.2

[a] Et$_2$Zn/ Bnbox = 1.0/1.2. [b] MeOH-insoluble. [c] By GPC. [d] $c = 1.0$ g dL^{-1}, $l = 10$ cm, THF. [e] $c = 0.5$ g dL^{-1}, $l = 10$ cm, THF.
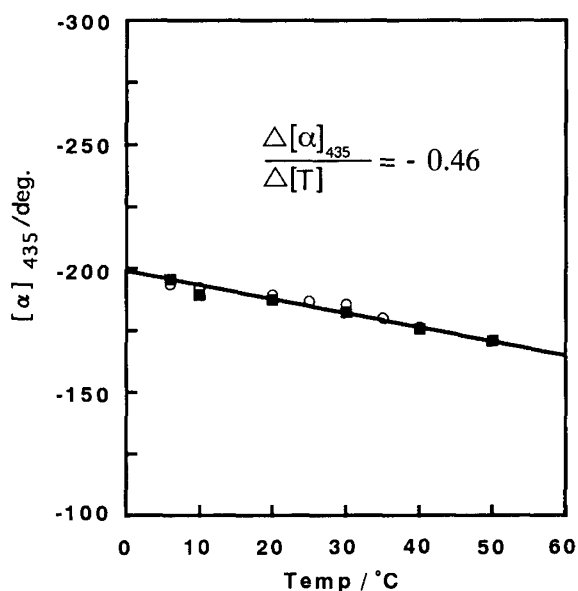
Figure 5. Effects of temperature on specific rotation $[\alpha]_{435}^{25}$ of poly(MBZMI) ($[\alpha]_{435}^{25} - 195.7°$) in solvent: THF, ■: heating, ○ : cooling.

Figure 6. GPC curves of poly(MBZMI) initiated by (1) Et$_2$Zn/Sp (run 10 in Table II) and (2) Et$_2$Zn/Bnbox (run 4 in Table IV). The top chromatogram was obtained by (A) polarimetric (α_{Hg}) and the bottom by (B) UV detector (254 nm).
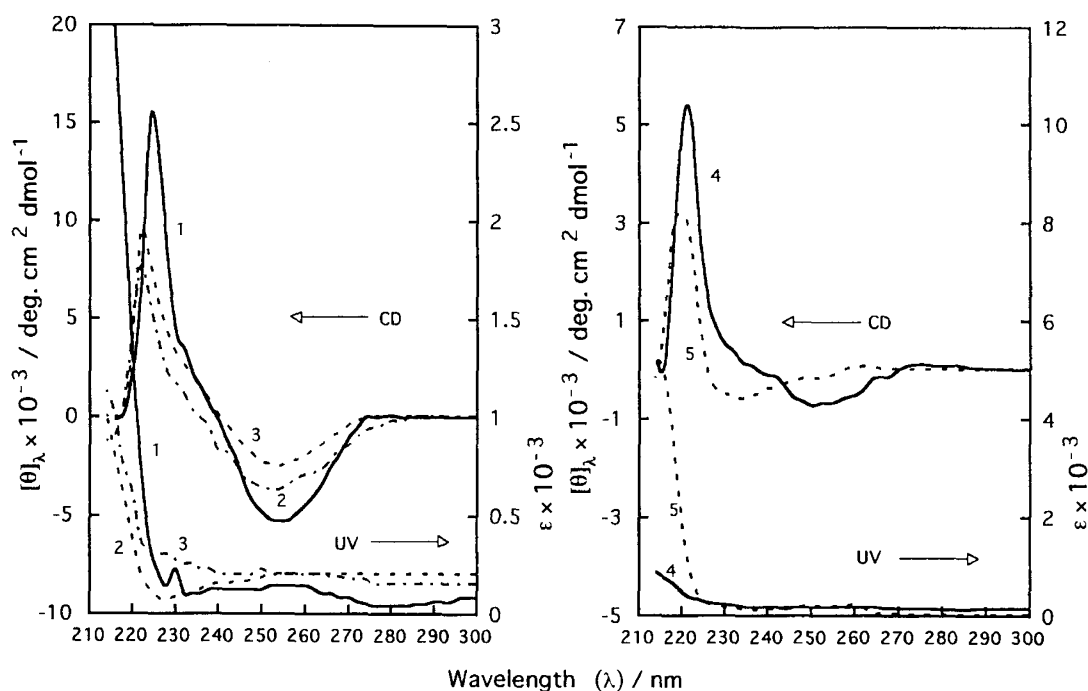
the polymer.[14]

(−)-Poly(MBZMI) (run 10 in Table II) and (+)-poly-(MBZMI) (run 4 in Table IV) were analyzed by GPC equipped with UV (A) and polarimetric detectors (B), as shown in Figure 6. In GPC curves detected by UV of the poly(MBZMI) obtained with Et$_2$Zn/Sp (A-1 in Figure 6), the polymer included only one high molecular weight fraction, and a peak appeared in the same region as by the polarimetric detector (B-1 in Figure 6). This suggests that the polymers are optically active. The GPC curves detected by UV (A-2) and polarimetric detector (B-2) of the poly(MBZMI) initiated by Et$_2$Zn/Bnbox exhibited similar peaks. But the GPC curve peaks by polarimetric detector were opposite that of poly(MBZMI) obtained with Et$_2$Zn/Sp. The curve (B-2) by polarimetric detector

indicated a positive sign in the whole region. $\overline{M}_n$ of the polymer obtained with Et$_2$Zn/Sp is higher than that of the polymer obtained with Et$_2$Zn/Bnbox.

Typical CD and UV spectra of the polymers are shown in Figure 7. The positive and negative CD peaks of the poly(MBZMI) initiated by Et$_2$Zn/Sp (1), n-BuLi (2) and AIBN (3) appeared at 213 nm and 255 nm, respectively, due to the n–π^* electron transition of carbonyl groups in the maleimide ring and the π–π^* electron transition of phenyl groups in MBZMI units of the main chain of

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Figure 7. CD and UV spectra for poly(MBZMI) obtained with (1) Et₂Zn/Sp (run 9 in Table II), (2) n-BuLi (run 1 in Table I), (3) AIBN (run 7 in Table I), and (4) MBZMI and (5) MBZSI in THF.

the polymer. CD peaks of the polymers obtained by Et₂-Zn/Sp, n-BuLi/Sp and AIBN were different from those of the chiral monomer MBZMI (4) and model compound MBZSI (5). The chirality of poly(MBZMI) may be attributed to not only chiral α-methylbenzyl groups of MBZMI but also to asymmetric induction by chiral ligand. CD spectral patterns of the poly(MBZMI) initiated by chiral ligand–organometal complexes were similar. These polymers may thus contain similar structure. The larger the absolute specific rotation, the larger was the peak at 255 nm. The asymmetric induction in main chain may thus become larger when peaks at 255 nm are higher.

SUMMARY

1. Asymmetric anionic polymerizations of chiral MBZMI were carried out with Et₂Zn/Sp or Et₂Zn/Bnbox to obtain optically active polymers. Poly(MBZMI) obtained with Et₂Zn/Sp in toluene at $-35°C$ showed the highest negative specific rotation of $-197.6°$ and highest $\overline{M}_n$ of 2.9×10^4. Poly(MBZMI) obtained with Et₂Zn / Bnbox at $0°C$ in THF showed the highest positive specific rotation of $+170.2°$.

2. The obtained polymers had different specific rotations and CD patterns from those of monomer MBZMI and model compounds MBZSI, suggesting that asymmetric induction takes place in the main chain of the polymers. The optical rotation of the polymers may result from not only optically active groups in the side chain of monomer MBZMI, but also different ratios of the existence of (S, S) or (R, R) in the polymer main chain.

3. From the ^{13}C NMR, CD spectra of the polymers, the main chain of the polymers with Et₂Zn/Sp showed higher stereoregularity.

4. The polymers obtained with the same initiator com-

plex in THF or toluene under the same conditions showed different specific rotations.

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