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ORIGINAL ARTICLE

Asymmetric anionic polymerization of maleimide bearing an *N*-4′-benzo 15-crown-5 ether with an organometal/chiral ligand complex

Motohisa Azechi, Kazuhiro Yamabuki, Kenjiro Onimura and Tsutomu Oishi

Asymmetric anionic homopolymerization of *N*-4′-benzo 15-crown-5 maleimide (B15C5MI) was carried out with a chiral anionic initiator consisting of organometal (*n*-butyllithium, diethylzinc (Et$_2$Zn)) and chiral ligand ((–)-sparteine ((–)-Sp), (*S, S*)-(1-ethylpropylidene)-bis(4-benzyl-2-oxazoline) ((*S, S*)-Bnbox)) to obtain optically active polymers. The polymer obtained with the chiral ligand had an optical rotation, suggesting that asymmetric induction occurred on the main chain of the polymer. Poly(B15C5MI) obtained with Et$_2$Zn/(*S, S*)-Bnbox in tetrahydrofuran showed the highest specific rotation of −64.1°. The chiroptical properties and structures of the polymers obtained were analyzed by circular dichroism, ultraviolet, nuclear magnetic resonance and gel permeation chromatography measurements. The effects of adding (*R*)-cyclohexylethylamine to the obtained poly(B15C5MI) were investigated.
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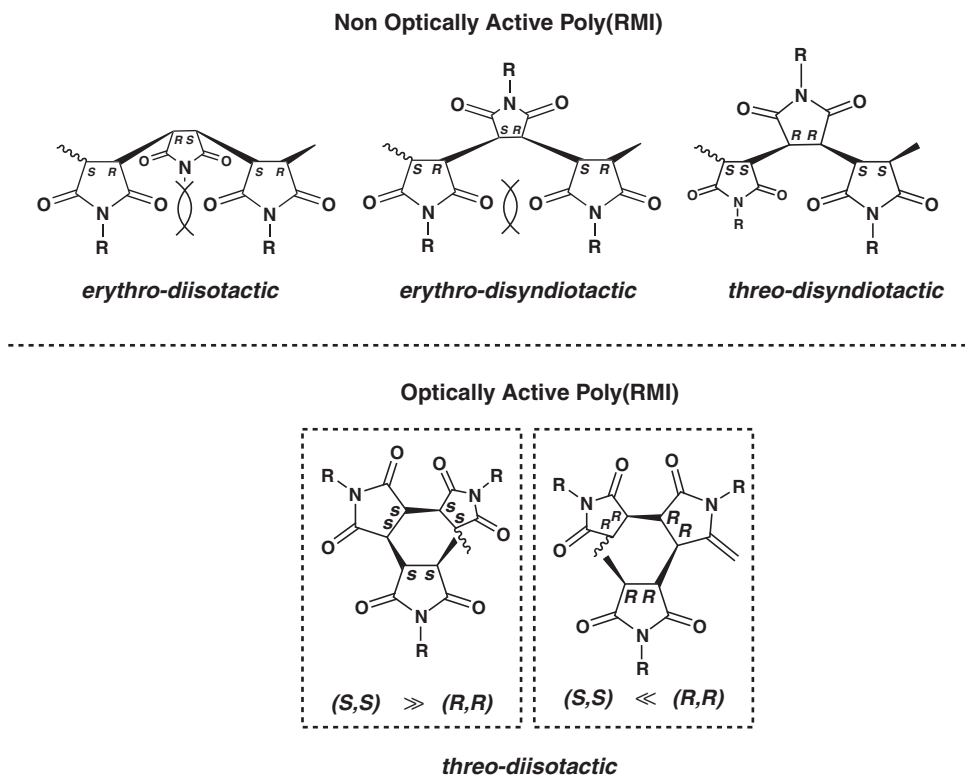
INTRODUCTION

In nature, macromolecules such as peptides, nucleic acids and polysaccharides have highly ordered structures, mostly forming left- or right-handed helicies. These structures are optically active and are crucial for the special functions of these molecules such as molecular recognition and catalysis. To artificially form a one-handed helical structure, it is necessary to synthesize an optically active polymer by asymmetric polymerization.[1–4]

We have previously investigated asymmetric anionic polymerizations of *N*-substituted maleimides (RMI) with organometal/chiral ligand complexes.[5–15] As RMI consists of a 1,2-disubstituted structure, poly(RMI) can be presumed to produce four types of structures: *threo-diisotactic*, *threo-disyndiotactic*, *erythro-diisotactic* and *erythro-disyndiotactic* (Scheme 1). *Erythro-diisotactic* and *erythro-disyndiotactic* structures cannot be formed with *cis*-additional reaction because of steric hindrance among monomeric units due to carbonyl groups in imide rings.[16] *Trans*-additional structures, that is, *threo-diisotactic* and *threo-disyndiotactic* structures, can be formed in the polymerization of RMI. *Threo-disyndiotactic* structures show no optical activity because (*S, S*)- and (*R, R*)-configurational pairs exist at equivalent levels in the polymer main chains. Poly(RMI) with a *threo-diisotactic* structure can show optical activity when one of the asymmetric carbon pairs in the monomeric unit exists in excess. Furthermore, the high continuity of the same configurational pair ((*S, S*) or (*R, R*)) in the *threo-diisotactic* structures may allow for a helical conformation. 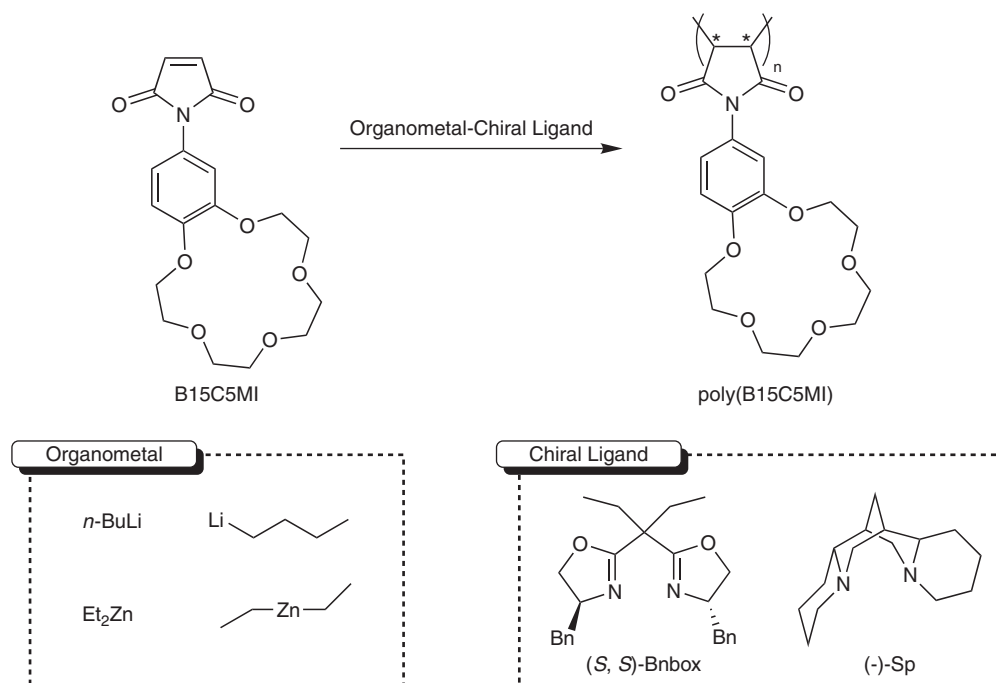Asymmetric induction of the polymer main chains was affected to a large extent by *N*-substituents, polymerization solvents, polymerization temperatures and other polymerization conditions. In our previous studies, we systematically investigated the polymerization of RMIs with various *N*-substituents. The RMI with a 1-naphthyl or (*S*)-methylbenzyl group as an *N*-substituent showed the highest specific optical rotation in chloroform ([α]$_{435}$=+762.3°, +551.7°).

Crown ether is a cyclic ether derivative and has attracted a great deal of attention as a host molecule that can incorporate metal cations (M$^+$) and alkyl ammonium salts (R-NH$_3^+$) such as amines and amino acids as guest molecules. These complexes are formed by dipole–dipole interactions between crown ether and cations. Recently, polymers bearing various crown ethers were investigated. For example, Yashima[17–21] and Kakuchi *et al.*[22–25] reported that poly(phenylacetylene) and poly(isocyanate) bearing aza crown ether or benzo crown ether as host molecules induced a one-handed helical structure on addition of alkyl ammonium salts, amino alcohols and chiral amino acids. However, there have been no reports on the asymmetric polymerization of maleimide bearing crown ether derivatives.

In this study, maleimide bearing *N*-4′-benzo 15-crown-5 ether (B15C5MI) was synthesized from maleic anhydride and the corresponding amine. Asymmetric anionic polymerizations of B15C5MI were performed with an organometal and a chiral ligand complex as initiators (Scheme 2). Random or block copolymerizations of B15C5MI were also carried out with *N*-1-naphthylmaleimide

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Non Optically Active Poly(RMI)

erythro-diisotactic   *erythro-disyndiotactic*   *threo-disyndiotactic*

Optically Active Poly(RMI)

(S,S) ≫ *(R,R)*   *(S,S)* ≪ *(R,R)*

threo-diisotactic

Scheme 1 Structure of poly(RMI).

Organometal-Chiral Ligand

B15C5MI   poly(B15C5MI)

Organometal

n-BuLi   Li

Et$_2$Zn   Zn
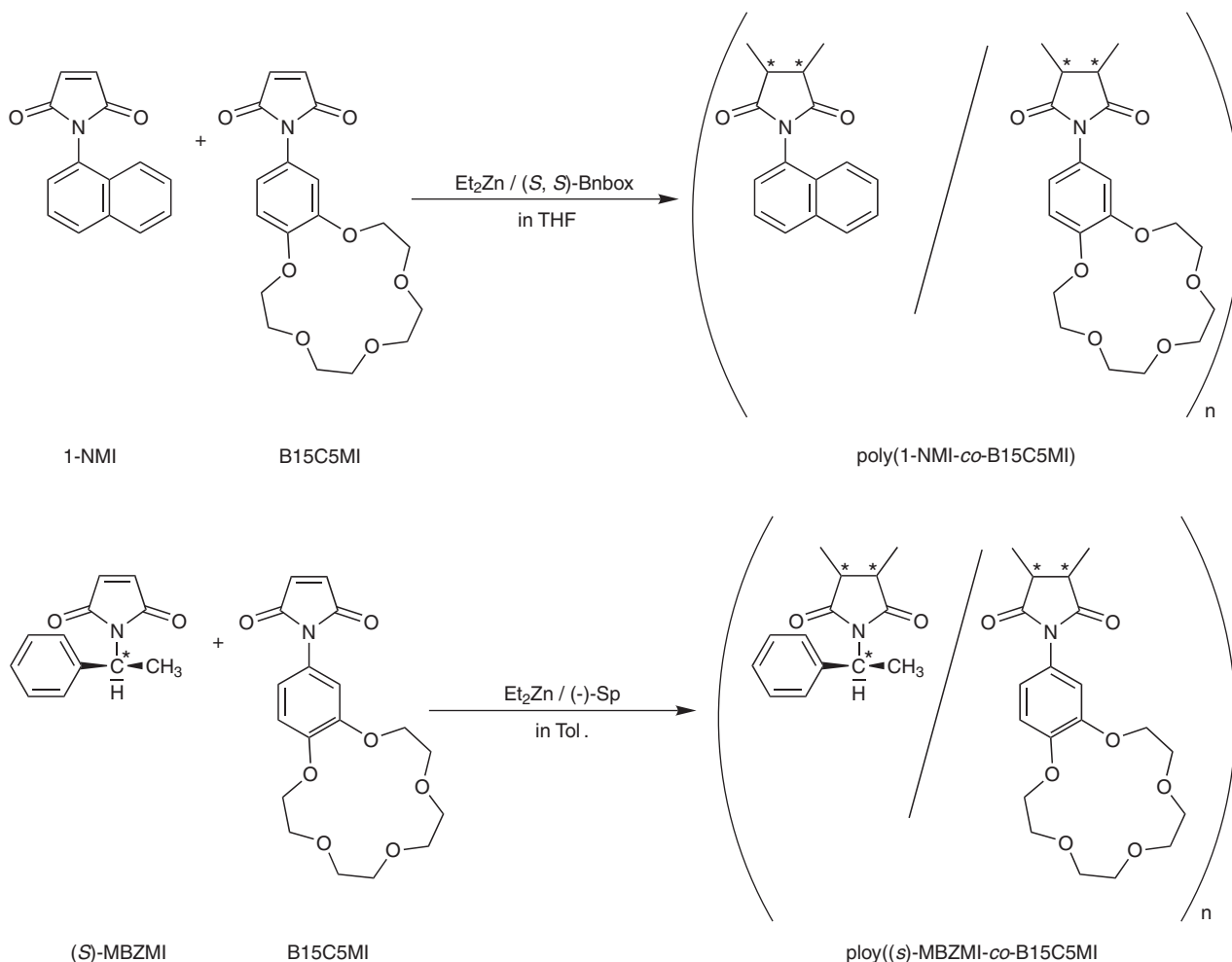
Chiral Ligand

(*S, S*)-Bnbox   (-)-Sp

Scheme 2 Asymmetric anionic polymerization of B15C5MI.

(1-NMI) or (*S*)-(−)-methylbenzylmaleimide ((*S*)-MBZMI) (Scheme 3). Chiroptical properties and structures of the polymers were investigated by ^{13}C nuclear magnetic resonance (NMR), gel permeation chromatography and circular dichroism (CD) measurements.

EXPERIMENTAL PROCEDURE

Materials

Scheme 3 Asymmetric anionic copolymerization of B15C5MI with 1-NMI and (*S*)-MBZMI.

(Kanto Chemical, Tokyo, Japan, in *n*-hexane, 1.55 mol l^{-1}) was used as purchased. Diethylzinc (Et$_2$Zn) (in *n*-hexane, 1.04 mol l^{-1}) was kindly supplied by Tosoh Corp. (Tokyo, Japan). (−)-Sparteine ((−)-Sp) (Tokyo Chemical Industry, Tokyo, Japan) was used after purification by distillation under reduced pressure ([α]$_{435}$=−10.3°, *c*=1.0 g per 100 ml, *l*=10 cm, tetrahydro-furan (THF)). (*S*, *S*)-(1-Ethylpropylidene)-bis(4-benzyl-2-oxazoline) ((*S*, *S*)-Bnbox) was prepared as reported previously ([α]$_{435}$=−123.5°, *c*=1.0 g per 100 ml, *l*=10 cm, THF).[26–28] 2, 2′-Azobisisobutylonitrile (Ishizu Seiyaku, Osaka, Japan) was used after recrystallization from methanol.

Monomer synthesis

The synthetic route of the monomer is shown in Scheme 4.

4′-Aminobenzo 15-crown-5 ether

4′-Nitrobenzo 15-crown-5 ether (Tokyo Chemical Industry, 5.1 g, 16.3 mmol) was dissolved in ethyl acetate (400 ml) in a Schlenk reaction tube, and then 10 wt % palladium-activated carbon (Wako Pure Chemical Industries, Osaka, Japan; 0.51 g) was added. The solution was evacuated by aspirator and replaced by hydrogen gas. After stirring under a hydrogen atmosphere for 1 week, the reaction tube was evacuated by aspirator, replaced by nitrogen gas and then filtered to remove palladium-activated carbon. The filtrate was concentrated under reduced pressure to yield a red–purple liquid (yield: 4.6 g (99.4 %), ^{1}H NMR (δ in p.p.m. from tetramethylsilane in CDCl$_3$): 3.75 (s, 8H, other -O-CH$_2$-), 3.84-3.93 (m, 4H, Ph-O-CH$_2$-*CH$_2$*-), 4.03-4.12 (m, 4H, Ph-O-*CH$_2$*-CH$_2$-), 6.21 (dd, 1H, Ar), 6.28 (d, 1H, Ar), 6.74 (d, 1H, Ar)).

N-4′-Benzo 15-crown-5 maleamic acid

A solution of 4′-Aminobenzo 15-crown-5 ether (4.6 g, 16.2 mmol) in dry THF (100 ml) was added dropwise to a solution of maleic anhydride (1.9 g, 19.4 mmol) in dry THF (100 ml) at room temperature, and then the mixture was stirred for 18 h. Yellow precipitates were collected by suction filtration to obtain *N*-4′-Benzo 15-crown-5 maleamic acid. *N*-4′-Benzo 15-crown-5 maleamic acid was dried under vacuum at room temperature for 2 days (yield: 5.1 g (82.7%), ^{1}H NMR (δ in p.p.m. from tetramethylsilane in CDCl$_3$): 3.72 (s, 8H, other -O-CH$_2$-), 3.82-3.92 (m, 4H, Ph-O-CH$_2$-*CH$_2$*-), 3.98-4.10 (m, 4H, Ph-O-*CH$_2$*-CH$_2$-), 6.40 (d, 1H, -CH=*CH*-CONH-), 6.44 (d, 1H, -CH=*CH*-COOH), 6.77 (d, 1H, Ar), 6.98 (dd, 1H, Ar), 7.29 (d, 1H, Ar), 9.24 (s, 1H, -CH=CH-CO*NH*-)).

B15C5MI

Acetic anhydride (30 ml) and anhydrous sodium acetate (0.13 g, 1.3 mmol) were combined in a flask. *N*-4′-Benzo 15-crown-5 maleamic acid (5.1 g, 13.4 mmol) was added, and the resulting suspension was dissolved by stirring and heating for 1 h. The reaction mixture was cooled almost to room temperature and then poured into a mixture of ice water (300 ml) and dichloromethane (200 ml). After acetic acid was neutralized with NaHCO$_3$, the precipitated product was removed by suction filtration. The filtrate was extracted three times with dichloromethane (200 ml×3) and the organic phase was washed with saturated NaHCO$_3$aq (200 ml) and water (200 ml×3) in sequence and then dried over Na$_2$SO$_4$. The organic phase was concentrated under reduced pressure to yield a yellow solid (yield: 3.0 g
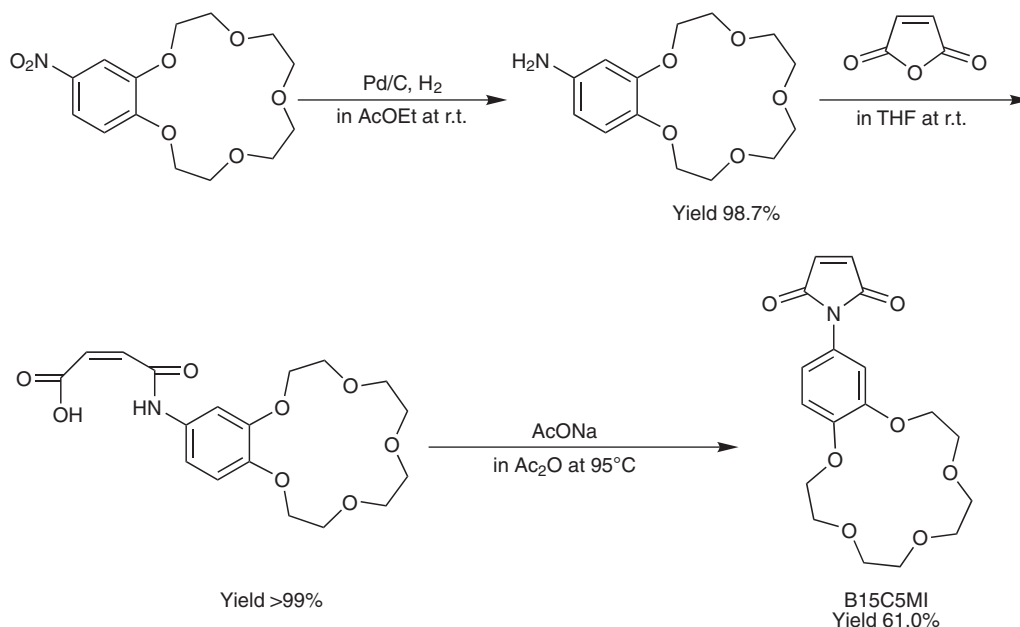
Scheme 4 Synthesis of B15C5MI.

(61.0%), m.p.: 149.5–150.5 °C, ^{1}H NMR (δ in p.p.m. from tetramethylsilane in CDCl$_3$): 3.70–3.80 (m, 8H, other -O-CH$_2$-), 3.85–3.95 (m, 4H, Ph-O-CH$_2$-CH_2-), 4.10-4.20 (m, 4H, Ph-O-CH_2-CH$_2$-), 6.80 (s, 2H, -CH=CH-), 6.88 (d, 1H, Ar), 6.90 (d, 1H, Ar), 6.95 (d, 1H, Ar), ^{13}C NMR (δ in p.p.m. from tetramethylsilane in CDCl$_3$): 69.5–69.1 (Ph-O-CH$_2$-CH_2-), 71.1–70.5 (other -O-CH$_2$-), 77.5–76.5 (Ph-O-CH_2-CH$_2$-), 112.4 (Ar), 113.9 (Ar), 119.2 (Ar), 124.3 (Ar), 134.1 (-CH=CH-), 148.9 (Ar), 149.3 (Ar), 169.7 (C=O)).

N-1-Naphthylmaleimide
1-NMI was synthesized from maleic anhydride and 1-naphthylamine according to a previously reported method.[29,30]

(S)-(–)-N-α-Methylbenzylmaleimide
(S)-MBZMI was synthesized from maleic anhydride and (S)-(-)-1-phenylethyl-amine according to a previously reported method.[29]

Anionic homopolymerization
Monomer and chiral ligand were placed in a Schlenk reaction tube and a pear-shaped flask, respectively. The flasks were evacuated by vacuum pump and then replaced by nitrogen gas. Polymerization solvent was added to each vessel by a syringe under nitrogen atmosphere. Organometal (n-BuLi or Et$_2$Zn) in an n-hexane solution was introduced into the chiral ligand solution with a syringe to prepare the initiator complex. The monomer solution was maintained at the polymerization temperature. The complex solution was added by a cannula in a stream of nitrogen to initiate polymerization. Polymerization without chiral ligand was initiated by directly adding organometal in an n-hexane solution to a monomer solution with a syringe. After the prescribed time (24 or 72 h), polymerization was terminated with a small amount of methanol containing two drops of 6 N aqueous hydrochloric acid. The polymerization solution was concentrated. Dichloromethane was added to the residue, and the solution was washed using 0.1 N aqueous hydrochloric acid. After the organic layer was concentrated, the residue was purified by three cycles of reprecipitation from THF-methanol. The pure polymers were dried in vacuo at room temperature for 2 days.

Anionic random copolymerization
The mixtures of B15C5MI and 1-NMI or (S)-MBZMI were placed in a Schlenk reaction tube. The tube was evacuated by vacuum pump and then replaced by nitrogen gas. Polymerization solvent was added to each vessel using a syringe under nitrogen atmosphere. From that point, the reaction proceeded in the same manner as the homopolymerization.

Anionic block copolymerization
After 1-NMI or (S)-MBZMI was homopolymerized with the organometal/chiral ligand complex for 6 h, a B15C5MI monomer solution was added to the solution and block copolymerization was initiated.

Radical polymerization
Radical polymerization was conducted in a sealed glass tube using 2, 2'-azobisisobutylonitrile as an initiator under nitrogen atmosphere. All reagents were added to the glass tube, and the mixture was degassed three times before sealing the tube under vacuum. Polymerization was conducted in an oil bath regulated at 60 °C for 24 h. The polymerization was terminated by cooling the reaction mixture to 0 °C. The obtained polymer was purified in a method similar to that of anionic polymerization.

Measurement
Specific optical rotations were measured in THF or chloroform at 25 °C using a quartz cell (l=5 cm) by a JASCO DIP-1030 polarimeter (JASCO, Tokyo, Japan). CD and ultraviolet (UV) spectra were recorded in THF or chloroform at 25 °C using a quartz cell with a path length of 0.1 mm by a JASCO J-805 spectro-polarimeter. The number-average molecular weights (M_ns) of the polymers were measured with gel permeation chromatography with a Shimadzu LC-10A instrument (Shimadzu Corp., Kyoto, Japan) equipped with an SPD-10A UV detector (Shimadzu Corp.), a JASCO OR-990 polarimetric detector and a C-R7Ae plus data processor. THF or chloroform was used as the eluent. The molecular weight calibration curve was obtained with polystyrene standards. ^{1}H and ^{13}C NMR spectra were obtained by JEOL-EX270 (JEOL, Tokyo, Japan).

RESULTS AND DISCUSSION
Homopolymerization of B15C5MI
Radical or asymmetric anionic polymerizations of B15C5MI were performed under several conditions. Table 1 summarizes the results of these polymerizations of B15C5MI. When only n-BuLi was used, the yield of poly(B15C5MI) obtained in toluene (Run 2 in Table 1) was lower than that in THF (Run 3 in Table 1), indicating that the polarity

Table 1 Polymerizations of B15C5MI[a]

Run	Initiator	Solvent (ml)	Temp. (°C)	Time (h)	Yield[b] (%)	$M_n{}^c \times 10^{-3}$	$M_w/M_n{}^c$	$[\alpha]_{435}^{25\,d}$ (deg.)
1	*n*-BuLi[e]	THF (60)	0	24	74.0[f]	0.5	1.0	—
2	*n*-BuLi[g]	Tol. (180)	0	24	3.1	1.9	2.6	—
3	*n*-BuLi[g]	THF (60)	0	24	76.7	2.3	2.5	—
4	*n*-BuLi/(−)-Sp (1/1.2)[g]	THF (60)	0	24	99>	ND	ND	20.1
5	*n*-BuLi/(*S*, *S*)-Bnbox (1/1.2)[g]	THF (60)	0	24	99>	5.4	2.8	22.6
6	Et₂Zn[e]	THF (60)	0	72	Trace	—	—	—
7	Et₂Zn/(−)-Sp (1/1.2)[e]	THF (60)	0	72	Trace	—	—	—
8	Et₂Zn/(−)-Sp (1/1.2)[g]	THF (60)	0	72	37.7	1.5	1.1	−24.2
9	Et₂Zn/(*S*, *S*)-Bnbox (1/0.5)[g]	THF (60)	0	72	21.1	2.0	1.1	64.1[h]
10	AIBN[i]	THF (12)	60	24	3.3	2.0	1.8	—
11	AIBN[i]	Tol. (24)	60	24	76.4	7.4	3.1	—

Abbreviations: AIBN, 2, 2'-azobisisobutylonitrile; ND, not determined; THF, tetrahydrofuran; Tol., toluene.
[a]0.3 g.
[b]Methanol-insoluble part.
[c]By gel permeation chromatography (CHCl₃).
[d]*c*=0.1 g per 100 ml, *l*=5 cm, in CHCl₃.
[e][Organometal]/[monomer]=0.1.
[f]*n*-Hexane-insoluble part.
[g][Organometal]/[monomer]=0.2.
[h]*c*=0.05 g per 100 ml, *l*=5 cm, in CHCl₃.
[i][AIBN]/[monomer]=0.1.

of the solvent significantly affects the yield of the polymerization of B15C5MI with *n*-BuLi. A similar phenomenon was found for the polymerizations of 1-NMI.[10] When the concentration of the initiator solution was 10 mol%, polymerization did not proceed, but a concentration of 20 mol% yielded a polymer. The yields of the methanol-insoluble part of poly(B15C5MI)s obtained with *n*-BuLi/ligand complexes were higher than those with Et₂Zn/ligand complexes. This may result from the differences in electronegativity and valence between *n*-BuLi and Et₂Zn, because the occurrence of anionic polymerization is generally influenced by the electronegativity of the metal. The M_n and yields of polymers obtained with the organometal/ligand complexes were higher than those obtained with only organometal. These results confirmed that the catalytic activity of the organometal/ligand complex was higher than that of organometal only. That is, the coordination of the organometal by the ligand would contribute to the enhancement of catalytic activity.[31] To investigate the interaction between crown ether and lithium or zinc in the polymerization, the ¹H NMR spectra of the monomer solution added to lithium chloride or zinc chloride were measured. No interaction was observed between crown ether and metal in the ¹H NMR spectra. Therefore, it can be concluded that lithium and zinc did not affect the polymerization of maleimide with crown ether. Poly(B15C5MI) was synthesized with M_n=1500–5400 by anionic polymerization. Previous papers reported M_n values from 1600 to 3400 of maleimide polymers with bulky substituents (*N*-substituted: 9-fluorenyl, diphenylmethyl, triphenyl-methyl and cyclododecyl),[6,7] similar to the molecular weights reported here for poly(B15C5MI)s. Therefore, these results suggest that the bulky substituent affected the polymerization ability of maleimide.

Optical properties of poly(B15C5MI)
All polymers obtained with organometal/chiral ligand complexes were optically active. The poly(B15C5MI) initiated by the Et₂Zn/(*S*, *S*)-Bnbox complex showed the highest specific optical rotation of the obtained polymers. The absolute values of the specific optical rotation of poly(B15C5MI)s formed with Et₂Zn/ligand complexes were higher than those with *n*-BuLi/ligand complexes. Polymerization was slow when Et₂Zn was used as an initiator, which could indicate that the stereoregularity of the polymer was improved because the growth end

attacked a monomer selectively. The specific optical rotations of the polymers synthesized with Et₂Zn/(−)-Sp and Et₂Zn/(*S*, *S*)-Bnbox initiators were negative and positive, respectively. In our previous study, poly(*N*-phenylmaleimide)s with a phenyl group as the *N*-substituent initiated with Et₂Zn/(−)-Sp had a negative specific optical rotation, and that initiated with Et₂Zn/(*S*, *S*)-Bnbox had a positive specific optical rotation.[31] Therefore, the polymerization mechanism of poly(B15C5MI)s tended to be similar to that when poly(*N*-phenyl maleimide) was used as the chiral ligand.

Structures of poly(B15C5MI)
¹³C NMR spectra of poly(B15C5MI) obtained with various initiators were measured. The methine carbons of the main chain with a phenyl group as the *N*-substituent and carbonyl groups of the maleimide ring showed peaks at about 38–48, 110–150 and 176 p.p.m., respectively. According to the ¹³C NMR spectra of poly(CHMI) obtained with anionic initiators, the methine carbons of the main chain exhibited two peaks at 40 and 43 p.p.m. assigned to *threo-diisotactic* and *threo-disyndiotactic* structures, respectively.[32] The *threo-diisotactic* and *threo-disyndiotactic* structures of the poly(B15C5MI)s obtained by anionic polymerization were indistinguishable by the ¹³C NMR spectra, but the peaks of those obtained by radical polymerization appeared around 39 and 42 p.p.m., respectively. The content of the *threo-diisotactic* structure in the polymer obtained by radical polymerization was higher than that obtained by anionic polymerization.

Copolymerization of 1-NMI and B15C5MI
In our previous report,[9,10] homopolymerizations of 1-NMI were performed with an organometal and a chiral ligand. As a result, poly(1-NMI) with the specific optical rotation of 762.3° was obtained with Et₂Zn/(*S*, *S*)-Bnbox in THF at room temperature for 72 h. This polymer showed the highest specific optical rotation among all maleimide polymers. Accordingly, asymmetric anionic copolymerizations of B15C5MI and 1-NMI were performed with Et₂Zn/(*S*, *S*)-Bnbox in THF at room temperature for 72 h. This polymerization condition is the same as the poly(1-NMI) condition that yielded the highest specific optical rotation. Table 2 shows the results of copolymerizations of B15C5MI and 1-NMI. In the case of both the random

Table 2 Asymmetric anionic random copolymerizations or block copolymerizatons of 1-NMI (*M₁*) and B15C5MI (*M₂*)[a] with Et₂Zn/(*S*, *S*)-Bnbox (1.0/0.5)[b] in THF at r.t. for 72 h.

Run	Solvent (ml)	M_1 in feed monomer (mol%)	Yield[c] (%)	M_1 in copolymer[d] (mol%)	M_n[e] $\times 10^{-3}$	M_w/ M_n[e]	$[\alpha]_{435}^{25}$[f] (deg.)
1[g]	12	90	4.0	78	1.7	1.7	−7.9
2[g]	12	95	99>	87	2.5	1.7	20.2
3[h]	16	90	73.3	86	2.0	1.5	15.6[i]
4[h]	10	95	96.5	98	3.1	1.9	46.1[i]

Abbreviations: r.t., room temperature; THF, tetrahydrofuran.
[a]M_1+M_2=0.5 g.
[b][Organometal]/[monomer]=0.1.
[c]Methanol-insoluble part.
[d]Determined by ¹H NMR.
[e]By gel permeation chromatography (THF).
[f]c=0.1 g per 100 ml, l=1 cm, in THF.
[g]By random copolymerization.
[h]By block copolymerization.
[i]c=0.1 g per 100 ml, l=5 cm, in THF.

copolymer and the block copolymer, a higher copolymer yield was obtained when 1-NMI was 95 mol% in the feed monomer (Runs 2 and 4 in Table 2). These results suggest that steric hindrance by a bulky benzocrown ether group of B15C5MI may have affected the copolymerization ability. Comparing block copolymers with random copolymers, the yields and M_n values of block copolymers (Runs 3 and 4 in Table 2) were higher than those of random copolymers (Runs 1 and 2 in Table 2) under the same conditions. The results of block copolymerizations suggested that 1-NMI was polymerized first because of its high polymerization ability. Therefore, copolymerization ability depends on the polymerization ability of 1-NMI.

Optical properties of poly(1-NMI-*co*-B15C5MI)
The specific optical rotation of the copolymer differed depending on the composition of the copolymer. Increasing the 1-NMI content in the copolymer tended to yield a positive specific optical rotation. In the homopolymerization of 1-NMI, poly(1-NMI) obtained with Et₂Zn/(*S*, *S*)-Bnbox as an initiator had a large positive specific optical rotation (+762.3°).[10] Therefore, these results demonstrate that the optical rotation of the copolymer depends on the 1-NMI content.

Figure 1 shows CD and UV spectra of the copolymers. The UV spectra of the copolymer showed peaks around 210–240 nm and 260–310 nm, which could be attributed to the ^1B_b (long axis) and ^1L_a (short axis) electron transition of naphthalene chromophore in the *N*-substituent, respectively.[9] Split CD spectra were observed around UV absorption bands on the basis of the π–π* transition of the naphthyl group. Split CD spectra of all copolymers showed a positive first and a negative second cotton effect. These results indicate that copolymers possess a positive exciton chirality. In other words, the transition dipole moment of each naphthyl group is arranged clockwise for the (+)-copolymer.[9]

To investigate the dependence of the optical activity of the polymer on molecular weight, gel permeation chromatograms were traced with UV and polarimetric detectors connected in series. Figure 2 shows typical chromatograms. The top and bottom curves were obtained by polarimetric and UV detections, respectively. For the poly(1-NMI-*co*-B15C5MI) obtained by copolymerization of 1-NMI and B15C5MI (Run 4 in Table 2), the polarimetric chromatogram was in good agreement with the UV spectrum, indicating that every poly(1-NMI-*co*-B15C5MI) possessed equivalent optical rotation.
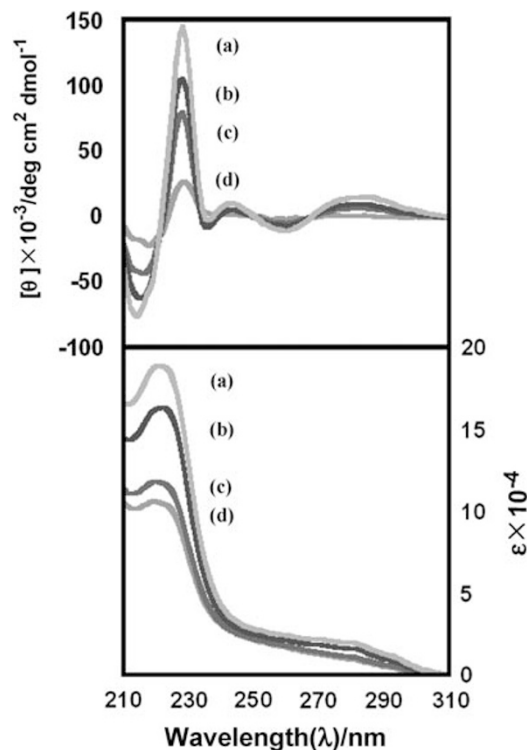
Figure 1 CD and UV spectra of poly(1-NMI-*co*-B15C5MI): (**a**) block copolymer (*M₁*/*M₂*=98:2, $[\alpha]_{435}$=+46.1°, Run 4 in Table 2), (**b**) block copolymer (*M₁*/*M₂*=86:14, $[\alpha]_{435}$=+15.6°, Run 3 in Table 2), (**c**) random copolymer (*M₁*/*M₂*=87:13, $[\alpha]_{435}$=+20.2°, Run 2 in Table 2) and (**d**) random copolymer (*M₁*/*M₂*=78:22, $[\alpha]_{435}$=−7.9°, Run 1 in Table 2).
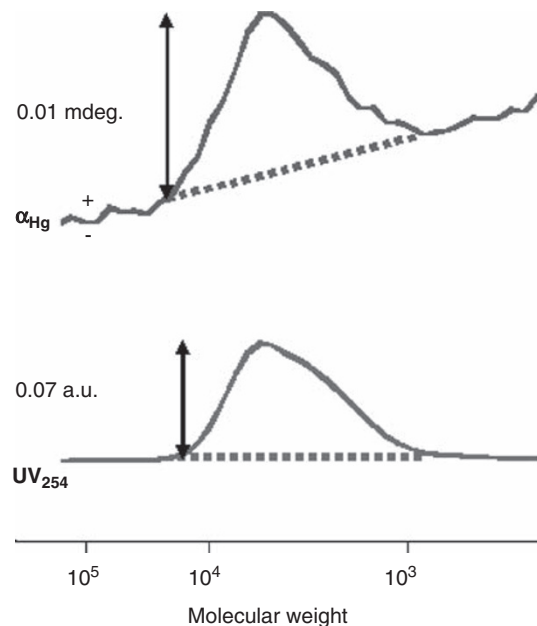
Figure 2 Gel permeation chromatography (GPC) curves for poly(1-NMI-*co*-B15C5MI) obtained by block copolymerization (*M₁*/*M₂*=98/2, $[\alpha]_{435}$=+46.1°, Run 4 in Table 2).
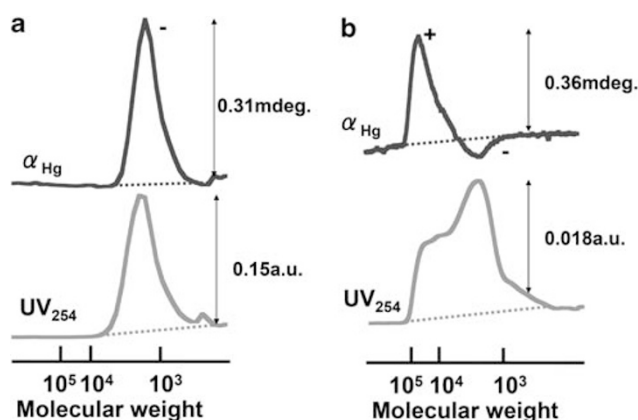
Copolymerization of (*S*)-MBZMI and B15C5MI
In our previous report,[8] homopolymerizations of (*S*)-MBZMI were performed with an organometal and a chiral ligand. As a result, when

Table 3 Asymmetric anionic random copolymerizations or block copolymerizatons of (*S*)-MBZMI (*M*₁) and B15C5MI (*M*₂)ᵃ with Et₂Zn/(−)-Sp (1.0/1.2)ᵇ in toluene at 0 °C for 72 h

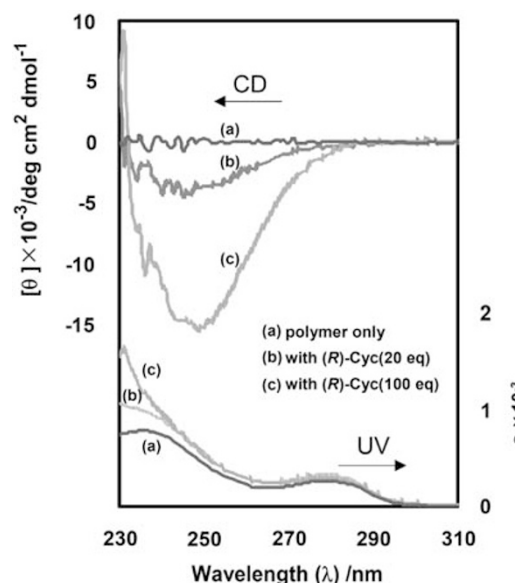| Run	Solvent (ml)	M₁ in feed monomer (mol%)	Yieldᶜ (%)	M₁ in copolymerᵈ (mol%)	M_nᵉ $\times 10^{-3}$	M_w/M_nᵉ	$[\alpha]_{435}^{25f}$ (deg.)
1�g	60	90	4.0	57	0.9	2.3	−20.4
2�g	30	95	6.0	96	1.6	1.4	−20.3ʰ
3ⁱ	60	90	13.2	98	4.8	5.0	154.0
4ⁱ	30	95	71.0	97	12.9	7.0	34.3

Abbreviation: THF, tetrahydrofuran.
ᵃM_1+M_2=0.5 g.
ᵇ[Organometal]/[monomer]=0.1.
ᶜMethanol-insoluble part.
ᵈDetermined by ¹H NMR.
ᵉBy gel permeation chromatography (THF).
ᶠc=0.1 g per 100 ml, l=5 cm, in THF.
ᵍBy random copolymerization
ʰc=0.1 g per 100 ml, l=1 cm, in THF.
ⁱBy block copolymerization.

Figure 3 Gel permeation chromatography (GPC) curves for poly((*S*)-MBZMI-*co*-B15C5MI) obtained by (**a**) random copolymerization (M_1/M_2=96/4, $[\alpha]_{435}$=−20.3°, Run 2 in Table 3) and (**b**) block copolymerization (M_1/M_2=97/3, $[\alpha]_{435}$=+34.3°, Run 4 in Table 3).

Figure 4 CD and UV spectra of poly(B15C5MI) (Run 11 in Table 1) in the presence of (*R*)-Cyc.

only *n*-BuLi and Et₂Zn were used, the yields, M_n values and specific optical rotations of the polymers were 38.9–76.4%, 3100–17 900 and −106.9 to +66.6°, respectively. When a complex of organometal and chiral ligand was used, the same parameters were 54.8–100%, 2600–74 800 and −77.8 to +551.7°, respectively. We found that the chiral ligand improved the polymerization ability and stereoselectivity of the polymer main chain. This polymer showed the highest specific optical rotation (+551.7°) among all polymers synthesized using chiral maleimides. Hence, asymmetric anionic copolymerizations of B15C5MI and (*S*)-MBZMI were performed with Et₂Zn/(−)-Sp in toluene at 0°C for 72 h. These polymerization conditions are the same as those that yielded the highest specific optical rotation of poly((*S*)-MBZMI). Table 3 shows the results of copolymerizations of B15C5MI and (*S*)-MBZMI. These results suggest that the copolymerization of B15C5MI and (*S*)-MBZMI tended to produce yields and M_n values similar to that of B15C5MI and 1-NMI.

Optical properties of poly((*S*)-MBZMI-*co*-B15C5MI)
The random copolymers and block copolymers synthesized here had negative and positive specific rotations, respectively.

Figure 3 displays the chromatograms of poly((*S*)-MBZMI-*co*-B15C5MI). The left chromatogram is from a random copolymer (Figure 3a) and the right chromatogram is from a block copolymer (Figure 3b). For the random copolymer (Run 1 in Table 3), the polarimetric chromatogram corresponded with the UV spectrum. This suggests that every poly((*S*)-MBZMI-*co*-B15C5MI) had an equivalent optical rotation, whereas the block copolymer had a positive optical rotation at a high molecular weight and a negative optical rotation at a low molecular weight. When Et₂Zn/(−)-Sp was used as an initiator, poly((*S*)-MBZMI) had a positive optical rotation[8] and poly(B15C5MI) had a negative optical rotation. The results for the block copolymer could be because the high-molecular-weight copolymers had a high (*S*)-MBZMI content, whereas the low molecular weight had a low (*S*)-MBZMI content.

Effect of adding (*R*)-cyclohexylamine to achiral poly(B15C5MI)
Figure 4 shows the CD and UV spectra of poly(B15C5MI) (Run 11, Table 1) with (*R*)-cyclohexylethylamine ((*R*)-Cyc) in CH₃CN/chloroform (1/1). Increasing the amount of (*R*)-Cyc, the cotton effect due to the carbonyl group of maleimide around 230–250 nm increased significantly. Therefore, these results suggest that the conformational chirality of the polymer main chain was changed by adding (*R*)-Cyc. In addition, to investigate the interaction between the polymer and ammonium salt, the CD and UV spectra of the polymer solution

containing the (R)-Cyc/HClO$_4$ complex were measured in CH$_3$CN/chloroform (1/1). The cotton effects of the polymer did not change when chiral ammonium salt was added. Chiral ammonium salts were previously shown to have an effect on polymers such as poly(phenylacetylene) and poly(isocyanate), which have flexible main chain structures.[17–25] In this study, we investigated the effect of adding a chiral ammonium salt to the maleimide polymer with a rigid main chain structure. Because the main chain structure is rigid, there is no space between the bulky crown ether side chains. Therefore, the chiral ammonium salt may have been unable to coordinate with the crown ether because of the steric hindrance between side chains.

CONCLUSIONS

(1) Optically active poly(B15C5MI)s were obtained by asymmetric anionic polymerizations with organometal/chiral ligand complexes.

(2) The effect of chiral ligand on the polymerization of poly(B15C5MI)s tended to be similar to that of poly(N-phenyl maleimide).

(3) The polymer obtained by radical polymerization was confirmed to have peaks indicating a *threo-diisotactic* structure by ^{13}C NMR spectra.

(4) The polymerization ability and optical rotation of copolymers depended on those of 1-NMI and (S)-MBZMI.

(5) The results of adding of (R)-Cyc to poly(B15C5MI) obtained by radical polymerization, suggest that the conformational chirality of the polymer main chain was changed by adding (R)-Cyc.

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