Asymmetric Polymerization of *N*-ortho- or *para*-Substituted Phenylmaleimide Using Chiral Anionic Initiators

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ABSTRACT: *N*-Phenylmaleimide (PhMI) and its derivatives were polymerized using chiral anionic initiators consisting of diethylzinc (Et₂Zn) and chiral ligands to investigate the effect of the bulkiness, flexibility and polarity of the *ortho*- or *para*-substituents on optical activity of the obtained polymer. The optical activity of the polymer was extremely influenced by *N*-substituents, initiators, and other polymerization conditions. Poly(*N*-2-biphenylmaleimide) (poly(2-BPMI)) formed with Et₂Zn-(–)-2,2'-(1-ethylpropylidene)bis(4-benzyl-2-oxazoline) (Bnbox) showed the highest specific rotation ($[\alpha]_{435}^{25}$) of +164.7°. From ¹³C NMR spectroscopy, optically active poly(2-BPMI) and poly(*N*-(2-phenoxy)-phenylmaleimide) (poly(2-POPMI)) mainly possessed *threo*-diisotactic structures in the main chains. Chiral stationary phase prepared from optically active poly(PhMI) optically resolved racemic 1,1'-bi-2-naphthol.

KEY WORDS *N*-Substituted Maleimide / Asymmetric Anionic Polymerization / Chiral Ligand / Optically Active Polymer /

N-Substituted maleimide (RMI) is one of the interesting monomers which can form an optically active polymer.^{1–5} Main chain carbons of poly(RMI) are chiral because polymerization of RMI proceeds through only *trans*-opening reaction of double bond in the imide ring.⁶ Structures of poly(RMI) produced by *trans*-addition reactions are displayed in Chart 1. In *threo*-disyndiotactic structures, stereogenic centers (*S*, *S*) and (*R*, *R*) in each monomeric unit equally exist, so that main chain carbons of poly(RMI) do not exhibit optical activity. *Threo*-diisotactic structures exert optical activity only if either of configurational pairs of (*S*, *S*) or (*R*, *R*) predominantly is formed in the *trans*-main chains. Furthermore, when the same configurational pairs are successively connected in the *threo*-diisotactic sequences, the polymer main chains can form a helical conformation. If poly(RMI) contains the sequences of helical conformation, the polymer has not only configurational chirality but also conformational one.

Systematic research on asymmetric anionic polymerization of achiral RMI bearing aromatic groups has been performed by the authors.^{4,5} Optical activity of poly(RMI) was significantly affected by a structure of *N*-substituent. The authors investigated the effect of bulkiness of *N*-substituent on optical activity of poly(RMI) prepared by asymmetric anionic polymerization. For example, poly(*N*-triphenylmethylmaleimide)⁴ (poly(TrMI)) containing a huge *N*-substituent exhibited small specific rotations ($[\alpha]_{435}^{25} = -31.5^\circ$ to -2.8°). On the other hand, optically active poly(*N*-phenylmaleimide)¹ (poly(PhMI))

having a small *N*-substituent showed a higher specific optical rotation ($[\alpha]_{435}^{25} = +94.6^\circ$) than poly(TrMI). Recently, the authors reported asymmetric anionic polymerizations of *N*-1-naphthylmaleimide⁵ (1-NMI). 1-NMI has a planar aromatic group which is not a very huge *N*-substituent. However, a specific rotation of poly(1-NMI) ($[\alpha]_{435}^{25} = -36.8^\circ$ to $+762.3^\circ$) formed by asymmetric anionic method was the highest in all of poly(RMI)s obtained so far. Thus, bulky *N*-substituents did not always provide high optical activity to the obtained poly(RMI). Therefore, further studies on the effect of *N*-substituents of RMI on optical activity of the polymer are currently desirable.

In this paper, we introduced a substituent into the *ortho*- or *para*-position of phenyl group of PhMI, and

Chart 1.

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asymmetric anionic homopolymerizations of PhMI and its derivatives with diethylzinc (Et_2Zn)–chiral ligand [(-)-2,2'-(1-ethylpropylidene)bis(4-benzyl-2-oxazoline) (Bnbox) or (-)-sparteine (Sp)] complexes were carried out under several polymerization conditions (Chart 2). The effects of bulkiness, flexibility, and polarity of the substituent on the optical activity and the stereoregularity of the obtained polymers were examined. Moreover, chiral recognition ability of optically active poly(PhMI) was evaluated by ^1H NMR and HPLC.

EXPERIMENTAL

Monomers

PhMI (Wako Pure Chemical Industries, Ltd.) was recrystallized from chloroform (mp $90\text{--}91^\circ\text{C}$). Other RMIs were synthesized from maleic anhydride and primary amines according to the reported procedures.^{7,8} The synthetic path is shown in Scheme 1.

N-2-Biphenylmaleamic Acid (2-BPMA)

A solution of 2-aminobiphenyl (2.0 g, 12 mmol) in benzene (50 mL) was slowly added dropwise to a solution of excess maleic anhydride (2.2 g, 24 mmol) in benzene (100 mL) over a period of 30 min at r.t.

The mixed solution was stirred for 1 d. The mixture was concentrated under reduced pressure. The obtained crude 2-BPMA was dissolved in ethyl acetate (200 mL), and washed with NaHCO_3 aq. (100 mL $\times$ 2), H_2O (100 mL $\times$ 2), and saturated NaCl aq. (100 mL) in order. The organic layer was dried over anhydrous MgSO_4 . The organic solution was evaporated to dryness to obtain 2-BPMA as a white powder. 2-BPMA was dried under vacuum at 25°C for 2 d. The obtained 2-BPMA was used in the next step without further purification [yield, 3.1 g (quant.); mp, $147\text{--}152^\circ\text{C}$; ^1H NMR (δ in ppm from TMS in $\text{DMSO}-d_6$): 6.23–6.32 (d, 1 H, $=\text{CH}-\text{CONH}-$), 6.35–6.45 (d, 1 H, $=\text{CH}-\text{COOH}$), 7.29–7.63 (m, 9 H, phenyl groups); ^{13}C NMR (δ in ppm from TMS in $\text{DMSO}-d_6$): 166.54, 164.75 (C=O), 133.78, 131.63 ($-\text{CH}=\text{CH}-$), 138.73, 136.80, 132.36, 130.68, 129.06, 128.74, 128.07, 12.69, 127.01, (phenyl groups)].

N-2-Biphenylmaleimide (2-BPMI)

2-BPMA (3.1 g, 12 mmol) was suspended in dry benzene (150 mL), and heated at 60°C . ZnBr_2 (2.7 g, 12 mmol) was added in one portion. A solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS, 3.9 mL, 12×1.5 mmol) in dry benzene (100 mL) was slowly added dropwise to the mixture with vigorous stirring over a period of 30 min at 80°C . After the dropping was completed, the reaction mixture was refluxed for 16 h with vigorous stirring. The reaction mixture was cooled to room temperature and filtered. The filtrate was evaporated to dryness under reduced pressure. The obtained residue was dissolved in ethyl acetate (200 mL). The solution was fully washed with 0.5 N HCl aq. (100 mL $\times$ 3), saturated NaHCO_3 aq. (100 mL $\times$ 2), and saturated NaCl aq. (100 mL) in that order. The organic solution was dried over anhydrous MgSO_4 and it was concentrated under reduced pressure. The obtained crude 2-BPMI was purified by column chromatography on silica gel (eluent, benzene), followed by recrystallization from *n*-hexane–ethyl acetate (1/9, v/v) to obtain pure 2-BPMI as a pale yellow crystal [yield, 1.6 g (56%); mp, $138\text{--}140^\circ\text{C}$ (Lit.⁹ mp, $141\text{--}142^\circ\text{C}$); ^1H NMR (δ in ppm from TMS in CDCl_3): 6.72 (s, 2 H, $-\text{CH}=\text{CH}-$), 7.31–7.97 (m, 9 H, phenyl groups); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 169.52 (C=O), 133.96 ($-\text{CH}=\text{CH}-$), 141.43, 138.58, 130.73, 129.47, 129.23, 128.63, 128.34, 128.25, 127.94, 127.42 (phenyl groups)].

Other RMA and RMI were prepared by almost similar method to 2-BPMA and 2-BPMI.

N-(2-Phenoxy)-Phenylmaleamic Acid (2-POPMA)

Gray powder [yield, quant.; mp, $159\text{--}161^\circ\text{C}$; ^1H

NMR (δ in ppm from TMS in DMSO- d_6): 6.28–6.35 (d, 1 H, =CH–CONH–), 6.49–6.58 (d, 1 H, =CH–COOH), 6.74–7.40 (m, 9 H, phenyl groups); ^{13}C NMR (δ in ppm from TMS in DMSO- d_6): 167.53, 167.08, 163.70 (C=O), 156.84, 148.07, 130.55, 130.33, 129.31, 126.00, 123.97, 123.94, 119.00 (phenyl groups), 131.79, 131.29 (–CH=CH–)].

N-(2-Phenoxy)-Phenylmaleimide (2-POPMI)

Crude 2-POPMI was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 2/1, v/v), followed by vacuum distillation (bp 170°C/5.8 × 10^{−2} mmHg). Yellow crystal; yield, 85%; mp, 87–90°C; ^1H NMR (δ in ppm from TMS in CDCl₃): 6.77 (s, 2 H, –CH=CH–), 6.93–7.39 (m, 9 H, phenyl groups); ^{13}C NMR (δ in ppm from TMS in CDCl₃): 169.61 (C=O), 134.72 (–CH=CH–), 156.59, 153.96, 130.87, 130.58, 130.15, 124.33, 123.94, 122.26, 119.59, 119.55 (phenyl groups). *Anal.* Calcd for C₁₆H₁₁NO₃: C, 72.45%; H, 4.18%; N, 5.28%. Found: C, 72.76%; H, 4.07%; N, 5.96%.

N-(4-Phenoxy)-Phenylmaleamic Acid (4-POPMA)

Yellowish green powder [yield, quant.; mp, 164–165°C; ^1H NMR (δ in ppm from TMS in DMSO- d_6): 6.34–6.42 (d, 1 H, =CH–CONH–), 6.54–6.61 (d, 1 H, =CH–COOH), 7.01–7.78 (m, 9 H, phenyl groups); ^{13}C NMR (δ in ppm from TMS in DMSO- d_6): 167.06, 163.42 (C=O), 155.74, 152.71, 130.80, 130.32, 123.45, 121.63, 119.67, 118.37 (phenyl groups), 134.57, 132.08 (–CH=CH–)].

N-(4-Phenoxy)-Phenylmaleimide (4-POPMI)

Crude 4-POPMI was purified by column chromatography (silica gel, *n*-hexane/ethyl acetate = 1/1, v/v), followed by recrystallization from *n*-hexane–ethyl acetate (1/4, v/v). Yellow crystal; yield, 85%; mp, 159–161°C (Lit.¹⁰ mp, 160°C); ^1H NMR (δ in ppm from TMS in CDCl₃): 6.78 (s, 2 H, –CH=CH–), 6.95–7.35 (m, 9 H, phenyl groups); ^{13}C NMR (δ in ppm from TMS in CDCl₃): 169.54 (C=O), 134.11 (–CH=CH–), 156.96, 156.39, 129.83, 127.57, 125.79, 123.81, 119.35, 118.83 (phenyl groups).

Chiral Ligands

Bnbox was prepared from diethylmalonyl dichloride and (*S*)-phenylalaninol according to the reported methods^{11,12} ($[\alpha]_{435}^{25} = -150.7^\circ$, $c = 1.0 \text{ g dL}^{-1}$, $l = 10 \text{ cm}$, THF; $[\alpha]_{\text{D}} = -21.9^\circ$, $c = 1.0 \text{ g dL}^{-1}$, $l = 10 \text{ cm}$, CHCl₃, (Lit.¹² $[\alpha]_{\text{D}} = -21.8^\circ$, $c = 2.55 \text{ g dL}^{-1}$, CHCl₃)). Sp (Aldrich) was purified by vacuum distillation immediately before use ($[\alpha]_{435}^{25} = -10.3^\circ$, $c = 1.0 \text{ g dL}^{-1}$, $l = 10 \text{ cm}$, THF).

Reagents and Solvents

Et₂Zn in a *n*-hexane solution ([Et₂Zn] = 1.02 M, Kanto Chemical Co., Inc., Tokyo, Japan) was used without further purification. Radical initiator, 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents used for syntheses, polymerizations, and several measurements were purified in the usual manner. (*RS*)-1,1'-Bi-2-naphthol ((*RS*)-BINOL) was purchased from Tokyo Chemical Industry Co., Ltd. (*S*)-BINOL was provided from Sumikin Chemical Co., Ltd.

Polymerization

Chiral anionic initiator was prepared by adding Et₂Zn to a solution of chiral ligand in toluene or THF at 0°C just before use. Asymmetric anionic polymerization of RMI was initiated by adding the chiral anionic initiator *via* a cannula to a monomer solution in a dry Schlenk tube under a dry nitrogen atmosphere. After passage of stated time, the polymerization was terminated with methanol containing a small amount of HCl aq. The reaction mixture was poured into a large amount of methanol. The precipitated polymer was collected by suction filtration through a glass filter, washed by methanol, and dried. The obtained polymer was purified by reprecipitation from THF-methanol systems 3 times. The obtained poly(RMI) was dried under vacuum at 25°C for 2 d before several measurements.

Radical polymerization was conducted in sealed glass tube using AIBN as an initiator under nitrogen atmosphere. All reagents were added to the glass tube, and the mixture was degassed 3 times before sealing tube under vacuum. Polymerization was conducted in a water 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 the similar method to the case of the anionic polymerization.

Measurements

Hg-line specific optical rotation ($[\alpha]_{435}^{25}$) was measured at 25°C using a JASCO DIP-140. ^1H and ^{13}C NMR spectra were recorded with tetramethylsilane as an internal standard using a JEOL EX-270 apparatus operating at 270 and 68 MHz, respectively. Gel permeation chromatography (GPC) was monitored with a Shimadzu chromatopac C-R7Ae plus furnished with a Shimadzu SPD-10A UV detector (254 nm) and a JASCO-OR 990 polarimetric detector (350–900 nm) using THF as an eluent at 50°C to calibrate number-average molecular weight ($\overline{M}_n$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with standard polystyrene. Elemental analysis was carried out with a PerkinElmer Series II CHNS10 Analyzer 2400.

Table I. Anionic polymerizations of RMI with Et₂Zn-Bnbox at 0 °C

Run	RMI ^a (mol L ⁻¹)	[Et ₂ Zn]/[Bnbox] ^b	Polym. ^c Solv. (mL)	Polym. Time (h)	Yield ^d (%)	$\overline{M}_n^e$ × 10 ⁻³	$\overline{M}_w/\overline{M}_n^e$	[α] ₄₃₅ ^{25 f} (deg.)	
1 ^g	PhMI	(0.29)	1.0/1.2	Tol. (10)	24	92	2.3	1.6	+94.6
2		(0.58)	1.0/1.2	THF (5)	24	100	2.9	1.8	+116.1
3		(0.29)	1.0/0.5	Tol. (10)	24	85	2.1	1.6	+156.4
4		(0.58)	1.0/0.5	THF (5)	24	100	2.9	1.8	+132.0
5	2-BPMI	(0.08)	1.0/0.5	Tol. (25)	48	34	1.9	1.5	+164.7
6		(0.20)	1.0/0.5	THF (10)	48	59	2.7	1.6	+132.1
7	2-POPMI	(0.08)	1.0/0.5	Tol. (25)	72	83	3.2	1.7	+17.2
8		(0.19)	1.0/0.5	THF (10)	72	95	—	—	—
9	4-POPMI	(0.05)	1.0/0.5	Tol. (35)	72	40	2.5	2.9	+27.2
10		(0.19)	1.0/0.5	THF (10)	72	89	3.1	3.9	+24.0

^aRMI; 0.5 g. ^b[Diethylzinc] / [RMI] = 0.1. ^cTol.: Toluene, THF: Tetrahydrofuran. ^dMethanol-insoluble part. ^eBy GPC. ^f $c = 1.0$ g dL⁻¹ (run 1–6 and 9), 0.2 g dL⁻¹ (run 7), 0.9 g dL⁻¹ (run 10), $l = 10$ cm, in THF. ^gref 1.

Preparation of Chiral Stationary Phase

Optically active poly(PhMI) (35 mg) was dissolved in CHCl₃. Macroporous silica gel (TOSOH Corporation, Silica-100, particle size 5 μm, pore size 100 Å, 700 mg) was added to the solution of poly(PhMI). The mixture was evaporated to dryness under reduced pressure to prepare chiral stationary phase (CSP). The prepared CSP was packed into a stainless-steel column (150 × 2.0 mm I.D.) by a high-pressure slurry method (maximum pressure, 400 kg cm⁻²) with 2-propanol as an eluent. Theoretical plate number (N) was estimated with 1,3,5-tri-*tert*-butylbenzene, and calculated by the following equation,

$$N = 5.54 \times (t_r/w_{1/2})^2$$

where t_r is a retention time and $w_{1/2}$ is a half band width.

HPLC

Optical resolution analysis was carried out using the same apparatus as GPC. Mixed solvent of *n*-hexane and 2-propanol (9.5/0.5, v/v) was used as a mobile phase at a flow rate of 0.5 mL min⁻¹.

RESULTS AND DISCUSSION

Asymmetric Anionic Polymerization of RMI

The results of asymmetric anionic homopolymerizations of PhMI, 2-BPMI, 2-POPMI, and 4-POPMI with Et₂Zn-Bnbox are listed in Table I. Yields for polymerizations of 2-BPMI and 4-POPMI in toluene (runs 5 and 9) were smaller than others, because of low solubility of the monomers and/or growing polymers. However, the polymerization of 2-POPMI, which has similar solubility to that of 2-BPMI in toluene and contains a substituent at *ortho*-position on the phenyl group as well as 2-BPMI, gave a relatively high yield

(run 7). These results can be explained by comparison of *ortho*-substituent on phenyl group of 2-BPMI with that of 2-POPMI. *ortho*-Phenoxy group of 2-POPMI is more flexible than *ortho*-phenyl group of 2-BPMI. In addition, the rigid *ortho*-phenyl group of 2-BPMI is in close proximity to reaction center. That is, high yield for polymerization of 2-POPMI is caused by high flexibility and low bulkiness of phenoxy group. The most part of poly(2-POPMI) prepared in THF (run 8) was insoluble in common organic solvents, such as THF, CHCl₃, *N,N*-dimethylformamide, dimethylsulfoxide, and mixed solvent of CHCl₃–trifluoroacetic acid. All polymerizations gave optically active polymers, and all specific rotations of the formed polymers were dextrorotatory ($[\alpha]_{435}^{25} = +17.2^\circ$ to $+164.7^\circ$). Specific rotations of poly(PhMI) obtained with Et₂Zn-Bnbox complex consisting of the molar ratio of 1.0/0.5 (runs 3 and 4) were higher than those of 1.0/1.2 (runs 1 and 2), suggesting that the optimum asymmetric field was constructed by the molar ratio of 1.0/0.5. This is also confirmed by previous research⁵ on asymmetric anionic polymerization of 1-NMI. We reported the syntheses and chiroptical properties of optically active *trans*-3,4-dimethyl-*N*-substituted succinimides (*trans*-DMRSI (R: phenyl (*trans*-DMPhSI), 1-naphthyl (*trans*-DMNSI) as model compound of poly(RMI)).¹³ Specific rotations of *trans*-DMPhSI and *trans*-DMNSI were -127.6 and -126.7 , respectively. The results suggested that values of specific rotations of poly(RMI) are little affected by structures of *N*-substituent. The magnitude of specific rotation is reflected in the configurational chirality of the main chain and conformational chirality. Specific rotations of poly(PhMI) and poly(2-BPMI) were much higher than those of poly(2-POPMI) and poly(4-POPMI), indicating that the polar phenoxy group of 2-POPMI and 4-POPMI are undesirable for the asymmetric anionic polymerization

Table II. Anionic polymerizations of RMI with Et₂Zn–Sp at 0 °C

Run	RMI ^a (mol L ⁻¹)	[Et ₂ Zn]/[Sp] ^b	Polym. ^c Solv. (mL)	Polym. Time (h)	Yield ^d (%)	$\overline{M}_n^e$ × 10 ⁻³	$\overline{M}_w/\overline{M}_n^e$	$[\alpha]_{435}^{25\text{ f}}$ (deg.)
1	PhMI (0.29)	1.0/0.5	Tol. (10)	72	67	2.2	2.1	-1.7
2	(0.58)	1.0/0.5	THF (5)	72	76	—	—	-5.3
3	2-BPMI (0.08)	1.0/0.5	Tol. (25)	72	38	2.3	1.9	-8.0
4	(0.20)	1.0/0.5	THF (10)	72	70	4.1	1.7	-20.7
5	2-POPMI (0.08)	1.0/0.5	Tol. (25)	72	70	1.8	1.8	+163.6
6	(0.19)	1.0/0.5	THF (10)	72	95	—	—	—
7	4-POPMI (0.05)	1.0/0.5	Tol. (35)	72	88	4.4	2.3	-5.2
8	(0.19)	1.0/0.5	THF (10)	72	86	8.0	3.7	-4.3

^aRMI; 0.5 g. ^b[Diethylzinc] / [RMI] = 0.1. ^cTol.: Toluene, THF: Tetrahydrofuran. ^dMethanol-insoluble part. ^eBy GPC. ^f $c = 0.2 \text{ g dL}^{-1}$ (run 1 and 2), 1.0 g dL^{-1} (run 3–5, 7, and 8), $l = 10 \text{ cm}$ (run 1–7), 5 cm (run 8), in THF (run 1, 3–5, 7, and 8), DMF (run 2).

Figure 1. GPC chromatograms of poly(PhMI) (a) ($[\alpha]_{435}^{25} = +156.4^\circ$, run 3 in Table I), poly(2-BPMI) (b) ($[\alpha]_{435}^{25} = +164.7^\circ$, run 5 in Table I), poly(2-POPMI) (c) ($[\alpha]_{435}^{25} = +163.6^\circ$, run 5 in Table II), and poly(4-POPMI) (d) ($[\alpha]_{435}^{25} = +27.2^\circ$, run 9 in Table I) monitored using UV (bottom curves) and polarimetric (α_{Hg} , top curves) detector.

of RMI using Et₂Zn–Bnbox complex as an initiator. On the other hand, specific rotations of poly(PhMI) formed in toluene (runs 3 and 4) were not very different from those of poly(2-BPMI) (runs 5 and 6). This indicates that Bnbox and a phenyl group bonding at *ortho*-position of phenyl group in 2-BPMI cannot build effective asymmetric fields at the polymer growth-ends.

Table II shows the polymerization results using Et₂Zn–Sp as an initiator. Polymerization of 2-BPMI in toluene also gave low yield as well as the result listed in run 5 in Table I. Polymerization of 2-POPMI in THF (run 6 in Table II) gave insoluble polymer in common organic solvents similarly to the case of polymerization using Et₂Zn–Bnbox as an initiator (run 8 in Table I). $\overline{M}_n$ of the poly(4-POPMI) prepared in THF was higher than that of other polymers shown in Ta-

ble I and II. All polymers exhibited optical activity. Specific rotations of poly(PhMI), poly(2-BPMI), and poly(4-POPMI) were very small ($[\alpha]_{435}^{25} = -20.7^\circ$ to -1.7°). However, poly(2-POPMI) obtained in toluene showed a high specific rotation ($[\alpha]_{435}^{25} = +163.6^\circ$). Et₂Zn–Sp complex may be suitable for the polymerization of PhMI derivatives bearing a bulky and polar substituent at *ortho*-position of a phenyl ring.

GPC chromatograms of optically active poly(RMI) were recorded using UV and polarimetric detector to evaluate the dependence of optical rotation on molecular weight. The obtained chromatograms were displayed in Figure 1 (a: poly(PhMI), $[\alpha]_{435}^{25} = +156.4^\circ$, run 3 in Table I; b: poly(2-BPMI), $[\alpha]_{435}^{25} = +164.7^\circ$, run 5 in Table I; c: poly(2-POPMI), $[\alpha]_{435}^{25} = +163.6^\circ$, run 5 in Table II; d: poly(4-POPMI), $[\alpha]_{435}^{25} = +27.2^\circ$,

Figure 2. Change of the specific optical rotation of poly(2-BPMI) (A) ($[\alpha]_{435}^{25} = +164.7^\circ$, run 5 in Table I) and poly(4-POPMI) (B) ($[\alpha]_{435}^{25} = +27.2^\circ$, run 9 in Table I) on measurement temperature ($\square$ and $\circ$: cooling, $\blacksquare$ and $\bullet$: heating).

run 9 in Table I). UV and α_{Hg} chromatograms of poly(PhMI), poly(2-BPMI), and poly(2-POPMI) were symmetrical. Namely, every molecular weight part of each polymer showed the same optical rotation. The results suggested that chirality of the poly(RMI)s were attributed to not chiral carbons of the main chain-ends but chiral stereogenicity of the whole main chain. On the other hand, the top of the α_{Hg} chromatogram displayed in Figure 1d shifted in a lower molecular weight range than the maximum position of the UV curve. This reflects that the optical rotation of low molecular weight part of poly(4-POPMI) prepared with Et_2Zn – Bnbox in toluene was higher than that of high molecular weight one.

Figure 2 depicts a change of specific rotation on measurement temperature. Figure 2a and 2b shows the results obtained from poly(2-BPMI) (run 5 in Table I, $[\alpha]_{435}^{25} = +164.7^\circ$) and poly(4-POPMI) (run 9 in Table I, $[\alpha]_{435}^{25} = +27.2^\circ$), respectively. Interestingly, the specific rotation of poly(2-BPMI) (Figure 2a) increased with rise of temperature. In contrast, the specific rotation of poly(4-POPMI) decreased with rise of temperature. The configuration of the polymer main chain is unchanged by heating and cooling, but the conformation of polymer is changeable by them. Therefore, these changes displayed in Figure 2 result from the relaxation of the chiral conformation rather than the configurational chirality due to asymmetric centers in the main chains. On the basis of previous researches,^{1,4,5} it can be explained that the change of specific rotation for poly(4-POPMI) is ascribed to the relaxation of partial chiral conformation of the main chains. The change of specific rotation for the poly(2-BPMI) is very unusual

result, so that the origin of the conformational chirality for the poly(2-BPMI) is different from that for poly(4-POPMI). The change of specific rotation for poly(2-BPMI) may be due to axial asymmetry of the biphenyl groups in the side chains, but the reason is not clear at present.

Structure of Poly(RMI)

To investigate the structure of poly(RMI), ^{13}C NMR spectra were measured. Figure 3 shows ^{13}C NMR spectra for optically inactive poly(PhMI) formed with AIBN (a) and optically active one (b, run 3 in Table I, $[\alpha]_{435}^{25} = 156.4^\circ$). A part of the poly(PhMI) obtained by radical method (Figure 3b) was not insoluble, so that the NMR spectrum was measured in a mixed solvent of CDCl_3 and trifluoroacetic acid (4/1, v/v). There were no differences in the signals due to phenyl and carbonyl groups among the polymers. However, the signals due to main chain carbons of optically inactive poly(PhMI) were different from those of optically active one. Main chain signals of poly(PhMI) obtained using AIBN appeared in two peaks, as shown Figure 3a. Main chain signals of optically active poly(PhMI) prepared by asymmetric anionic method exhibited one broad peak. On the basis of our previous works,^{1,4,5} the peaks at lower magnetic field and higher one are assigned to *threo*-disyndiotactic and *threo*-diisotactic structures, respectively. Interestingly, the main chains of the optically inactive polymer had more *threo*-diisotactic content than those of optically active one. Optical activity of poly(PhMI) was ascribed to small amounts of *threo*-diisotactic structures which contain the same configurational stereogenic centers such as $-(S, S)-(S, S)-(S,$

Figure 3. ^{13}C NMR spectra for poly(PhMI) obtained with AIBN in toluene (a) and $\text{Et}_2\text{Zn-Bnbox}$ in toluene (b) ($[\alpha]_{435}^{25} = +156.4^\circ$, run 3 in Table I) in CDCl_3 .

S)-(*S*, *S*)- or -(*R*, *R*)-(*R*, *R*)-(*R*, *R*)-(*R*, *R*)-. In addition, poor solubility of the poly(PhMI) formed by radical polymerization might be attributed to large quantity of the *threo*-diisotactic sequences in the main chains.

Figure 4 displays the ^{13}C NMR spectra for optically inactive poly(2-BPMP) prepared by radical polymerization in toluene using AIBN as an initiator (a, $\overline{M}_n = 1600$, $\overline{M}_w/\overline{M}_n = 1.5$) and optically active one (b, run 1 in Table I, $[\alpha]_{435}^{25} = +164.7^\circ$). The signal due to phenyl groups of the poly(2-BPMP) prepared by radical polymerization was similar to that by $\text{Et}_2\text{Zn-Bnbox}$. Signals due to carbonyl and main chain carbons of optically active poly(2-BPMP) (Figure 4b) were different from those of optically inactive one (Figure 4a). Main chain signals of optically active poly(2-BPMP) was sharper than that of optically inactive one. This indicates that poly(2-BPMP) obtained by asymmetric anionic polymerization has more stereoregular structures than that obtained by radical polymerization. From the previous researches by the authors,^{1,4,5} the main chain signals appearing at higher and lower magnetic field are assigned to *threo*-diisotactic and *threo*-disyndiotactic structures, respectively, as shown in Figure 4. As compared Figure 4a with 4b, it became apparent that optically active poly(2-BPMP) possessed more *threo*-diisotactic structures, which are important for produc-

tion of chiral main chains, than optically inactive one.

^{13}C NMR spectra for optically active poly(2-POPMP) (a, run 5 in Table II, $[\alpha]_{435}^{25} = +163.6^\circ$) and poly(4-POPMP) (b, run 9 in Table I, $[\alpha]_{435}^{25} = +27.2^\circ$) are shown in Figure 5. In Figure 5a, signals assigned to phenyl groups around 120 ppm were complicated and broad than those of Figure 5b, suggesting that *N*-substituent of the poly(2-POPMP) forms more various conformations than that of the poly(4-POPMP). Signals due to carbonyl group of the poly(2-POPMP) were broader than those of poly(4-POPMP), nevertheless main chain signals mainly appeared at the higher magnetic field around 40 ppm, as shown in Figure 5a. Carbonyl groups of the poly(2-POPMP) is close to flexible phenoxy group, so that peak positions of the carbonyl groups are liable to be influenced not by stereoregularity of the main chains but by movement of the phenoxy group. From the main chain signals depicted in Figure 5, it was clarified that poly(2-POPMP) with a high specific rotation contains more *threo*-diisotactic content than poly(4-POPMP) with low one.

Optical Resolution Ability of Optically Active Poly(PhMI)

Chiral recognition ability of optically active poly(PhMI) was examined by ^1H NMR spectroscopy,

Figure 4. ^{13}C NMR spectra for poly(2-BPMI) obtained with AIBN in toluene (a) ($\overline{M}_n = 1600$, $\overline{M}_w/\overline{M}_n = 1.5$) and Et_2Zn –Bnbox in toluene (b) ($[\alpha]_{435}^{25} = +164.7^\circ$, run 5 in Table I) in CDCl_3 .

Figure 5. ^{13}C NMR spectra for poly(2-POPMI) (a) (Et_2Zn –Sp in toluene, $[\alpha]_{435}^{25} = +163.6^\circ$, run 5 in Table II) and poly(4-POPMI) (b) (Et_2Zn –Bnbox in toluene, $[\alpha]_{435}^{25} = +27.2^\circ$, run 9 in Table I) CDCl_3 .

Figure 6. ^1H NMR spectra of (RS) -BINOL (a), mixture of (RS) -BINOL and poly(PhMI) (b), and mixture of (RS) -BINOL, poly(PhMI) ($[\alpha]_{435}^{25} = +156.4^\circ$, run 3 in Table I) and (S) -BINOL (c) in CDCl_3 . Concentrations: $[(RS)\text{-BINOL}] = 0.04 \text{ mol L}^{-1}$; $[\text{poly(PhMI)}] = 0.08 \text{ mol L}^{-1}$ (succinimide unit); $[(S)\text{-BINOL}] = 0.04 \text{ mol L}^{-1}$.

as shown in Figure 6. Figure 6a shows ^1H NMR spectra of racemic BINOL in CDCl_3 ($[(RS)\text{-BINOL}] = 0.04 \text{ mol L}^{-1}$). When the optically active (+)-poly(PhMI) (run 3 in Table I, $[\alpha]_{435}^{25} = 156.4^\circ$) was added in the solution of (RS) -BINOL ($[\text{poly(PhMI)}] = 0.08 \text{ mol L}^{-1}$), ^1H NMR peak due to hydroxyl groups of (RS) -BINOL shifted in the lower magnetic field and split into two signals, as shown in Figure 6b. This indicates that the optically active (+)-poly(PhMI) interacts with (R) - or (S) -BINOL by hydrogen bond between carbonyl and hydroxyl group and/or π - π stacking between phenyl and naphthyl. The strength of interaction differs among two enantiomers of (RS) -BINOL. To clarify the enantiomer which strongly interacts with optically active (+)-poly(PhMI), (S) -BINOL was added in the solution of (RS) -BINOL and (+)-poly(PhMI) in CDCl_3 . The obtained spectrum depicts in Figure 6c. On the basis of the change of peak intensity of two hydroxyl groups, it was revealed that optically active (+)-poly(PhMI) selectively and strongly interacts with (S) -BINOL.

Optically active poly(PhMI) (run 3 in Table I, $[\alpha]_{435}^{25} = 156.4^\circ$) was coated on macroporous silica gel to prepare CSP, and the CSP was packed into a

Figure 7. HPLC chromatograms of (RS) -BINOL resolved using CSP prepared from optically active poly(PhMI) ($[\alpha]_{435}^{25} = +156.4^\circ$, run 3 in Table I) and silica gel.

column ($N = 850$, 1,3,5-tri-*tert*-butylbenzene). HPLC chromatogram of (RS) -BINOL on the CSP is displayed in Figure 7 (conditions: flow rate, 0.5 mL min^{-1} ; mobile phase, n -hexane/2-propanol = 9.5/0.5 (v/v); temperature; r.t.). The top and the bottom chromatograms were monitored with a polarimetric and a UV detectors, respectively. Split UV chromatograms appeared at 3.7 and 4.0 min, indicating that BINOL was optically resolved by the CSP. On the basis of the sign of α_{Hg} chromatogram, it was clarified that the first eluted isomer was (R) -(+)-BINOL, and the second one was (S) -(-)-BINOL. Capacity factors, k'_1 and k'_2 were estimated to be 2.75 and 3.09, respectively. Separation factor, α was calculated to be 1.12. Resolution factor could not be estimated because UV chromatograms of (R) - and (S) -BINOL were not completely separated. As shown in Figure 6, (+)-poly(PhMI) selectively interacted with (S) -(-)-BINOL, and elution order of the enantiomers displayed in Figure 7 reflected the result.

SUMMARY

1. Asymmetric anionic homopolymerizations of *N*-phenylmaleimide and its derivatives were carried out with Et_2Zn -chiral ligand complexes to obtain optically active polymers.

2. Polymerizability of RMI and optical activity of poly(RMI) obtained were greatly influenced by structures of *N*-substituents and chiral ligand-initiator complex.

3. Poly(2-BPMI) formed with Et_2Zn -Bnbox in toluene exhibited the highest specific optical rotation of $+164.7^\circ$.

4. From ^{13}C NMR spectra, it was ascertained that op-

tically active poly(2-BPMI) and poly(2-POPMI) possess large amounts of *threo*-diisotactic structures in the main chains.

5. Optically active poly(PhMI) selectively interacted with (*S*)-BINOL, and CSP prepared from the polymer and silica gel optically resolved (*RS*)-BINOL.

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