Asymmetric Polymerization of *N*-1-Anthrylmaleimide with Diethylzinc-Chiral Ligand Complexes and Optical Resolution Using the Polymer

Yukio Isobe, Kenjiro Onimura, Hiromori Tsutsumi, and Tsutomu Oishi[†]

Department of Applied Chemistry & Chemical Engineering, Faculty of Engineering, Yamaguchi University, 2–16–1 Tokiwadai, Ube, Yamaguchi 755–8611, Japan

ABSTRACT: Asymmetric anionic homopolymerizations of *N*-1-anthrylmaleimide (1-AMI) were performed with diethylzinc (Et$_2$Zn)-chiral ligand complexes to obtain optically active polymers. The optical activity of poly(1-AMI) was influenced by polymerization conditions such as temperature, solvents and structures of chiral ligands. Poly(1-AMI) obtained with Et$_2$Zn/(−)-2,2′-(1-ethylpropylidene)bis(4-benzyl-2-oxazoline) (Bnbox) in THF at 0°C showed the highest specific optical rotation ($[\alpha]_D^{25} = +92.5°$). CD spectra of (+)-poly(1-AMI) exhibited negative exciton chirality around 230–300 nm, indicating that ^1B_b transition moments of anthryl groups were twisted counterclockwise. Chiral recognition ability of poly(1-AMI) was investigated by ^1H NMR and HPLC, and the polymer coated on silica gel optically resolved 1, 1′-bi-2-naphthol.
KEY WORDS N-Substituted Maleimide / *N*-1-Anthrylmaleimide / Asymmetric Anionic Polymerization / Chiral Ligand / Exciton Chirality Method / Optical Resolution /

The asymmetric anionic polymerization of *N*-substituted maleimide (RMI) was previously studied.[1–10] RMI is polymerized through only *trans* additional reactions,[11] so that the obtained poly(RMI) contains two chemical structures, *threo-disyndiotactic* and *threo-diisotactic* structures in the main chains. The main chains consisting of *threo-disyndiotactic* sequences show no optical activity because (*S*, *S*)–configurational pair is equal to (*R*, *R*)–one. *Threo-diisotactic* sequences exhibit optical activity when the same configurational pairs predominate in the main chains. If the same configurational pairs successively exist, the polymer main chains form a helical conformation. Optical activity of poly(RMI) is influenced by polymerization conditions. In particular, molecular design of *N*-substituents and initiator complexes are very important. Recently, the authors reported asymmetric anionic polymerizations of *N*-1-naphthylmaleimide (1-NMI).[6, 9, 10] Poly(1-NMI) prepared with Et$_2$Zn–Bnbox in THF exhibited the highest specific rotation of all poly(RMI) obtained so far.[10] The highly optical activity of the polymer was attributed not only to configurational chirality but partial helical conformation as well.

Chiral recognition is shown by optically active polymer. Therefore, optically active polymers are used as chiral stationary phases (CSP) for HPLC. For example, CSP prepared from optically active polymethacrylate derivatives bearing bulky substituents developed by Okamoto *et al.* optically resolved many racemates.[12–17] Polysaccharide derivatives[18, 19] prepared from natural polymers give excellent CSP. These polymers possess highly ordered structures such as helical conformations effective for chiral recognition. There are only a few reports on chiral recognition or optical resolution using optically active poly(RMI) to our knowledge.

This article presents asymmetric anionic homopolymerizations of 1-AMI with diethylzinc-chiral ligand complexes (Scheme 1). The effects of polymerization conditions such as chiral ligands, solvents, and temperature on optical activity of the obtained polymers were studied. The chiral conformation of the polymer was investigated by the exciton–coupled circular dichroic method. Chiral recognition ability of the optically active polymer was characterized by ^1H NMR and HPLC.

EXPERIMENTAL

Monomer

1-AMI was prepared from maleic anhydride and 1-anthrylamine as reported previously.[20, 21]

N-1-Anthrylmaleamic Acid (1-AMA)

A solution of 1-anthrylamine (1.0 g, 5.2 mmol) in glacial acetic acid (20 mL) was added dropwise to a solution of excess maleic anhydride (1.0 g, 10.0 mmol) in

---

[†]To whom all correspondence should be addressed (Phone: +81-836-85-9281, Fax: +81-836-85-9201, E-mail: oishi@po.cc.yamaguchi-u.ac.jp).
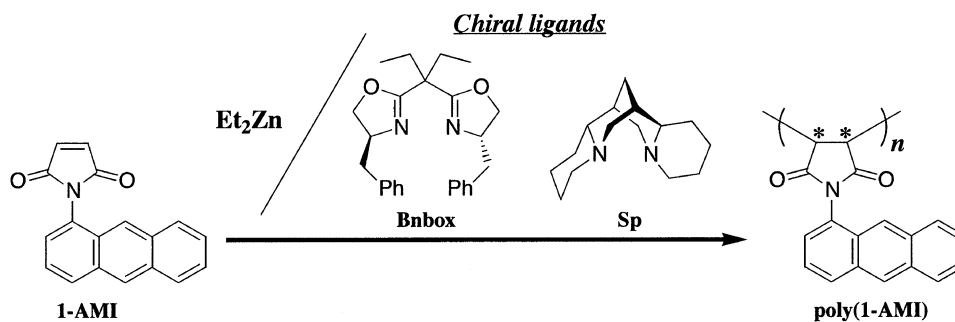
Scheme 1.

glacial acetic acid (20 mL) at r.t., and the mixture was stirred overnight. The mixture was poured into a large amount of water (300 mL). Yellow precipitates were collected by suction filtration and washed with water (100 mL × 2). The obtained 1-AMA was dried under vacuum at 25°C for 2 days [yield, 1.3 g (87%); mp, 200–206°C; ^{1}H NMR (δ in ppm from TMS in DMSO-d_6): 6.38 (d, 1H, =C$\underline{H}$–CONH–), 6.79 (d, 1H, =C$\underline{H}$–COOH), 7.46–8.79 (m, 9H, aromatic protons), 10.63 (br, 1H, –N$\underline{H}$–), 13.35 (br, 1H, –COO$\underline{H}$); ^{13}C NMR (δ in ppm from TMS in DMSO-d_6): 166.94, 164.53 (C=O), 13135.00, 133.82 (–CH=CH–), 132.81, 130.46, 129.47, 128.23, 127.93, 126.67, 126.26, 126.11, 126.00, 125.70, 125.64, 122.95, 122.03 (aromatic carbons)]. 1-AMA was used without further purification.

N-1-Anthrylmaleimide (1-AMI)

A suspension of 1-AMA (0.1 g, 0.3 mmol) in dry benzene (60 mL) was heated at 65°C, and then ZnBr$_2$ (0.05 g, 3.4 mmol) was added in one portion. A solution of 1, 1, 1, 3, 3, 3-hexamethyldisilazane (HMDS, 11.0 mL, 3.4 × 1.5 mmol) in dry benzene (30 mL) was slowly added dropwise to a suspension with vigorous stirring at 80°C. The reaction mixture was refluxed for 4 h with vigorous stirring. The solution was cooled to r.t., and poured into 0.5 N aqueous hydrochloric acid (70 mL). The aqueous phase was extracted with ethyl acetate (30 mL × 2). The organic layers were combined and washed with saturated aqueous sodium hydrogencarbonate (30 mL × 2) and saturated aqueous sodium chloride (30 mL × 2) and dried over anhydrous magnesium sulfate. The organic solution was concentrated using evaporator under reduced pressure. The crude 1-AMI was purified by column chromatography on silica gel using a eluent of n-hexane–CH$_2$Cl$_2$ (1/3, v/v), followed by recrystallization from n-hexane–ethyl acetate (1/1, v/v) to obtain pure 1-AMI as a yellow crystal [yield, 0.05 g (51%); mp, > 300°C; ^{1}H NMR (δ in ppm from TMS in CDCl$_3$): 7.03 (s, 2 H, –CH=CH–), 7.35–8.55 (m, 9 H, aromatic protons); ^{13}C NMR (δ in ppm from TMS in CDCl$_3$): 170.08 (C=O), 134.59 (–CH=CH–), 132.24, 132.09, 131.95, 130.40, 128.54,

128.36, 128.01, 127.66, 127.57, 127.40, 127.30, 126.79, 126.38, 126.25, 126.3 (anthryl group)].

Chiral Ligands

Bnbox was synthesized from (*S*)-phenylalaninol and diethylmalonyl dichloride according to literatures[22, 23] ($[\alpha]_{435}^{25} = -150.7°$, $c = 1.0 \, \text{g dL}^{-1}$, $l = 10 \, \text{cm}$, THF). Commercially available Sp (Aldrich Chemical Company, Inc.) was distilled under reduced pressure immediately before use ($[\alpha]_{435}^{25} = -10.3°$, $c = 1.0 \, \text{g dL}^{-1}$, $l = 10 \, \text{cm}$, THF).

Reagents and Solvents

Commercially available Et$_2$Zn in a n-hexane solution ([Et$_2$Zn] = 1.02 M, Kanto Chemical Co., Inc., Tokyo, Japan) was used without further purification. Solvents used for syntheses, polymerizations, HPLC and other measurements were purified by the general method. (*RS*)-1,1′-bi-2-Naphthol (BINOL) used for ^{1}H NMR study and optical resolution purchased from Tokyo Chemical Industry Co., Ltd.

Polymerization

A Schlenk reaction tube containing 1-AMI was degassed by vacuum pump, and replaced with dry nitrogen gas 3 times to get dry 1-AMI. Chiral ligand in a pear-shaped flask was dried in the same manner. Polymerization solvent was placed in each vessel using a syringe under nitrogen atmosphere. Et$_2$Zn in a n-hexane solution was introduced into chiral ligand solution by syringe to prepare the initiator complex. 1-AMI solution was kept at polymerization temperature. Initiator solution was added by a cannula in stream of nitrogen to initiate the polymerization. After a prescribed time, polymerization was terminated with a small amount of methanol containing 2 drops of 6 N aqueous hydrochloric acid. The solution was poured into a large amount of methanol. The precipitated polymer was collected by suction filtration, washed with methanol, and dried. The obtained polymer was purified by reprecipitation from THF-methanol systems 3 times. The obtained poly(1-AMI) was dried under vacuum at 25°C for 2

days before measurements.

Measurements

Specific optical rotation ($[\alpha]_D^{25}$ or $[\alpha]_{435}^{25}$) was measured at 25°C in THF using a JASCO DIP-140. ^{1}H (270 MHz) and ^{13}C (68 MHz) NMR spectra were obtained with tetramethylsilane as internal standard using a JEOL EX-270 apparatus. GPC was carried out with a Shimadzu chromatopac C-R7Ae plus equipped with a Shimadzu SPD-10A UV detector (254 nm) and JASCO-OR 990 polarimetric detector (350–900 nm) using THF as an eluent at 50°C to evaluate number–average molecular weight ($\overline{M}_n$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with polystyrene as a standard. HPLC analysis was carried out with apparatus consisting of a TOSOH CCPM pump, a TOSOH CCPM controller, a Shimadzu CHROMATOPAC C-R7Ae plus, a TOSOH UV-8010 UV detector (254 nm), and a JASCO-OR 990 polarimetric detector (350–900 nm).

Preparation of Chiral Stationary Phase

Modification of Silica Gel. A mixture of macroporous silica gel (TOSOH Corporation, Silica-100, particle size 5 μm, pore size 100 Å, 5.0 g), triethylamine (4.0 mL, 28.7 mmol), and diphenyldichlorosilane (4.0 mL, 19.3 mmol) in dry toluene (30 mL) was refluxed for 1 day. The mixture was poured into a large amount of methanol (100 mL). The precipitate was collected by suction filtration and washed with methanol (30 mL × 2) to obtain a modified silica gel (6.5 g).

Packing Material. Optically active poly(1-AMI) (0.1 g, 10 wt%) was dissolved in THF. The modified silica gel (1.0 g) was added to a solution of poly(1-AMI). The mixture was degassed by ultrasonication. THF was removed under reduced pressure to prepare modified silica gel coated with poly(1-AMI).

Packing

CSP consisting of modified silica gel and optically active poly(1-AMI) was packed into a stainless-steel column (150 × 2.0 mm I.D.) using a high-pressure slurry method (maximum pressure, 400 kg cm^{-2}) with a methanol as an eluent. Theoretical plate number (N) was calculated using toluene according to 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 half a band width.

RESULTS AND DISCUSSION

Asymmetric Anionic Polymerization of 1-AMI

Table I shows the results of asymmetric anionic polymerizations of 1-AMI. Polymerizations with Et$_2$Zn–Bnbox in THF at 0°C (run 1 in Table I) and at r.t. (run 5 in Table I) gave quantitative yields. When polymerization was performed at −40°C (run 4 in Table I), only a trace amount of poly(1-AMI) was obtained as the methanol insoluble portion. During polymerization at −40°C, polymerization solution color remained yellow, and no red color due to carbanion was observed, indicating no initiation reaction because of low temperature. All polymerizations gave optically active poly(1-AMI)s ($[\alpha]_D^{25} = +1.1°$ to $+92.5°$). In particular, poly(1-AMI) initiated with Et$_2$Zn–Bnbox ([Et$_2$Zn] / [Bnbox] = 1.0/0.5) in THF at 0°C had the highest specific optical rotation ($[\alpha]_D^{25} = +92.5°$). In our previous reports,[6, 7, 9, 10] the Et$_2$Zn–Bnbox complex was a suitable initiator for asymmetric anionic polymerization of RMI, and the optimum molar ratio of [Et$_2$Zn]/[Bnbox] was 1.0/0.5. In polymerizations of 1-AMI, specific optical rotation of poly(1-AMI) obtained using the ratio of 1.0/0.5 (run 5 in Table I, $[\alpha]_D^{25} = +92.5°$) was higher than that obtained using the ratio of 1.0/1.2 (run 3 in Table I, $[\alpha]_D^{25} = +56.4°$). Optimum asymmetric fields for the propagating polymer ends may thus form by the complex consisting of the molar ratio of 1.0/0.5. Poly(1-AMI) obtained with Et$_2$Zn–Sp in THF exhibited very small specific optical rotation ($[\alpha]_D^{25} = +1.1°$) and relatively low yield (32.0%). Because 1-AMI bears a bulky substituent of an anthryl group, relatively small ligand like Sp may be difficult to control stereospecific growth during asymmetric polymerization.

To monitor directly the change of optical activity during polymerization, asymmetric anionic polymerization of 1-AMI was carried out with Et$_2$Zn–Bnbox in 1 cm quartz cell at r.t. at feed ratios of [Et$_2$Zn]/[1-AMI] = 0.2 and [Et$_2$Zn]/[Bnbox] = 1.0/0.5, and the monomer concentration [1-AMI] = 0.036 mol L^{-1} in THF. The results are shown in Figure 1. Specific rotation of the polymerization solution rapidly increased for 15 min, and then gradually increased with reaction time. Optical rotation (α_D^{25}) reached a constant value after 40 min. Optical rotation and polymerization yield at this time were 0.07° and 92.0%, respectively. The specific optical rotation ($[\alpha]_D^{25}$) of the polymer was calculated as +70.0° from optical rotation, yield, and monomer concentration.

Figure 2 shows change in specific optical rotation of poly(1-AMI) prepared by run 5 in Table I with tem-

Table I. Asymmetric anionic polymerizations of 1-AMI

Run	1-AMI[a] $\overline{\text{mol L}^{-1}}$	Initiator[b] $\overline{([Et_2Zn]/[Ligand])}$	Polym.[c] Solvent $\overline{\text{mL}}$	Polym.[d] Temp. $\overline{^\circ C}$	Polym. Time $\overline{\text{h}}$	Yield[e] $\overline{\%}$	$\overline{M}_n$[f] $\overline{\times 10^{-3}}$	$\overline{M}_w/\overline{M}_n$[f]	$[\alpha]_D^{25\,g}$ $\overline{\text{deg.}}$
1	0.12	Et$_2$–Bnbox (1.0/1.2)	THF (15)	r.t.	72	100	2.2	3.3	+48.0
2	0.04	Et$_2$–Bnbox (1.0/1.2)	Tol. (50)	r.t.	144	49.1	1.9	2.8	+38.7
3	0.07	Et$_2$–Bnbox (1.0/1.2)	THF (15)	0	72	33.0	3.0	2.7	+56.4
4	0.07	Et$_2$–Bnbox (1.0/1.2)	THF (16)	−40	72	trace	–	–	–
5	0.12	Et$_2$–Bnbox (1.0/0.5)	THF (6)	0	72	100	4.0	4.1	+92.5
6	0.04	Et$_2$–Bnbox (1.0/0.5)	Tol. (20)	0	72	45.0	2.9	2.3	+47.3
7	0.12	Et$_2$–Sp (1.0/0.5)	THF (6)	0	72	32.0	2.3	3.7	+1.1

[a] 1-AMI; 0.5 g (run 1, 2), 0.3 g (run 3, 4), 0.2 g (run 5, 6, 7). [b] [Et$_2$Zn]/[1-AMI] = 0.1. [c] THF: tetrahydrofuran, Tol.: toluene. [d] r.t.: room temperature. [e] Methanol-insoluble part. [f] By GPC. [g] c = 1.0 g dL^{-1} (run 1, 2, 3, 5), c = 0.76 g dL^{-1} (run 6), c = 0.64 g dL^{-1} (run 7), l = 10 cm, in THF.
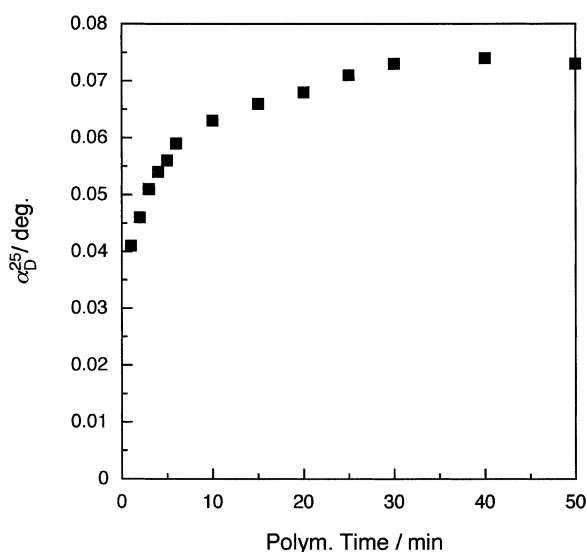

Figure 1. Change in optical rotation (α_D^{25}) during polymerization of 1-AMI with Et$_2$Zn–Bnbox in THF at r.t. Conditions: Cell length, 1.0 cm; [1-AMI], 0.36 mol L^{-1}; Initiator, [Et$_2$Zn]/[1-AMI] = 0.2; [Et$_2$Zn]/[Bnbox] = 1.0/0.5.

Figure 2. Change in specific optically rotation of poly(1-AMI) ([α]$_D^{25}$ = +92.5°, run 5 in Table I) depending on temperature (○: cooling, ●: heating).

perature. Specific optical rotation decreased with temperature. The temperature coefficient ($\Delta[\alpha]_D/\Delta T$) was 0.22° °C^{-1}. For the poly(1-AMI) adopts one–handed helical conformation observed for optically active poly-isocianates[24–26] reported by Okamoto and co-workers, the coefficient value is expected to be more larger. Therefore, change in specific optical rotation shown in Figure 2 may result from thermal relaxation of incomplete helical conformations of the polymer.

To investigate the optical activity of the poly(1-AMI) (run 5 in Table I, [α]$_D^{25}$ = +92.5°) in relation to molecular weight, GPC chromatograms were obtained by monitoring with UV and polarimetric detectors connected in series. The obtained curves are displayed in Figure 3. Top and bottom curves are due to polarimetric and UV (254 nm) detection, respectively. The shapes of the curves were very similar, indicating that the poly(1-AMI)s with different molecular weights possess equivalent optical rotation. That is, optical activity of
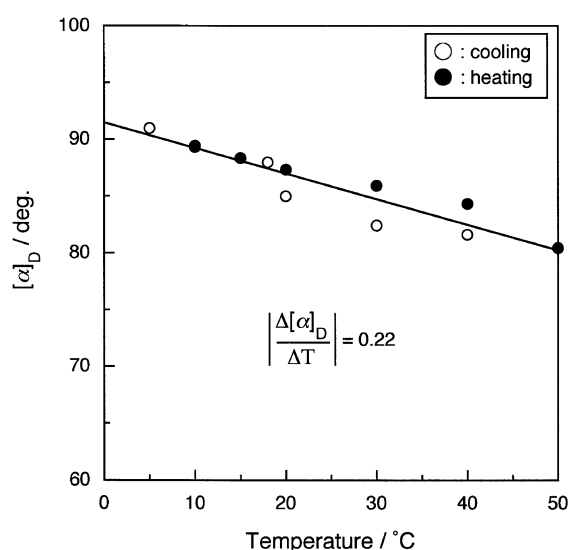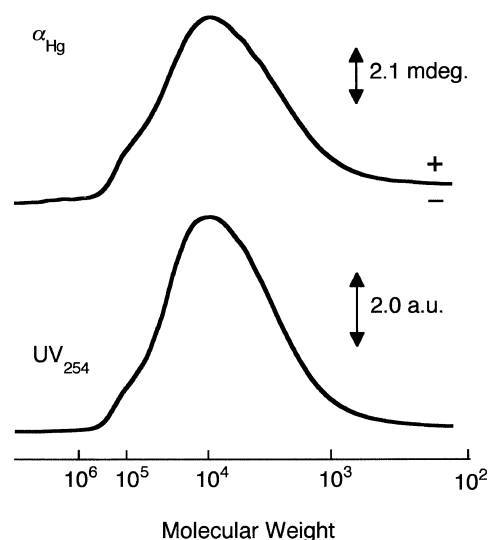

Figure 3. GPC chromatograms of poly(1-AMI) ([α]$_D^{25}$ = +92.5°, run 5 in Table I) monitored with polarimetric (top curve, α_{Hg}) and UV (bottom curve, 254 nm) detectors.

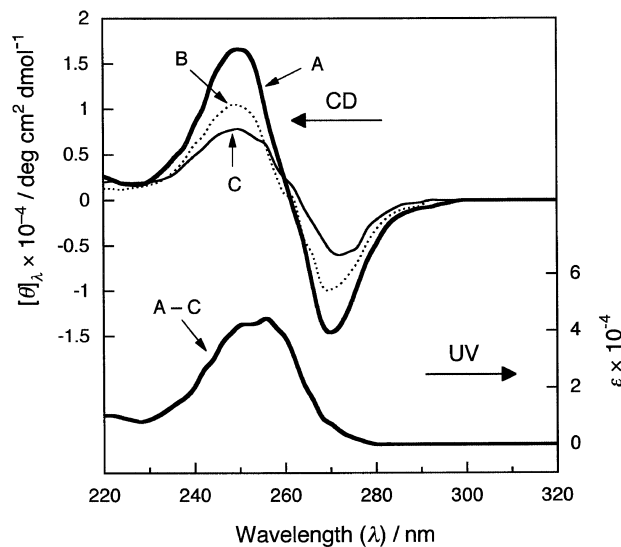**Figure 4.** CD (top curve) and UV (bottom curve) spectra of poly(1-AMI): (A) $[\alpha]_D^{25}$ = +92.5° (run 5 in Table I), (B) $[\alpha]_D^{25}$ = +48.0° (run 1 in Table I), (C) $[\alpha]_D^{25}$ = +38.7° (run 2 in Table I).

the poly(1-AMI) is independent of molecular weight. From this, optical activity of poly(1-AMI) is mainly attributable to chiral centers in the *threo-diisotactic* main chains. Information on chiral conformation for optically active poly(1-AMI) was obtained by CD and UV spectra in THF. Both spectra are depicted in Figure 4. Top and bottom curves represent CD and UV spectra, respectively. In UV spectra, all polymers exhibited similar curves. In CD spectra, as specific optical rotation increased, peak intensity increased. Each CD curve split in two peaks at 270 nm and 249 nm around the UV absorption bands, indicating the CD curves to be due to exciton coupling of ^1B_b electric transition dipole moments on the long axis of anthryl groups. The exciton–coupled circular dichroic method[27] can be applied to poly(1-AMI). (+)-Poly(1-AMI) showed negative exciton chirality with negative Cotton effect at longer wavelength and positive one at shorter wavelength. That is, long axis ^1B_b bands of anthryl groups are twisted coun-
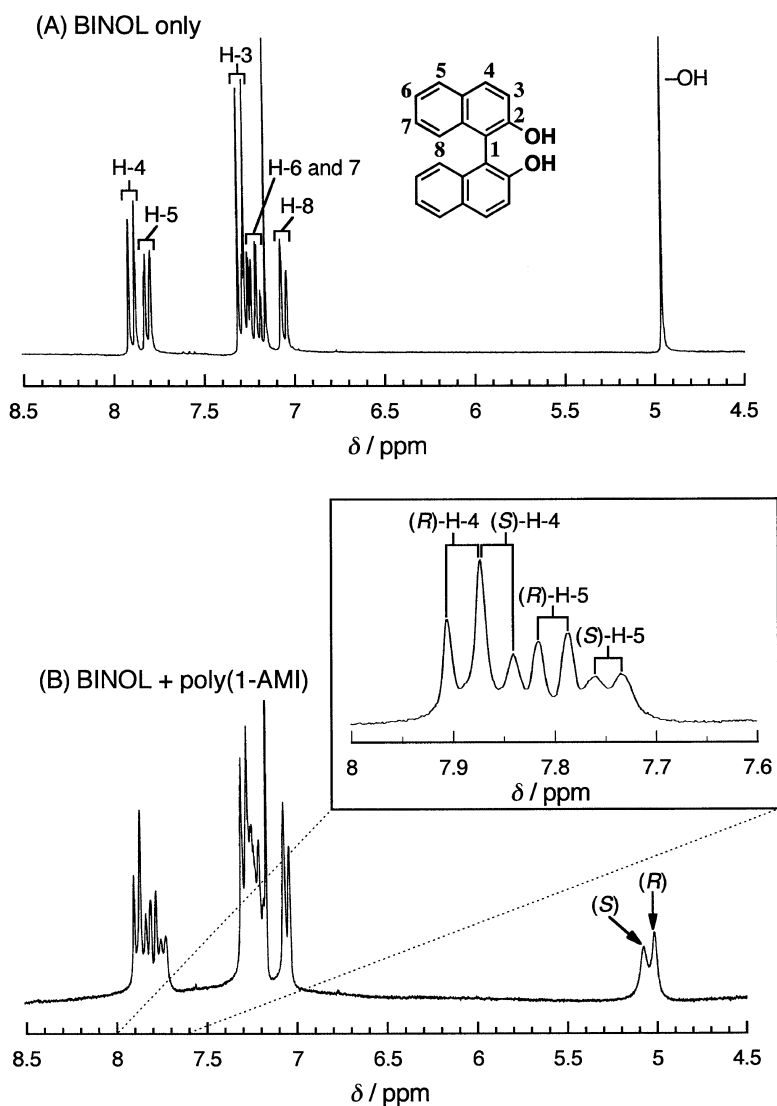

Figure 5. ^{1}H NMR spectra of BINOL (A) and a mixture (B) of BINOL and optically active poly(1-AMI) ($[\alpha]_D^{25}$ = +92.5°, run 5 in Table I) in CDCl$_3$.

terclockwise along the main chain of (+)-poly(1-AMI), indicating that the anthryl groups build chiral conformations. These chiral conformations are attributable to anthryl groups in *threo-diisotactic* sequences consisting of the same absolute configuration, such as –(*S*, *S*)–(*S*, *S*)– or –(*R*, *R*)–(*R*, *R*)–. However, no information on the main chain configuration was obtained by the spectra since no CD peaks due to ^1L_a electric transition dipole moments in parallel to the C_2 axis of succinimide unit in the polymer were observed.

Optical Resolution Ability for Poly(1-AMI)

Since optically active poly(1-AMI) possesses not only configurational chirality but also conformational one, the polymer should show the chiral recognition of some racemates. A NMR spectroscopy is a most effective method for monitoring chiral discrimination.[18, 28] Figure 5 shows ^{1}H NMR spectra of BINOL (A) and mixture (B) of BINOL and optically active poly(1-AMI) (run 5 in Table I, $[\alpha]_D^{25} = +92.5°$) in CDCl$_3$. As shown in Figure 5 (B), signals due to hydroxyl protons and methine ones at 4– and 5–positions of naphthyl groups were split, implying the polymer to interact with one enantiomer of BINOL, and intermolecular forces are due to hydrogen bonds and π–stacking. Detailed examination using chiral BINOL revealed that (+)-poly(1-AMI) selectively interacts with (*S*)-(–)-BINOL.

Optically active poly(1-AMI) (run 5 in Table I, $[\alpha]_D^{25} = +92.5°$) was coated on macroporous silica gel. The prepared slurry was packed into a HPLC column. Figure 6 shows HPLC chromatograms of BINOL monitored with polarimetric and UV detectors. BINOL was optically resolved into each enantiomer. (*R*)-(+)-BINOL was eluted first, followed by (*S*)-one. This order reflects selectivity of interaction confirmed by ^{1}H NMR spectra in Figure 5. A possible separation mechanism is shown in Chart 1. Stereochemistry of succinimide units of (+)-poly(1-AMI) is more suitable for (*S*)-(–)-BINOL interposed by hydrogen bonds and π–stacking interactions than for (*R*)-BINOL. Therefore, (+)-poly(1-AMI) interacts more strongly with (*S*)-(–)-BINOL than with (*R*)-BINOL. In this case, two chiral centers in the succinimide unit of (+)-poly(1-AMI) possess (*S*, *S*)-configurational pairs, as shown in Chart 1. Previously, the authors reported the absolute stereochemistry of poly(1-NMI).[6, 9] This report shows that (+)-poly(1-NMI) possesses more (*S*, *S*)-configurational carbon pairs than (*R*, *R*)-ones in the main chains. (+)-Poly(1-NMI) selectively interacts with (*S*)-(–)-BINOL.[29] These (+)-polymers have the same selectivity for BINOL, suggesting that (+)-polymers contain similar configurations in the main
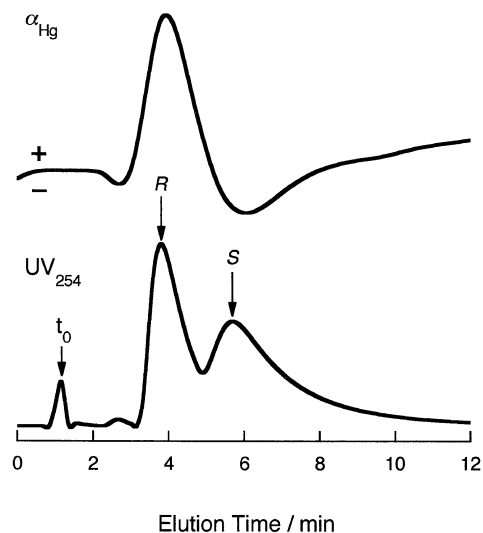

Figure 6. Chromatographic resolution of BINOL with a column of poly(1-AMI) coated on silica gel. Top and botom chromatograms were monitored by polarimetric (α_{Hg}) and UV (254 nm) detector, respectively. Conditions: Column size, 150×2.0 mm I.D.; Flow rate, 0.5 mL min^{-1}; Eluent, hexane/2-propanol = 9/1 (v/v).
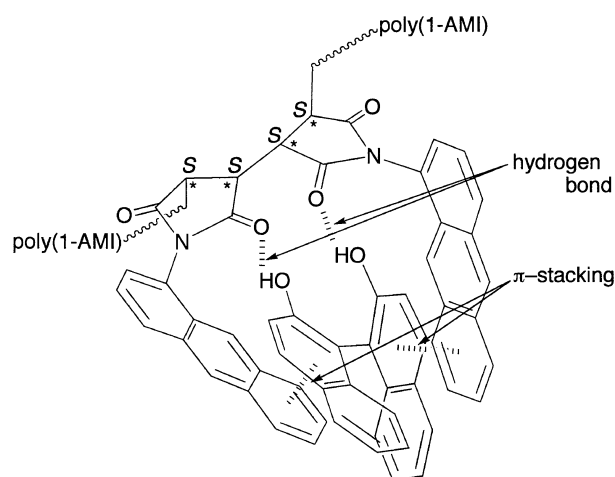

Chart 1.

chains. The main chain of (+)-poly(1-AMI) thus contains more (*S*, *S*)-configurational carbon pairs than (*R*, *R*)-ones.

CONCLUSIONS

1. Asymmetric anionic polymerizations of 1-AMI were carried out with chiral ligand–diethylzinc complexes to obtain optically active polymers.
2. Poly(1-AMI) obtained with a Et$_2$Zn–Bnbox complex showed relatively high D-line specific optical rotations of 38.7° to 92.5°.
3. ^{1}H NMR signals due to protons at 4, 5-positions and hydroxyl groups in (*RS*)-BINOL split in the presence of optically active poly(1-AMI), suggesting the polymer has chiral recognition ability to resolve BINOL.

4. (*RS*)-BINOL could be resolved by HPLC using the column prepared from optically active poly(1-AMI) coated on silica gel. (*R*)-Enantiomer was eluted first, followed by (*S*)-enantiomer.

REFERENCES

1. T. Oishi, H. Yamasaki, and M. Fujimoto, *Polym. J.*, **23**, 795 (1991).
2. K. Onimura, H. Tsutsumi, and T. Oishi, *Polym. Bull.*, **39**, 437 (1997).
3. K. Onimura, H. Tsutsumi, and T. Oishi, *Macromolecules*, **31**, 5971 (1998).
4. K. Onimura, H. Tsutsumi, and T. Oishi, *Chem. Lett.*, 791 (1998).
5. T. Oishi, K. Onimura, K. Tanaka, W. Horimoto, and H. Tsutsumi, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 473 (1999).
6. T. Oishi, K. Onimura, Y. Isobe, and H. Tsutsumi, *Chem. Lett.*, 673 (1999).
7. T. Oishi, K. Onimura, Y. Isobe, H. Yanagihara, and H. Tsutsumi, *J. Polym. Sci., Part A: Polym. Chem.*, **38**, 310 (2000).
8. Y. Isobe, K. Onimura, H. Tsutsumi, and T. Oishi, *Polym. J.*, **32**, 1052 (2000).
9. Y. Isobe, K. Onimura, H. Tsutsumi, and T. Oishi, *J. Polym. Sci., Part A: Polym. Chem.*, **39**, 3556 (2001).
10. Y. Isobe, K. Onimura, H. Tsutsumi, and T. Oishi, *Macromolecules*, **34**, 7617 (2001).
11. R. C. P. Cubbon, *Polymer*, **6**, 419 (1965).
12. Y. Okamoto and T. Nakano, *Chem. Rev.*, **94**, 349 (1994).
13. T. Nakano, K. Taniguchi, and Y. Okamoto, *Polym. J.*, **29**, 540 (1997).
14. T. Nakano, Y. Hidaka, and Y. Okamoto, *Polym. J.*, **30**, 596 (1998).
15. T. Nakano, Y. Satoh, and Y. Okamoto, *Polym. J.*, **30**, 635 (1998).
16. J. Wu, T. Nakano, and Y. Okamoto, *J. Polym. Sci., Part A: Polym. Chem.*, **36**, 2013 (1998).
17. J. Wu, T. Nakano, and Y. Okamoto, *J. Polym. Sci., Part A: Polym. Chem.*, **37**, 2645 (1999).
18. Y. Okamoto and E. Yashima, *Angew. Chem. Int. Ed.*, **37**, 1020 (1998).
19. For example:
    a) G. Hesse and R. Hagel, *Chromatographia*, **6**, 277 (1973).
    b) Y. Okamoto, M. Kawashima, K. Yamamoto, and K. Hatada, *Chem. Lett.*, 739 (1984).
    c) Y. Okamoto, M. Kawashima, and K. Hatada, *J. Am. Chem. Soc.*, **106**, 5357 (1984).
    d) I. W. Wainer, M. C. Alembic, *J. Chromatogr.*, **358**, 85 (1986).
    e) Y. Okamoto, M. Kawashima, and K. Hatada, *J. Chromatogr.*, **363**, 173 (1986).
    f) Y. Okamoto, R. Aburatani, and K. Hatada, *J. Chromatogr.*, **389**, 95 (1987).
    g) I. W. Wainer, R. M. Stiffin, and T. Shibata, *J. Chromatogr.*, **411**, 139 (1987).
    h) Y. Okamoto, K. Hatano, R. Aburatani, and K. Hatada, *Chem. Lett.*, 715 (1989).
    i) N. Enomoto, S. Furukawa, Y. Ogasawara, H. Akano, Y. Kawamura, E. Yashima, and Y. Okamoto, *Anal. Chem.*, **68**, 2798 (1996).
20. P. Y. Reddy, S. Kondo, T. Toru, and Y. Ueno, *J. Org. Chem.*, **62**, 2652 (1997).
21. P. Y. Reddy, S. Kondo, S. Fujita, and T. Toru, *Synthesis*, 999 (1998).
22. A. Abiko and S. Masamune, *Terrahedron Lett.*, **33**, 5517 (1992).
23. S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, A.-M. Faucher, and J. P. Edwards, *J. Org. Chem.*, **60**, 4884 (1995).
24. Y. Okamoto, M. Matsuda, T. Nakano, and E. Yashima, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 309 (1994).
25. K. Maeda and Y. Okamoto, *Macromolecules*, **31**, 1046 (1998).
26. K. Maeda and Y. Okamoto, *Macromolecules*, **31**, 5164 (1998).
27. N. Harada and K. Nakanishi, "Circular Dichroic Spectroscopy–Exciton Coupling in Organic Stereochemistry", University Science Books, Sausalito, CA, 1983.
28. E. Yashima, C. Yamamoto, and Y. Okamoto, *J. Am. Chem. Soc.*, **118**, 4036 (1996).
29. K. Onimura, H. Tsutsumi, and T. Oishi, 10th Int. Symp. on Chiral Discrimination, Vienna, Aug. 30–Sep. 2, Abstracts, 1998, p 106.