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Asymmetric Anionic Polymerization of N-Substituted Maleimides with *n*-Butyllithium−Methylene-Bridged 2,2-Bis(oxazoline) Complexes

Kenjiro Onimura, Hiromori Tsutsumi, and Tsutomu Oishi*

Department of Applied Chemistry & Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2557 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

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ABSTRACT: Asymmetric anionic homopolymerizations of achiral N-substituted maleimide (RMI: R = cyclohexyl (CHMI), R = phenyl (PhMI), R = *tert*-butyl (TBMI)) were carried out with *n*-butyllithium (*n*-BuLi)−chiral bis(oxazoline) complexes to obtain optically active polymers. (−)-2,2′-(1-Ethylpropylidene)-bis(4-alkyl-2-oxazoline) derivatives [4-alkyl (R′): R′ = benzyl ((*S*,*S*)-Bnbox), R′ = isobutyl ((*S*,*S*)-*i*-Bubox), R′ = isopropyl ((*S*,*S*)-*i*-Prbox), and R′ = phenyl ((*R*,*R*)-Phbox)] were prepared from amino alcohols and diethylmalonic acid. The polymer initiated by *n*-BuLi−(*S*,*S*)-Bnbox showed the highest specific rotation (poly(CHMI), $[\alpha]^{25}_{435}$ +111.4°). The poly(PhMI) prepared with (*S*,*S*)-*i*-Prbox as chiral ligand showed a negative specific rotation (−19.1°). The poly(TBMI) initiated by *n*-BuLi−(*R*,*R*)-Phbox showed a large specific rotation (−63.2°). The specific rotations were attributed to different contents between stereogenic centers (*S*,*S*) and (*R*,*R*) based on threo-diisotactic structures of the main chain.

Introduction

Recently, optically active polymers have aroused wide interest.[1] Polymerizations of 1,2-disubstituted ethylene type monomers, i.e., N-substituted maleimide (RMI), have been extensively investigated. The polymerization of RMI forms four types of structures for poly(RMI), as shown in Chart 1. The polymerization of RMI proceeds via stereoregularity of cis and trans addition. If the polymerizations of RMI proceed through cis addition, the structure of poly(RMI) has two types of configuration, i.e., erythro-diisotactic and erythro-disyndiotactic structures. The stereochemistry of the main chain of erythro-diisotactic poly(RMI) is −(*R*,*S*)−(*S*,*R*)−(*R*,*S*)−(*S*,*R*)−. The stereochemistry of the main chain of erythro-disyndiotactic poly(RMI) is −(*R*,*S*)−(*R*,*S*)−(*R*,*S*)−(*R*,*S*)−. But Cubbon reported that the polymerizations of RMI cannot proceed through cis addition because of steric hindrance between the vicinal succinimide ring at the 3,4-position of succinimide.[2] When the polymerizations of RMI proceed through trans addition, the structure of the polymer has two types of configurations, i.e., threo-diisotactic and threo-disyndiotactic structures (Chart 1).

The polymers of threo-disyndiotactic structure cannot exhibit optical activity because of the equivalence of chiral stereogenic centers (*S*,*S*) or (*R*,*R*) in the structure of the polymer. Chiroptical properties of poly(RMI) could be attributed to threo-diisotactic structures, which arise from the excess of chiral stereogenic centers (*S*,*S*) or (*R*,*R*). The authors synthesized and copolymerized optically active RMI bearing α-amino acid residues, (*R*)-α-methylbenzyl, *l*-menthyl, and cholesteryl groups.[3−7] The results suggested that chiroptical properties of the polymers and copolymers were ascribed to *asymmetric induction*, that is, formation of new asymmetric centers in the polymer main chain and *asymmetric perturbation* by the side chain chromophores. On the other hand, a few studies on *asymmetric synthesis polymerization* of achiral RMI using chiral ligands have been made.[8−10] In this polymerization, the propagating species attack monomers selectively on one enantioface. The authors reported that the polymerizations of several RMIs initiated by *n*-butyllithium (*n*-BuLi)−(−)-sparteine ((−)-Sp) complex gave optically active polymers: poly(*N*-cyclohexylmaleimide) (poly(CHMI); $[\alpha]_D$ −39.5°, $[\alpha]^{25}_{435}$ −74.9°).[8] Okamoto and co-workers reported anionic polymerizations of *N*-phenylmaleimide (PhMI) with chiral ligands and a few anionic initiators.[9] Recently, the authors reported asymmetric synthesis

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* To whom all correspondence should be addressed (tel & fax +81-836-35-9427, e-mail oishi@po.cc.yamaguchi-u.ac.jp).

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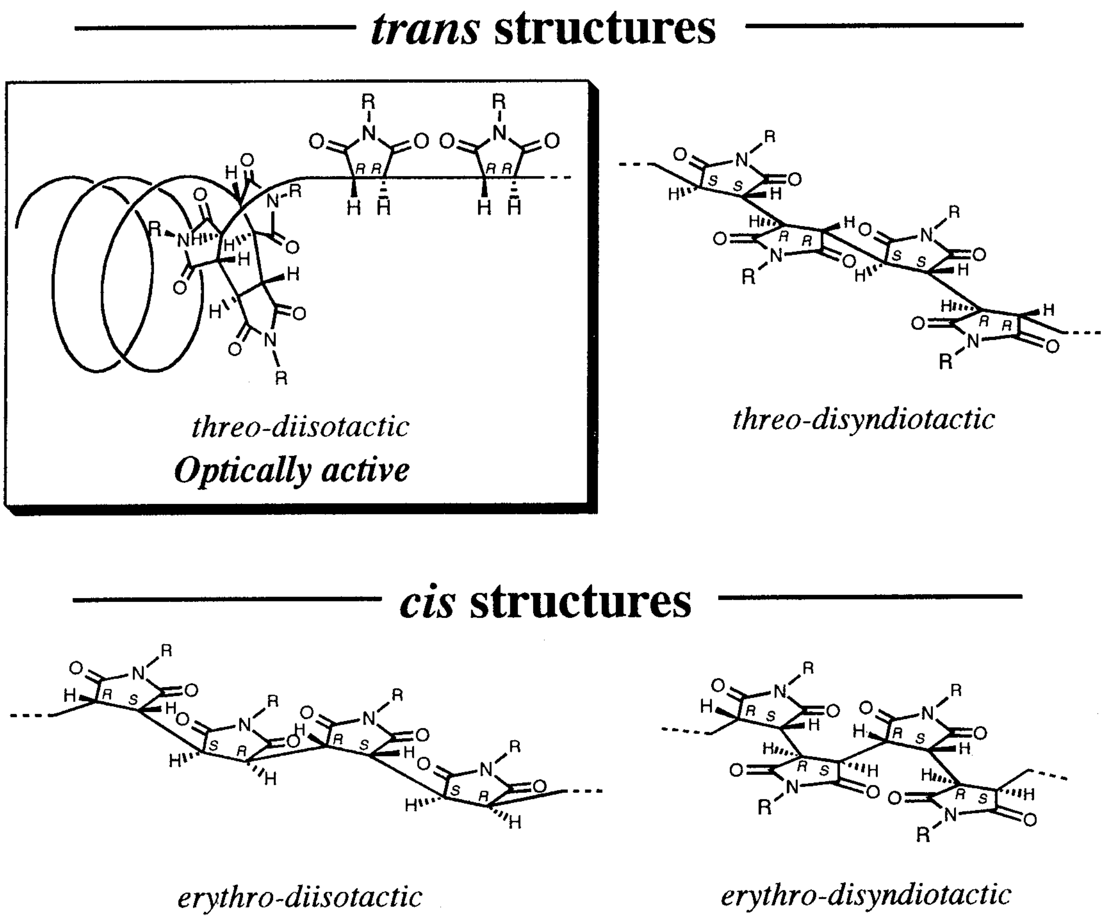
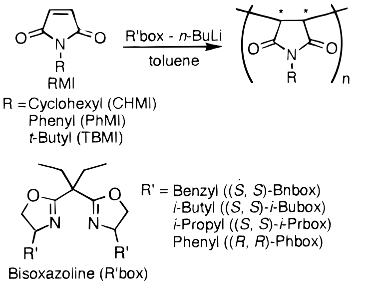
Chart 1



Scheme 1



polymerizations of achiral RMI with directly coupled bis(oxazoline)s as chiral ligands.[10] However, the obtained poly(RMI)s showed low specific rotations ($[\alpha]^{25}_{435}$ −2.9° to −8.2°). The reason for this could be attributed to the fact that the directly coupled bis(oxazoline)s were not capable of building a better asymmetric field at the growing end of polymers.

In this paper, four chiral methylene-bridged bis(oxazoline)s (R′box) are prepared from diethylmalonic acid and optically active amino alcohols, and achiral RMIs (CHMI, PhMI, *N*-*tert*-butylmaleimide (TBMI)) are polymerized with *n*-BuLi−R′box complexes (Scheme 1). The authors discuss chiroptical properties of poly(RMI) obtained with bis(oxazoline)s or (−)-Sp based on specific rotations and circular dichroism (CD) and ^{13}C NMR spectra of the polymers.

Experimental Section

RMI Monomers. RMI was prepared from maleic anhydride and the corresponding primary amine by usual methods.[11] Melting points and boiling points of RMI are as follows: CHMI mp 89 °C, PhMI mp 90−91 °C, and TBMI bp 55 °C/2 mmHg.

Reagents and Solvents. Commercially available *n*-BuLi (1.63 mol/L in a hexane solution) was used without further purification. Solvents, toluene, and methanol were purified by usual methods. Methylene-bridged bis(oxazoline)s were synthesized by the published procedure:[12] (4*S*)-2,2′-(1-ethylpropylidene)bis(4-benzyl-4,5-dihydrooxazole) ((*S*,*S*)-Bnbox), $[\alpha]^{25}_{435}$ = −150.7° (*c* 1.0 g dL^{-1}, THF); (4*S*)-2,2′-(1-ethylpropylidene)bis[(2-methylpropyl)-4,5-dihydrooxazole) ((*S*,*S*)-*i*-Bubox), $[\alpha]^{25}_{435}$ = −241.1° (*c* 1.0 g dL^{-1}, THF); (4*S*)-2,2′-(1-ethylpropylidene)bis[(1-methylethyl)-4,5-dihydrooxazole) ((*S*,*S*)-*i*-Prbox), $[\alpha]^{25}_{435}$ = −198.4° (*c* 1.0 g dL^{-1}, THF); (4*S*)-2,2′-(1-ethylpropylidene)bis(4-phenyl-4,5-dihydrooxazole) ((*R*,*R*)-Phbox), $[\alpha]^{25}_{435}$ = +286.7° (*c* 1.0 g dL^{-1}, THF).

Polymerization. Anionic homopolymerizations of RMI were carried out in toluene under dry nitrogen. Chiral R′box and *n*-BuLi were mixed at 0 °C just before use. An initiator solution was added to the monomer solution cooled to 0 °C. The reaction was terminated by the addition of a few drops of methanol. The polymer was precipitated in excess methanol containing a small amount of hydrochloric acid, separated by filtration, and purified by reprecipitation from chloroform−methanol or THF−methanol systems three times.

Measurements. Gel permeation chromatography (GPC) measurement of the polymer was accomplished on a LC-10AS (Shimadzu) equipped with a UV detector SPD-A (Shimadzu) and on a polarimetric detector OR-990 (Japan Spectroscopic Co.) using THF as the eluent. Four GPC columns, HSG-10, -15, -20, -40H (Shimadzu), were connected in series, and the molecular weight was calibrated with standard polystyrene. Hg-line or D-line specific rotations were measured with a JASCO DIP-140 (Japan Spectroscopic Co.) at 25 °C (quartz cell length, 10 cm; 1.0 g dL^{-1} in THF or CHCl$_3$). CD spectra

Table 1. Anionic Polymerization of N-Substituted Maleimide with *n*-BuLi−Bis(oxazoline) Ligands

run	RMI (mol/L)	initiator[a]	time (h)	yield (%)	$10^{-3}\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	$[\alpha]_{435}^{25}$[c] (deg)
1	CHMI (0.28)	BuLi−(*S*,*S*)-Bnbox	24	97	4.1	2.36	+111.4
2	PhMI (0.28)	BuLi−(*S*,*S*)-Bnbox	24	83	1.6	1.86	+0.9
3	TBMI (0.64)	BuLi−(*S*,*S*)-Bnbox	24	25	9.2	1.24	−1.5
4	CHMI (0.28)	BuLi−(*S*,*S*)-*i*-Bubox	24	89	3.4	2.35	+84.1
5	PhMI (0.28)	BuLi−(*S*,*S*)-*i*-Bubox	24	99	2.8	1.84	+8.7
6	TBMI (0.64)	BuLi−(*S*,*S*)-*i*-Bubox	24	49	10.2	1.46	+37.1
7	CHMI (0.28)	BuLi−(*S*,*S*)-*i*-Prbox	24	93	4.2	1.24	+43.5
8	PhMI (0.28)	BuLi−(*S*,*S*)-*i*-Prbox	24	96	4.0	1.46	−19.1
9	TBMI (0.64)	BuLi−(*S*,*S*)-*i*-Prbox	24	62	16.6	1.84	+9.4
10	CHMI (0.28)	BuLi−(*R*,*R*)-Phbox	24	99	3.0	2.05	−49.4
11	PhMI (0.28)	BuLi−(*R*,*R*)-Phbox	24	99	1.6	1.87	−18.3
12	TBMI (0.64)	BuLi−(*R*,*R*)-Phbox	24	20	9.3	1.35	−63.2
13[d]	CHMI (0.14)	BuLi−(−)-Sp	19	73	4.1	2.55	−74.9

[a] 10 mol %, [*n*-BuLi]/[R′box] = 1.0/1.2. [b] By GPC. [c] $c = 1.0$ g dL^{-1}, $l = 10$ cm, THF (runs 2, 3, 5, 6, 8, 9, 11, 12), $CHCl_3$ (runs 1, 4, 7, 10, 13). [d] See ref 8.

Table 2. Dependence of [(*S*,*S*)-Bnbox]/[*n*-BuLi] Ratio on Specific Rotaions of CHMI Polymers Obtained at 0 °C

run	RMI (mol/L)	initiator[a] [(*S*,*S*)-Bnbox]/[BuLi]	time (h)	yield (%)	$10^{-3}\bar{M}_n$[b]	$\bar{M}_w/\bar{M}_n$	$[\alpha]_{435}^{25}$[c] (deg)
1	CHMI (0.28)	0.5/1.0	24	93	6.5	2.44	+107.6
2	CHMI (0.28)	0.8/1.0	24	89	4.8	2.71	+108.7
3	CHMI (0.28)	1.0/1.0	24	91	5.4	3.55	+110.7
4	CHMI (0.28)	1.2/1.0	24	97	4.1	2.36	+111.4
5	CHMI (0.28)	1.6/1.0	24	99	4.3	2.41	+105.4
6	CHMI (0.28)	2.0/1.0	24	99	9.3	2.55	+100.8

[a] 10 mol %. [b] By GPC. [c] $c = 1.0$ g/dL, $l = 10$ cm, in $CHCl_3$.

were obtained at 25 °C using a JASCO J-20C (Japan Spectroscopic Co.), equipped with a xenon source and a computing data processor (quartz cell length, 0.1 and 0.2 mm; ca. 0.5−1.0 g dL^{-1} in THF). Ultraviolet (UV) spectra were obtained with a Shimadzu UV 2200 spectrophotometer (quartz cell length, 1 mm; ca. 0.5−1.0 g dL^{-1} in THF). ^{1}H and ^{13}C NMR spectra of the polymers were measured in chloroform-*d* at room temperature in the presence of tetramethylsilane (TMS) as an internal standard using a JEOL EX-270 (^{1}H, 270 MHz, ^{13}C, 68.7 MHz) spectrometer.

Results and Discussion

Homopolymerizations of RMI. The results of homopolymerizations of RMI with *n*-BuLi−chiral R′box complexes in toluene at 0 °C are summarized in Table 1.

All obtained polymers were optically active. The poly(CHMI) initiated by the *n*-BuLi−(*S*,*S*)-Bnbox complex showed the highest specific rotation ($[\alpha]_{435}^{25}$ +111.4°; run 1) in the poly(RMI) reported so far.[8−10] But poly(PhMI) and poly(TBMI) exhibited low specific rotations under the same conditions (runs 2 and 3). The absolute values of specific rotation ($[\alpha]_{435}^{25}$ +84.1°; run 4) of the poly(CHMI) obtained with (*S*,*S*)-*i*-Bubox were similar to that of poly(CHMI) initiated by the *n*-BuLi−(−)-Sp complex ($[\alpha]_{435}^{25}$ −74.9°; run 13).[8] The poly(CHMI) initiated by the *n*-BuLi−(*S*,*S*)-*i*-Prbox and *n*-BuLi−(*R*,*R*)-Phbox complexes showed $[\alpha]_{435}^{25}$ +43.5° and −49.4°, which suggests that the sign of specific rotation of poly(CHMI) depended on the stereochemistry at the 4-position in the oxazoline ring. Thus, poly(CHMI)s prepared with *n*-BuLi−(*S*,*S*)-R′box exhibited positive rotation, and that prepared with *n*-BuLi−(*R*,*R*)-R′box had a negative one. The absolute values of specific rotation of poly(PhMI)s initiated by *n*-BuLi−(*S*,*S*)-*i*-Prbox and *n*-BuLi−(*R*,*R*)-Phbox (runs 8 and 11) were larger than those polymerized with *n*-BuLi−(*S*,*S*)-Bnbox and *n*-BuLi−(*S*,*S*)-*i*-Bubox (runs 2 and 5). Despite different stereochemistries between *n*-BuLi−(*S*,*S*)-*i*-Prbox and *n*-BuLi−(*R*,*R*)-Phbox, the obtained poly(PhMI) showed the same sign (negative) of optical rotations. Poly(TBMI) polymerized with *n*-BuLi−(*S*,*S*)-*i*-Bubox and *n*-BuLi−(*R*,*R*)-Phbox showed larger specific rotations than those synthesized with *n*-BuLi−(*S*,*S*)-Bnbox and *n*-BuLi−(*S*,*S*)-*i*-Prbox. CHMI and TBMI have a bulky and an aliphatic substituent, and PhMI has a plane and an aromatic substituent. Therefore, it can be considered that CHMI and TBMI are affected by *only* steric repulsions of the substituent at the 4-position in the oxazoline ring. When the polymerization of PhMI was initiated by *n*-BuLi−(*S*,*S*)-Bnbox or *n*-BuLi−(*R*,*R*)-Phbox, the phenyl ring of PhMI might participate in a π-stacking interaction with the benzyl or phenyl group in oxazoline rings. Consequently, the sign of specific rotation of poly(RMI) depends on the substituents in the oxazoline ring and the RMI monomer.

Polymerizations of CHMI were performed under several conditions in order to clarify the relation between the specific rotations of poly(CHMI) and polymerization conditions. The effects of the molar ratios of (*S*,*S*)-Bnbox and *n*-BuLi on the specific rotations of poly(CHMI)s obtained were summarized in Table 2. The specific rotation showed the highest magnitude when the molar ratio of (*S*,*S*)-Bnbox and *n*-BuLi was 1.2/1.0. The number-average molecular weight ($\bar{M}_n$) was the largest when the ratio of (*S*,*S*)-Bnbox and *n*-BuLi was 2.0/1.0. The results could be explained as follows: *n*-BuLi is present in two or three aggregates. The aggregates of *n*-BuLi are deaggregated by (*S*,*S*)-Bnbox. The polymerizability of RMI initiated by the complex of *n*-BuLi and (*S*,*S*)-Bnbox is higher than that of the aggregates of *n*-BuLi. Almost all the polymerizations were initiated by the *n*-BuLi−(*S*,*S*)-Bnbox complex in the range of 0.5/1.0 to 0.8/1.0 to give the poly(CHMI) as shown in Table 2. But the obtained poly(CHMI)s had lower specific rotations than those obtained by the polymerization with the ratio 1.0/1.0. The reason could result from small amounts of the polymers initiated by

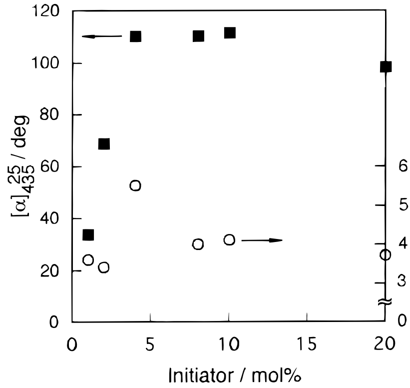


Figure 1. Dependence of concentrations of initiator ((*S,S*)-Bnbox−*n*-BuLi complex) on specific rotations ([α]$^{25}_{435}$) and $\bar{M}_n$ of poly(CHMI) obtained at 0 °C.

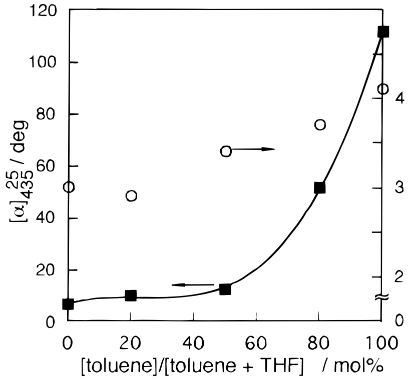


Figure 2. Effects of anionic polymerization solvent (mixture of toluene and THF) on specific rotations ([α]$^{25}_{435}$) and $\bar{M}_n$ of poly(CHMI) obtained with the *n*-BuLi−(*S,S*)-Bnbox complex at 0 °C.

the aggregates of *n*-BuLi. The poly(CHMI)s initiated by *only* the *n*-BuLi−(*S,S*)-Bnbox complex in the range of 1.0/1.0 to 1.2/1.0 showed higher specific rotations. By use of an excess of (*S,S*)-Bnbox, *n*-BuLi−2[(*S,S*)-Bnbox] complexes existed in a reaction mixture. But the *n*-BuLi−2[(*S,S*)-Bnbox] complexes, as well as the *n*-BuLi−[(*S,S*)-Bnbox] complex, could polymerize for CHMI. The complex was not capable of building better asymmetric fields at the polymer growth ends. Thus, poly(CHMI)s initiated by *n*-BuLi−(*S,S*)-Bnbox complex in the range of 1.6/1.0 to 2.0/1.0 showed low specific rotations.

The dependence of concentrations of the initiator on the specific rotations of poly(CHMI) obtained is shown in Figure 1. The specific rotations of the polymer showed high values ([α]$^{25}_{435}$ +98.1° to +111.4°) when the initiator was more than 4.0 mol %. But the specific rotations ([α]$^{25}_{435}$ +33.6° and +68.6°) and the yields were lower under the conditions of 1.0 and 2.0 mol % of the initiator. The authors reported that the specific rotation of poly(CHMI) obtained by the polymerizations with a 10 mol % concentration of chiral initiator showed the highest value.[8]

To clarify the effects of the polymerization solvents on the specific rotations of poly(CHMI), the polymerizations of CHMI were performed with *n*-BuLi−(*S,S*)-Bnbox in the mixture of solvents of toluene and THF at 0 °C for 24 h. The results are summarized in Figure 2. The specific rotations of the poly(CHMI) decreased with an increase of the amount of THF. The number-average molecular weight ($\bar{M}_n$) increased with increasing concentration of toluene in the mixture.

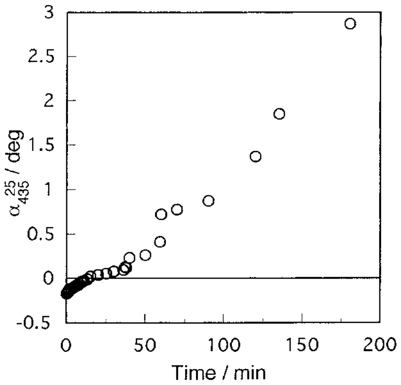


Figure 3. Change in optical rotation of polymerization system of CHMI with *n*-BuLi−(*S,S*)-Bnbox in toluene at 25 °C. Conditions: cell length, 1.0 cm; 0.28 mol/L in toluene.

The polymerization was performed in a quartz cell in order to observe directly a change of optical rotation in the asymmetric polymerization. The polymerization of CHMI was carried out with *n*-BuLi−(*S,S*)-Bnbox in a 1.0 cm quartz cell in toluene at 25 °C, and the change of optical rotation in the reaction mixture was followed. Figure 3 shows changes of optical rotation during the reaction at a feed ratio of [initiator]/[CHMI] = 10 mol %, [*n*-BuLi]/[(*S,S*)-Bnbox] = 1.0/1.2, and 0.28 mol/L in toluene. The optical rotation of only (*S,S*)-Bnbox in the same concentration was α$^{25}_{435}$ −0.26° (*c* = 1.34 g dL^{-1}; *l* = 1.0 cm in toluene). The optical rotation initially was negative and then increased in a positive direction as the polymerization proceeded and reached the largest positive values after 180 min (α$^{25}_{435}$ +2.9°). Monitoring of the optical rotation was disturbed ca. 200 min after initiation polymerization because the solution of polymerization became dark red. From this value (α$^{25}_{435}$ +2.9°) the specific rotation ([α]$^{25}_{435}$) of the polymer, assuming complete polymerization, was roughly estimated as +632°. But the poly(CHMI) purified by reprecipitation showed [α]$^{25}_{435}$ +61.8° (*c* = 1.0 g dL^{-1}; *l* = 10 cm in toluene). It is considered that the high specific rotation of poly(CHMI) polymerized in a quartz cell could be attributed to conformations such as helical structures under the conditions of anionic polymerizations. But the reprecipitated poly(CHMI) may relax to a random conformation. A similar phenomenon was observed by Cram et al. in the asymmetric anionic polymerization of methyl methacrylate.[13]

The polymerization conditions to obtain poly(RMI) with larger specific rotations were as follows: (i) the molar ratio of R′box and *n*-BuLi = 1.2/1.0, (ii) the concentration of *n*-BuLi−R′box complex = 10 mol %, and (iii) nonpolar solvents such as toluene.

Structure of Poly(CHMI). The (+)-poly(CHMI) (run 1 in Table 1) and (−)-poly(CHMI) (run 13 in Table 1) were analyzed by GPC equipped with UV (A) and polarimetric detectors (B) (Figure 4). In the GPC curves of the poly(CHMI) initiated by *n*-BuLi−(*S,S*)-Bnbox by UV detection (A-1), the polymer included small amounts of high molecular weight fractions, and the peaks appeared in the same region as that by polarimetric detection (B-1). This suggests that whole polymers including both high and low molecular weight parts are optically active. However, more data are necessary to explain two molecular weight fractions. While the GPC curves (A-2, B-2) of the poly(CHMI) initiated by *n*-BuLi−(−)-Sp exhibited approximately simple peaks. The GPC

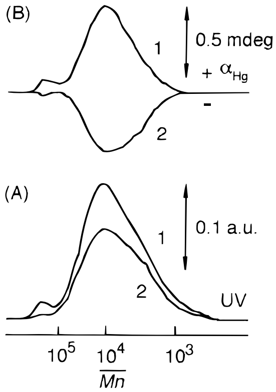


Figure 4. GPC curves of poly(CHMI). The top chromatogram was obtained by polarimetric detection (α_{Hg}) and the bottom by UV detection (254 nm): (1) initiated by *n*-BuLi−(*S*,*S*)-Bnbox (run 1 in Table 1); (2) initiated by *n*-BuLi−(−)-Sp (run 13 in Table 1).

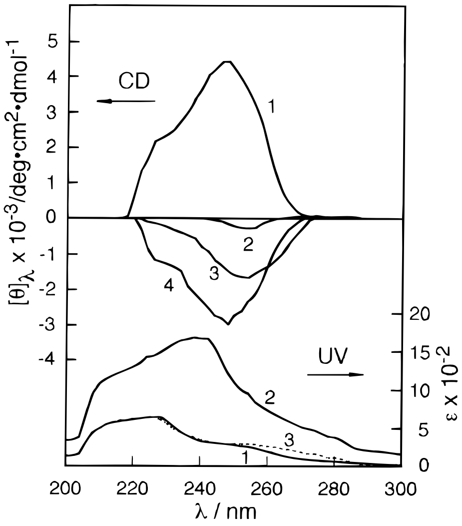


Figure 5. CD and UV spectra for poly(RMI): (1) poly(CHMI), run 1 in Table 1; (2) poly(PhMI), run 8 in Table 1; (3) poly(TBMI), run 12 in Table 1; (4) poly(CHMI) initiated by *n*-BuLi−(−)-Sp, run 13 in Table 1.

curve (B-2) by polarimetric detection indicated a negative sign in the whole region.

Typical CD and UV spectra of the polymers are shown in Figure 5. The CD peaks of the poly(RMI) initiated by R′box appeared at about 250 nm, due to the n → π^* electric transition of carbonyl groups in the maleimide ring. The spectral patterns of the poly(CHMI) obtained with *n*-BuLi−(*S*,*S*)-Bnbox and *n*-BuLi−(−)-Sp were nearly mirror images each other. These results suggest that the ratios of existence of (*S*,*S*) or (*R*,*R*) stereogenic centers at the main chain of poly(CHMI) are opposite. The optical rotations of poly(RMI) were ascribed to the polymer main chain chirality induced by lithium−chiral R′box complexes.

RMI can yield two trans-openings of a double bond to produce stereogenicity (*S*,*S*) and (*R*,*R*).[14] Figure 6 shows ^{13}C NMR spectra of the polymers obtained with (a) chiral oxazoline *n*-BuLi−(*S*,*S*)-Bnbox and (b) *n*-BuLi−(−)-Sp. According to ^{13}C NMR studies on poly(CHMI) and model compounds of poly(CHMI), i.e., *trans*- and *cis*-3,4-dimethyl-*N*-cyclohexylsuccinimide (CHDMSI), methine carbons due to the main chain of poly(CHMI) showed peaks at about 40 and 43 ppm assigned to trans configurations, namely, threo-diisotactic and threo-disyndiotactic structures, respectively.[10] Threo-diisotactic and threo-disyndiotactic structures of poly(CHMI) obtained with anionic initiators were assigned by comparing with the polymer initiated by AIBN. The structure of poly(CHMI) obtained with radical initiator could be threo-disyndiotactic configuration because of the smallest steric repulsion. The signal based on the poly(CHMI) main chain appeared only at 43.5 ppm in the ^{13}C NMR spectrum.[15] The peak at the lower magnetic field of about 43 ppm for the poly(CHMI) initiated by the *n*-BuLi−(*S,S*)-Bnbox complex was assigned to threo-disyndiotactic structures. Another peak at the higher magnetic field of about 40 ppm was assigned to the threo-diisotactic structure. The ^{13}C NMR spectrum of the poly(CHMI) initiated by *n*-BuLi−(*S*,*S*)-Bnbox was similar to that by *n*-BuLi−(−)-Sp (run 13 in Table 1). But chiroptical properties (the sign and intensity of CD spectra, GPC curves by polarimetric detector and specific rotations) for the poly(CHMI) initiated by *n*-BuLi−(*S*,*S*)-Bnbox (run 1 in Table 1) were extremely different from those for the poly(CHMI) initiated by *n*-BuLi−(−)-Sp (run 13 in Table 1).

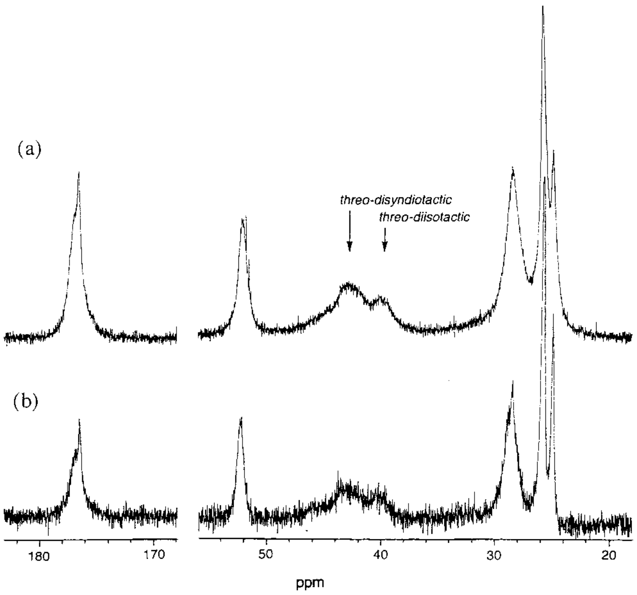


Figure 6. ^{13}C NMR spectra for poly(CHMI) obtained with (a) *n*-BuLi−(*S*,*S*)-Bnbox and (b) *n*-BuLi−(−)-Sp in $CDCl_3$.

To clarify the influence of temperature effects on the specific rotation of optically active poly(CHMI), the specific rotations of poly(CHMI) ($[\alpha]_{435}^{25} = +111.4°$, run 1 in Table 1) obtained with *n*-BuLi−(*S*,*S*)-Bnbox were measured in chloroform at the several temperatures. Figure 7 shows the results of the change of specific rotation at various temperatures. The magnitude of specific rotation slightly decreased with an increase in temperatures. But the value of the temperature coefficient ($\Delta[\alpha]/\Delta T$) was very small (−0.22). It is considered that the poly(CHMI) scarcely contains helical conformations. If the polymers contained helical structures such as poly(isocyanate),[16−20] the values of the specific rotation should remarkably vary with temperatures. The authors reported that homopolymerizations of optically active (*R*)-(+)-α-methylbenzylmaleimide produced the polymers without helical fragments in the main chain because of the very small value of the temperature coefficient ($\Delta[\alpha]/\Delta T$) (ca. 0.1).[21] In addition, the optical rotations of the polymer were much smaller than those of the polymer having a helical conformation such as poly(triphenylmethyl methacry-

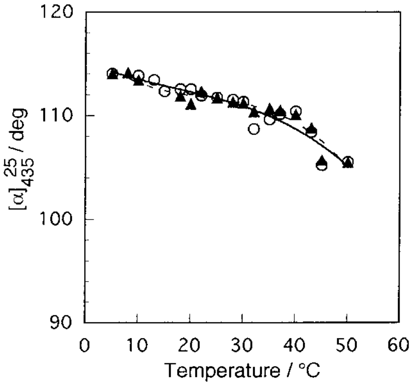


Figure 7. Effects of measurement temperature on specific rotation ($[\alpha]^{25}_{435}$) of poly(CHMI) (run 1 in Table 1) in $CHCl_3$: (○) heating (full line); (▲) cooling (dashed line).

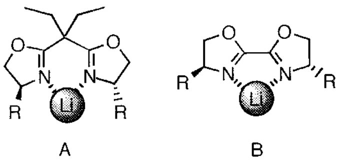


Figure 8. Bis(oxazoline)−lithium complex structures: (A) methylene-bridged bis(oxazoline); (B) directly coupled bis(oxazoline).

late).[1] Judging from these results, the optical rotations of poly(RMI) are practically ascribed to not *completely* helical structures but excessive chiral centers of (*R*,*R*) or (*S*,*S*) based on threo-diisotactic structures in the main chain. The sign and the magnitude of the specific rotation of the polymer were attributed to different structures of chiral ligands.

The authors reported that anionic homopolymerizations of RMI obtained with *n*-BuLi−directly coupled bis(oxazoline)s and fluorenyllithium−directly coupled bis(oxazoline)s complexes gave poly(RMI) with low optical activity ($[\alpha]^{25}_{435}$ −2.9° to −8.2°).[10] The bis(oxazoline)s can form a conformationally rigid framework consisting of a metal chelate with nitrogen atoms and impose a chiral environment at the growing end of the polymer. The size of the chelate consisting of bis(oxazoline)−Li complex is one important factor since it can control orientation of the substituents on two oxazoline rings around the metal ion. As bite angles of the bidentate bis(oxazoline) ligand consisting of a six-membered chelate in A (Figure 8) are larger than those of a five-membered chelate in B, R groups can approach in closer proximity to the metal ion. Since the methylene-bridged bis(oxazoline)s were capable of building better asymmetric fields at the polymer growth ends, chirality could be induced to the polymer main chain. Thus, the obtained polymers showed high specific rotations.

Conclusions

(1) Anionic homopolymerizations of RMI with *n*-BuLi−four chiral methylene-bridged bis(oxazoline) complex systems provided optically active polymers with high specific rotations (poly(CHMI), $[\alpha]^{25}_{435} = +111.4°$).

(2) The specific rotations of the polymers were influenced by solvent, concentrations of initiator, and [R′box]/[*n*-BuLi] ratios. The polymerization conditions to obtain the poly(RMI) with the highest specific rotation were as follows: (i) concentration of initiator 10 mol %, (ii) [R′box]/[*n*-BuLi] = 1.2/1.0, and (iii) nonpolar solvent as toluene.

(3) The main-chain signals of the polymer exhibited two peaks at 40 and 43 ppm in the ^{13}C NMR spectra. The peak at higher magnetic field was assigned to threo-diisotactic and the other to threo-disyndiotactic structure.

(4) The optical rotations of poly(RMI) are practically attributable to excessive chiral centers of (*R*,*R*) or (*S*,*S*) in the main chain.

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