Macromolecules **2001,** *34,* 7617−7623

Asymmetric Polymerization of *N*-1-Naphthylmaleimide with Chiral Anionic Initiator: Preparation of Highly Optically Active Poly(*N*-1-naphthylmaleimide)

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

Received May 14, 2001; Revised Manuscript Received August 14, 2001

ABSTRACT: Asymmetric anionic homopolymerizations of *N*-1-naphthylmaleimide (1-NMI) were carried out with chiral anionic initiator consisting of diethylzinc (Et_2Zn) and (4*S*)-2,2′-(1-ethylpropylidene)bis-(4-benzyl-4,5-dihydrooxazole) (Bnbox) to obtain optically active polymers. Poly(1-NMI) obtained with diethylzinc (Et_2Zn)−Bnbox complex in THF exhibited high specific optical rotation of +296.6°. The high molecular weight part of the poly(1-NMI) resolved by gel permeation chromatography (GPC) showed the highest specific optical rotation of +762.3°. Optical activity of poly(1-NMI) with high specific optical rotation was attributed to not only configurational chirality due to asymmetric carbons in the polymer main chain but also a conformational one based on higher-order structures, i.e., partial helical conformation, judging from the dependence of specific optical rotation on temperatures and molecular weights.

Introduction

The authors have investigated asymmetric anionic polymerizations of N-substituted maleimides (RMI) with organometal−chiral ligand complexes.[1−8] Since RMI consists of a 1,2-disubstituted structure, it can be presumed that poly(RMI) produces four types structures, i.e., *threo-diisotactic, threo-disyndiotactic, erythro-diisotactic*, and *erythro-disyndiotactic* (see Chart 1). *Erythro-diisotactic* and *erythro-disyndiotactic* structures provided with *cis*-additional reaction cannot be formed because of steric hindrance due to carbonyl groups in imide ring among monomeric units.[9] That is, *trans*-additional structures, i.e., *threo-diisotactic* and *threo-disyndiotactic* structures, can be formed in the polymerization of RMI. *Threo-disyndiotactic* structures show no optical activities because (*S*,*S*)- and (*R*,*R*)-configurational pairs equivalently exist in the polymer main chains. Poly(RMI) having the *threo-diisotactic* structures can show optical activity when one of asymmetric carbon pair in monomeric unit exists in excess. Furthermore, high continuity of the same configurational pair ((*S*,*S*)- or (*R*,*R*)-) in the *threo-diisotactic* structures may afford helical conformation. Asymmetric induction to the polymer main chains was extremely affected by N-substituents, polymerization solvents, polymerization temperatures, and other polymerization conditions. Recently, the authors reported asymmetric anionic polymerizations of *N*-1-naphthylmaleimide (1-NMI, see Chart 2) with organometal−chiral ligand complexes in toluene.[10] Poly(1-NMI)s obtained with Et_2Zn−bisoxazoline derivatives in toluene exhibited high specific optical rotations ($[\alpha]_{435}^{25} = +119.2°$ to $+191.4°$). These values were higher than those of other poly(RMI). That is to say, Et_2Zn−bisoxazoline derivative complexes were suitable for the asymmetric anionic polymerizations of 1-NMI. Particularly, the use of Bnbox (see Chart 2) as bisoxazoline derivative gave high optical activity to poly(1-NMI) ($[\alpha]_{435}^{25} = +152.3°$ to $+191.4°$). On the other hand, circular dichroism spectra of the poly(1-NMI)s exhibited a split Cotton effect in the region of the ultraviolet (UV) absorption band. According to the exciton chirality method, the absolute configuration of polymer main chain was determined as follows: (+)-Poly(1-NMI) main chains can contain more (*S*,*S*)- than (*R*,*R*)-configurations. (−)-Poly(1-NMI) main chains can contain more (*R*,*R*)- than (*S*,*S*)-configurations.[10,11]

In this paper, asymmetric anionic homopolymerizations of 1-NMI with Et_2Zn−Bnbox were studied in further detail to obtain higher optically active polymers. Effects of polymerization conditions, such as polymerization solvents, initiators, and polymerization temperatures, on optical activity of poly(1-NMI) were investigated. In addition, high molecular weight part of the poly(1-NMI) was resolved by GPC. Specific optical rotation of the high molecular weight part was the highest in all poly(RMI) prepared so far.

Experimental Section

Monomer. 1-NMI was synthesized from maleic anhydride and 1-naphthylamine according to a method reported previously.[12,13] The synthetic path is shown in Scheme 1.

***N*-1-Naphthylmaleamic Acid (1-NMA).** A solution of 1-naphthylamine (4.9 g, 34 mmol) in dry benzene (50 mL) was added dropwise to a solution of maleic anhydride (3.4 g, 34 mmol) in dry benzene (100 mL) at room temperature, and then the mixture was stirred for 1 h. Yellow precipitates were collected by suction filtration to obtain 1-NMA. 1-NMA was dried under vacuum at 25 °C for 2 days [yield, 8.2 g (quant); mp 140−141 °C. ^1H NMR (δ in ppm from TMS in $CDCl_3$): 6.31 (d, 1H, $=CH-CONH-$), 6.59 (d, 1H, $=CH-COOH$), 7.46−8.17 (m, 7H, aromatic protons), 9.49 (br, 1H, $-NH-$), 10.95 (br, 1H, $-COOH$)].

***N*-1-Naphthylmaleimide (1-NMI).** 1-NMA (8.2 g, 34 mmol) in benzene (150 mL) was heated at 50 °C, and then $ZnBr_2$ (7.8 g, 34 mmol) was added in one portion. The mixture was heated at 80 °C. 1,1,1,3,3,3-Hexamethyldisilazane (HMDS, 11.0 mL, 34×1.5 mmol) was slowly added dropwise to the suspension with vigorous stirring. The reaction mixture was refluxed for 4 h. The solution was cooled to room temperature. The solution was poured into 0.5 N aqueous hydrochloric acid (100 mL) and

---

* 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.

10.1021/ma010845a CCC: $20.00

Chart 1

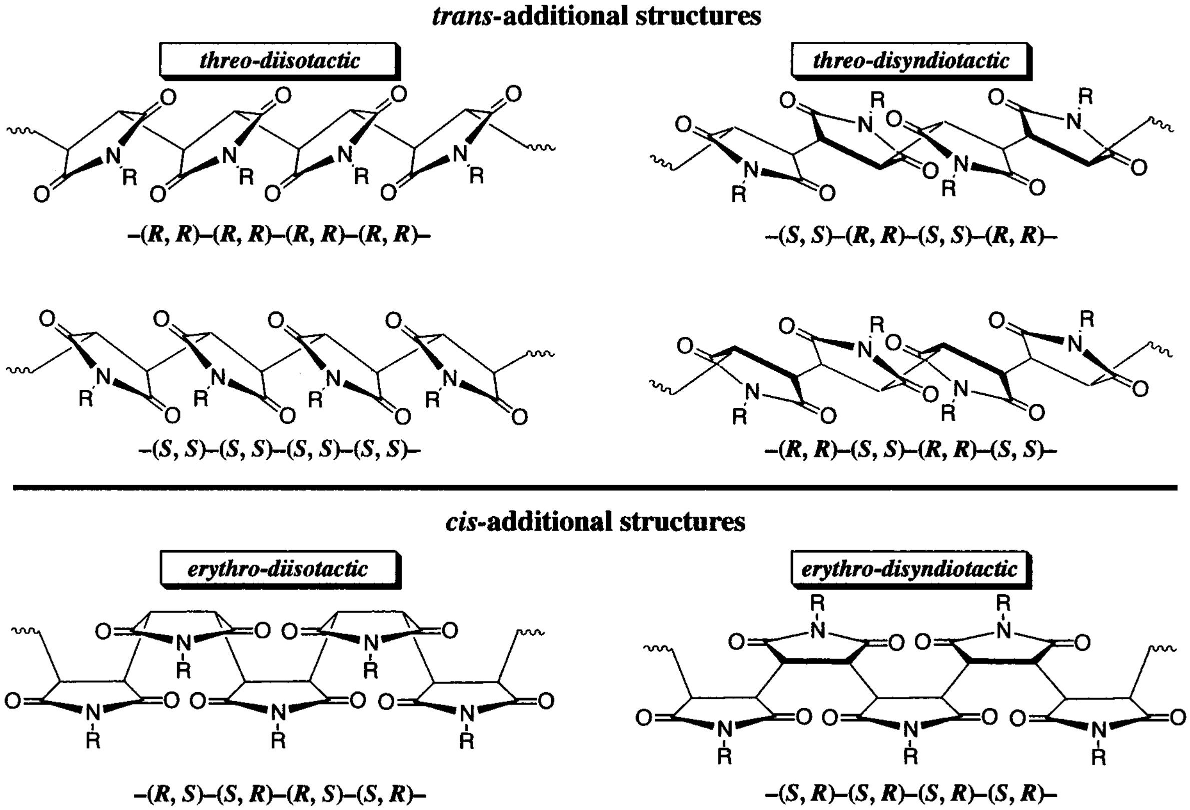
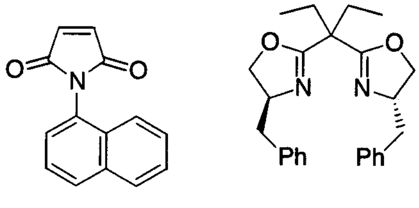


Chart 2



1-NMI **Bnbox**

extracted with ethyl acetate (50 mL × 2). The organic phase was combined and washed with saturated aqueous sodium hydrogen carbonate (50 mL × 2) and saturated brine (50 mL × 2) and dried over anhydrous magnesium sulfate. The organic solution was concentrated using an evaporator. The crude 1-NMI was purified by column chromatography using benzene as an eluent, followed by recrystallization from *n*-hexane–ethyl acetate (1/1, v/v) to obtain pure 1-NMI as a yellow crystal [yield, 6.0 g (79%); mp 114–115 °C. ^{1}H NMR (δ in ppm from TMS in $CDCl_3$): 6.96 (s, 2H, –CH=CH–), 7.35–7.97 (m, 7H, aromatic protons)].

Chiral Ligand. Bnbox was prepared from (*S*)-phenylalaninol and diethylmalonyl dichloride according to the literature[14,15] ($[\alpha]^{25}_{435} = -150.7°$, $c = 1.0$ g/dl, $l = 10$ cm, THF). Structure of Bnbox was depicted in Chart 2.

Reagents and Solvents. Commercially available organometals, i.e., *n*-BuLi and Et_2Zn in a *n*-hexane solution (Kanto Chemical Co., Inc., Tokyo, Japan), were used without purification. Solvents used for syntheses, polymerizations, and measurements were purified in the usual manner.

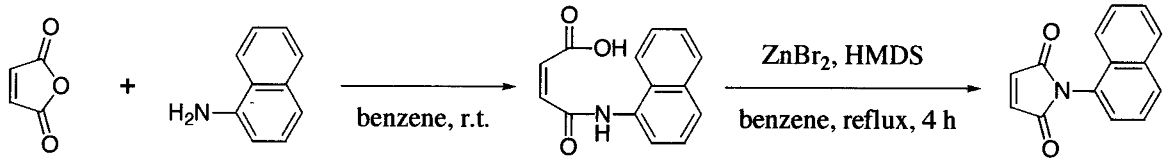
Polymerization. 1-NMI and chiral ligand were placed in a Schlenk reaction tube and pear-shaped flask, respectively. They were evacuated by vacuum pump and then replaced by dry nitrogen gas. Polymerization solvent was added to each vessel by a syringe under nitrogen atmosphere. Et_2Zn in a *n*-hexane solution was introduced into a chiral ligand solution with a syringe to prepare initiator complex. 1-NMI solution was kept at polymerization temperature. Complex solution was added by a cannula in stream of nitrogen to initiate the polymerization. Polymerization without chiral ligand was initiated by adding organometal (*n*-BuLi or Et_2Zn) in a *n*-hexane solution to a monomer solution directly with a syringe. After progress of 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 to precipitate polymer, and it was stood until the polymer precipitated. The precipitated polymer was collected by suction filtration, washed by methanol, and dried. Purification of the polymer was carried out by reprecipitation from THF–methanol systems three times. Obtained poly(1-NMI) was dried under vacuum at 25 °C for 2 days before measurements.

Measurements. Hg- ($[\alpha]^{25}_{435}$) or D-line ($[\alpha]^{25}_{D}$) specific optical rotations were measured at 25 °C in THF or $CHCl_3$–trifluoroacetic acid (9/1, v/v) using a JASCO DIP-140. ^{1}H (270 MHz) and ^{13}C NMR (68 MHz) spectra were obtained with tetramethylsilane as an internal standard using a JEOL EX-270. GPC was performed using a Shimadzu chromatopac C-R7Ae plus equipped 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 calculate number-average molecular weight ($\bar{M}_n$) and molecular weight distribution ($\bar{M}_w/\bar{M}_n$) with polystyrene as a standard.

Results and Discussion

Asymmetric Anionic Polymerization of 1-NMI. Table 1 shows the results of anionic and asymmetric anionic polymerizations of 1-NMI. Polymerizations using *only* organometals (runs 1 and 3 in Table 1) in toluene gave low polymerization yields (24.9% and 21.1%). On the other hand, the polymerizations with *n*-BuLi in THF (run 2 in Table 1) gave quantitative yield. But the yield of polymerization with *only* Et_2Zn in THF was not quantitative (55.7%; run 4 in Table 1). All asymmetric anionic polymerizations using Bnbox as chiral ligand produced optically active poly(1-NMI)s ($[\alpha]^{25}_{435} = +152.3°$ to $+422.5°$; runs 5–10 in Table 1).

Scheme 1



1-NMA **1-NMI**

Table 1. Anionic Polymerizations of 1-NMI[a]

run	initiator[b]	polym[c] solv (mL)	polym[d] temp (°C)	polym time (h)	yield[e] (%)	$\bar{M}_n$[f] × 10^{-3}	$\bar{M}_w/\bar{M}_n$[f]	$[\alpha]_{435}^{25}$[g] (deg)
1	*n*-BuLi	Tol (15)	0	24	24.9	1.7	2.1	
2	*n*-BuLi	THF (5)	0	24	100	3.1	2.1	
3	Et_2Zn	Tol (15)	20	72	21.1	1.2	1.6	
4	Et_2Zn	THF (5)	20	72	55.7	2.3	1.8	
5	Et_2Zn−Bnbox	Tol (15)	0	72	55.0	3.6	1.8	+152.3
6	Et_2Zn−Bnbox	Tol (15)	r.t.	72	92.6	3.3	1.8	+191.4
7	Et_2Zn−Bnbox	THF (5)	0	72	69.7	3.9	1.7	+190.1
8	Et_2Zn−Bnbox	THF (5)	r.t.	72	100	3.2	2.2	+296.6
9	Et_2Zn−Bnbox	THF (10)	r.t.	72	100	3.2	1.7	+282.0
10	Et_2Zn−Bnbox	THF (5)	−40	72	100 (11.3[h])	3.3	2.7	+222.6 (+422.5[i])

[a] 1-NMI; 0.5 g (runs 1−8 and 10), 1.0 g (run 9), [1-NMI] = 0.15 mol/L (in tol), 0.45 mol/L (in THF). [b] [Organometal]/[1-NMI] = 0.1, [Bnbox]/[Et_2Zn] = 1.2. [c] Tol = toluene, THF = tetrahydrofuran. [d] r.t. = room temperature. [e] Methanol-insoluble part. [f] By GPC. [g] $c = 1.0$ g/dL, $l = 10$ cm, in THF. [h] THF-insoluble part. [i] THF-insoluble part, $c = 0.6$ g/dL, $l = 10$ cm, in $CHCl_3$/trifluoroacetic acid = 9/1 (v/v).

Table 2. Anionic Polymerizations of 1-NMI[a] at Room Temperature for 72 h

run	initiator[b]	polym solv[c] Tol (mL)	polym solv[c] THF (mL)	molar ratio [Tol]/[Tol + THF] (mol %)	yield[d] (%)	$\bar{M}_n$[e] × 10^{-3}	$\bar{M}_w/\bar{M}_n$[e]	$[\alpha]_{435}^{25}$[f] (deg)
1	Et_2Zn−Bnbox	15	0	100	92.6	3.3	1.8	+191.4
2	Et_2Zn−Bnbox	12	3	75.3	100	2.5	2.0	+287.6
3	Et_2Zn−Bnbox	7.5	7.5	43.3	100	2.7	1.9	+335.3
4	Et_2Zn−Bnbox	3	12	16.0	100	2.7	2.0	+327.8
5	Et_2Zn−Bnbox	0	15	0	100	3.2	2.2	+296.6

[a] 1-NMI; 0.5 g, [1-NMI] = 0.15 mol/L. [b] [Et_2Zn]/[1-NMI] = 0.1, [Bnbox]/[Et_2Zn] = 1.2. [c] Tol = toluene, THF = tetrahydrofuran. [d] Methanol-insoluble part. [e] By GPC. [f] $c = 1.0$ g/dL, $l = 10$ cm, in THF.

These specific optical rotations were all dextrorotatory. From the results of our previous work,[10,11] the main chain carbons in these optically active poly(1-NMI)s possess more (*S*,*S*)-configurational pairs than (*R*,*R*)-ones. Yields of these polymerizations were higher than those of polymerizations using *only* Et_2Zn. Particularly, the yields of polymerizations with Et_2Zn−Bnbox (quant; runs 8−10 in Table 1) in THF were much higher than that with *only* Et_2Zn (55.7% yield; run 4 in Table 1). In comparison with runs 5−8 in Table 1, specific optical rotations of poly(1-NMI)s obtained at room temperature ($[\alpha]_{435}^{25}$ = +191.4° and +296.6°; runs 6 and 8 in Table 1) were higher than those of poly(1-NMI)s obtained at 0 °C ($[\alpha]_{435}^{25}$ = +152.3° and +190.1°; runs 5 and 7 in Table 1). In addition, the specific optical rotations of poly(1-NMI)s prepared in THF ($[\alpha]_{435}^{25}$ = +190.1° and +296.6°; runs 7 and 8 in Table 1) were higher than those in toluene ($[\alpha]_{435}^{25}$ = +152.3° and +191.4°; runs 5 and 6 in Table 1). In general, use of polar polymerization solvents such as THF and increasing temperature are undesirable for asymmetric anionic polymerizations because growing anions are liable to exist in free ions in polar solvents. Also, high temperature may cause side reactions. Therefore, asymmetric anionic polymerizations are usually carried out in nonpolar solvents at low temperature. Interestingly, the polymerizations of 1-NMI in polar solvent at relatively high-temperature tended to increase optical activity of the obtained polymers. When the polymerization was performed at −40 °C (run 10 in Table 1), the obtained poly(1-NMI) contained 11.3% of the THF-insoluble part in the methanol-insoluble one. The THF-insoluble part of the poly(1-NMI) was also insoluble in common organic solvents, such as $CHCl_3$, *N*,*N*-dimethylformamide, and dimethyl sulfoxide. But it was completely soluble in a mixed solvent consisting of $CHCl_3$−trifluoroacetic acid (9/1, v/v). The specific optical rotation ($[\alpha]_{435}^{25}$) of the THF-insoluble part was +422.5°. The value was much higher than that of THF-soluble one ($[\alpha]_{435}^{25}$ = +222.6°). This result suggested that the highly optically active poly(1-NMI) has poor solubility because of crystallinity induced by stereoregularity, i.e., *threo-diisotactic* structures.

To observe directly the change of optical rotations (α_{435}^{25}) during the asymmetric anionic polymerization of 1-NMI using the Et_2Zn−Bnbox complex in THF, the polymerization was performed in 1 cm quartz cell under the same conditions as run 8 in Table 1. The result is shown in Figure 1. The polymerization solution turned red after initiation. The solution was homogeneous during the polymerization. Optical rotations (α_{435}^{25}) of the polymerization solution increased with the progress of polymerization time, as shown in Figure 1. The optical rotation was +0.58° after 72 h, and the polymerization was terminated at this time. Specific optical rotation of the poly(1-NMI) in situ polymerization was calculated to be +236.4° by assuming that polymerization yield was quantitative. The yield and specific optical rotation ($[\alpha]_{435}^{25}$) of poly(1-NMI) after purification by

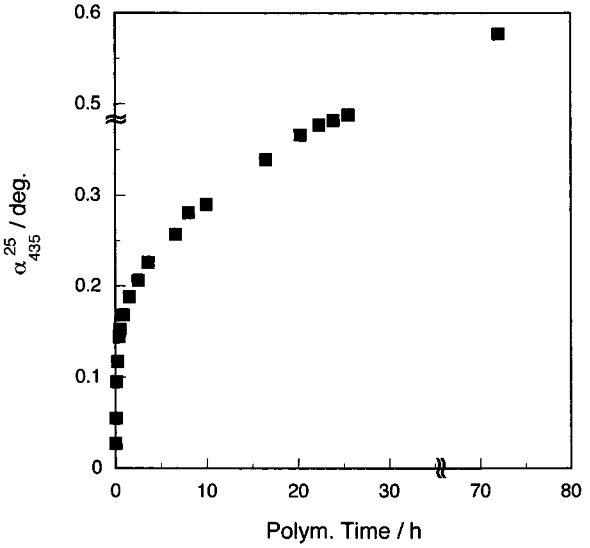


Figure 1. Optical rotation in the polymerization of 1-NMI with Et_2Zn−Bnbox in THF in quartz cell at room temperature. Conditions: cell length, 1.0 cm; 1-NMI, 0.14 mol/L; $[Et_2Zn]/[1\text{-NMI}] = 0.1$; $[Bnbox]/[Et_2Zn] = 1.2$.

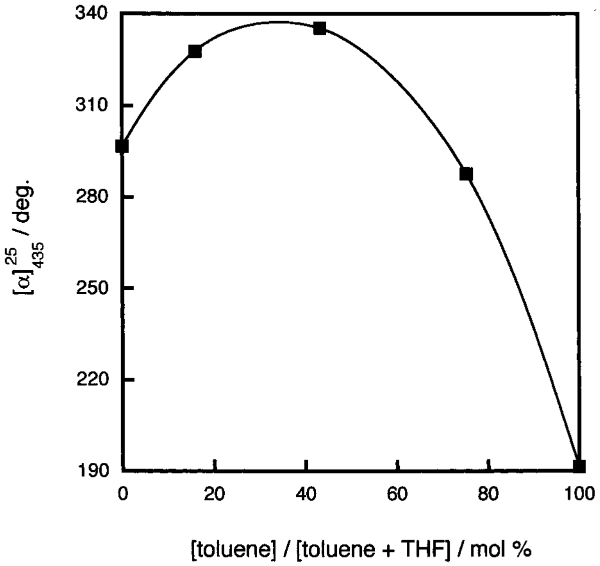


Figure 2. Effect of polymerization solvent on specific optical rotation of poly(1-NMI) (Table 2).

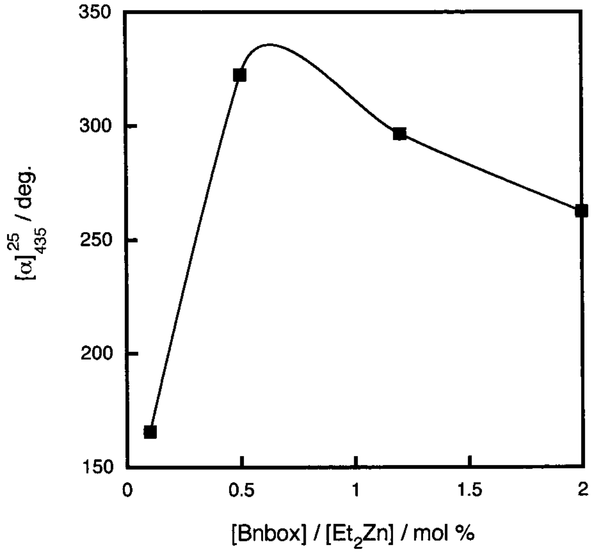


Figure 3. Effect of $[Bnbox]/[Et_2Zn]$ ratio on specific optical rotation of poly(1-NMI) (Table 3).

Table 3. Anionic Polymerizations of 1-NMI[a] in THF (5 mL) at Room Temperature for 72 h

run	initiator[b] $[Bnbox]/[Et_2Zn]$	yield[c] (%)	$\bar{M}_n$[d] × 10^{-3}	$\bar{M}_w/\bar{M}_n$[d]	$[\alpha]^{25}_{435}$[e] (deg)
1	2.0	100	1.7	2.1	+262.5
2	1.2	100	3.2	2.2	+296.6
3	0.5	100	2.8	2.2	+322.5
4	0.1	81.9	2.7	2.0	+165.6

[a] 1-NMI; 0.5 g, [1-NMI] = 0.45 mol/L. [b] $[Et_2Zn]/[1\text{-NMI}] = 0.1$. [c] Methanol-insoluble part. [d] By GPC. [e] $c = 1.0$ g/dL, $l = 10$ cm, in THF.

Table 4. Anionic Polymerizations of 1-NMI[a] in Toluene (7.5 mL) and THF (7.5 mL) for 72 h

run	initiator[b]	polym temp (°C)	yield[d] (%)	$\bar{M}_n$[e] × 10^{-3}	$\bar{M}_w/\bar{M}_n$[e]	$[\alpha]^{2}_{435}$[f] (deg)
1	Et_2Zn−Bnbox	−40	40.9	3.2	2.1	+376.7
2	Et_2Zn−Bnbox	0	100	3.5	2.4	+392.4
3	Et_2Zn−Bnbox	15	100	3.4	2.5	+383.8
4	Et_2Zn−Bnbox	20	100	2.8	1.9	+343.3
5	Et_2Zn−Bnbox	25	74.4	3.0	2.9	+287.6

[a] 1-NMI; 0.5 g, [1-NMI] = 0.15 mol/L. [b] $[Et_2Zn]/[1\text{-NMI}] = 0.1$, $[Bnbox]/[Et_2Zn] = 0.5$. [c] Tol = toluene, THF = tetrahydrofuran. [d] Methanol-insoluble part. [e] By GPC. [f] $c = 1.0$ g/dL, $l = 10$ cm, in THF.

reprecipitation from the THF−methanol system were 78.5% (methanol-insoluble part) and +215.5° ($c = 1.0$ g/dl, $l = 10$ cm, in THF), respectively. The magnitude of the specific optical rotation of poly(1-NMI) after purification ($[\alpha]^{25}_{435} = +215.5°$) was similar to that of poly(1-NMI) before termination ($[\alpha]^{25}_{435} = +236.4°$), indicating that the curve displayed in Figure 1 approximately reflected the change of optical rotations during polymerization of 1-NMI with Et_2Zn−Bnbox in THF.

Polymerization of 1-NMI was carried out under several conditions to clarify the effect of chiral ligands, polymerization solvents, and polymerization temperatures on optical activity of the poly(1-NMI) obtained and to synthesize poly(1-NMI) having more highly specific optical rotation. Table 2 shows the results of the polymerizations of 1-NMI using Et_2Zn−Bnbox in a mixed solvent of the toluene−THF system at room temperature for 72 h. The relationship between molar ratios of [toluene] and [toluene + THF] and specific optical rotations is plotted in Figure 2. When the molar ratio of [toluene] and [toluene + THF] was 43.3% (run 3 in Table 2), specific optical rotation of the poly(1-NMI) was the maximum ($[\alpha]^{25}_{435} = +335.3°$). This value was larger than that of poly(1-NMI) obtained in *only* THF ($[\alpha]^{25}_{435} = +296.6°$; run 5 in Table 2) and in *only* toluene ($[\alpha]^{25}_{435} = +191.4°$; run 1 in Table 2).

Previously, Oishi and co-workers[3] reported asymmetric anionic polymerization of *N*-cyclohexylmaleimide with the *n*-BuLi−Bnbox complex, and specific optical rotation was the highest when the molar ratio of [Bnbox] and [*n*-BuLi] was 1.0/1.2. But the effect of the molar ratio of [Bnbox] and $[Et_2Zn]$ on specific optical rotation of the polymer was unknown. The effect of the molar ratio of [Bnbox] and $[Et_2Zn]$ on the polymerization of 1-NMI is shown in Table 3 and Figure 3. When the ratio was 0.1/1.0 (run 4 in Table 3), the polymerization yield and specific optical rotation decreased, indicating that

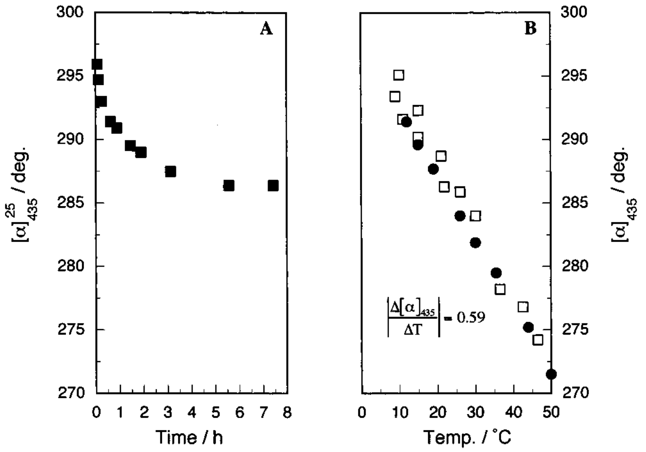


Figure 4. Change of the specific optical rotation of poly(1-NMI) (run 8 in Table 1, $[\alpha]^{25}_{435}$ = +296.6°) on time (left, A, ■) and temperature (right, B, (□) cooling, (●) heating).

a part of the polymerization was initiated by *only* Et$_2$Zn, which was achiral initiator and exhibited low catalytic activity (see run 4 in Table 1). Specific optical rotation of the poly(1-NMI) obtained using the ratio of 0.5/1.0 (run 3 in Table 3) was the highest value of +322.5°, presuming that a better structure of the initiator complex was coordinated by the molar ratio.

Table 4 shows the results of the asymmetric anionic polymerizations of 1-NMI using the optimum conditions summarized in Tables 2 and 3 (toluene = 7.5 mL, THF = 7.5 mL, [Bnbox]/[Et$_2$Zn] = 0.5/1.0) at several temperatures. When the polymerization temperature was −40 °C (run 1 in Table 4) and 25 °C (run 5 in Table 4), polymerization yields were lower than others. The low yield at −40 °C (40.9%) was attributable to poor solubility of the monomer and/or growing polymer. The low yield at 25 °C (74.4%) might be responsible for some partial side reactions. Poly(1-NMI) obtained at 0 °C exhibited the maximum specific optical rotation ($[\alpha]^{25}_{435}$ = +392.4°; run 2 in Table 4). This was the highest value in all poly(RMI)s yielded as methanol-insoluble part.

Optical Activity of Poly(1-NMI). Poly(1-NMI) obtained with Et$_2$Zn−Bnbox in THF at room temperature for 72 h (run 8 in Table 1) revealed an interesting optical property. Figure 4 displays the change in specific optical rotations of the poly(1-NMI) on time (left graph, A) and measurement temperature (right graph, B). The poly(1-NMI) showed a specific optical rotation of +296.6° at the beginning of the measurement. However, the specific optical rotations decreased with the progress of time and were constant after 5.5 h ($[\alpha]^{25}_{435}$ = +286.4°), as shown in Figure 4A. In succession, the specific optical rotations of poly(1-NMI) decreased with increasing measurement temperature as shown in Figure 4B. The temperature coefficient ($\Delta[\alpha]_{435}/\Delta T$) was 0.59. The value was relatively large among optically active poly(RMI) obtained so far.[3,6,7] If the optical activity of the poly(1-NMI) is attributable to only asymmetric centers in the polymer main chains, specific optical rotation would be scarcely changed by time or measurement temperature. The main chain of (+)-poly(1-NMI) with high specific optical rotation can contain high excess of (*S*,*S*)-configurations in *threo-diisotactic* structures.[10,11] When the continuity of (*S*,*S*)-configurations is relatively high, the poly(1-NMI) may form partial helical conformations. That is, the decrease in specific optical rotation displayed in parts A and B of Figure 4 may be due to relaxation of partial helical conformations caused by solvation and heating, respectively.

Figure 5 displays GPC chromatograms of poly(1-NMI) ($[\alpha]^{25}_{435}$ = +286.4°; run 8 in Table 1) monitored by UV (bottom curves) and polarimetric detector (top curves). A chromatogram (A) in Figure 5 was due to original poly(1-NMI) (methanol-insoluble polymer). The α_{Hg} chromatogram in the range of high molecular weight part exhibited a shoulder curve. A UV chromatogram at the range exhibited no shoulder curves. This indicates that optical rotation of high molecular weight part of the poly(1-NMI) is higher than that of low one. To separate high molecular weight part from the original poly(1-NMI), it was suspended in toluene. The toluene-insoluble part was separated from the solution by filtration. Chromatograms B and C in Figure 5 were due

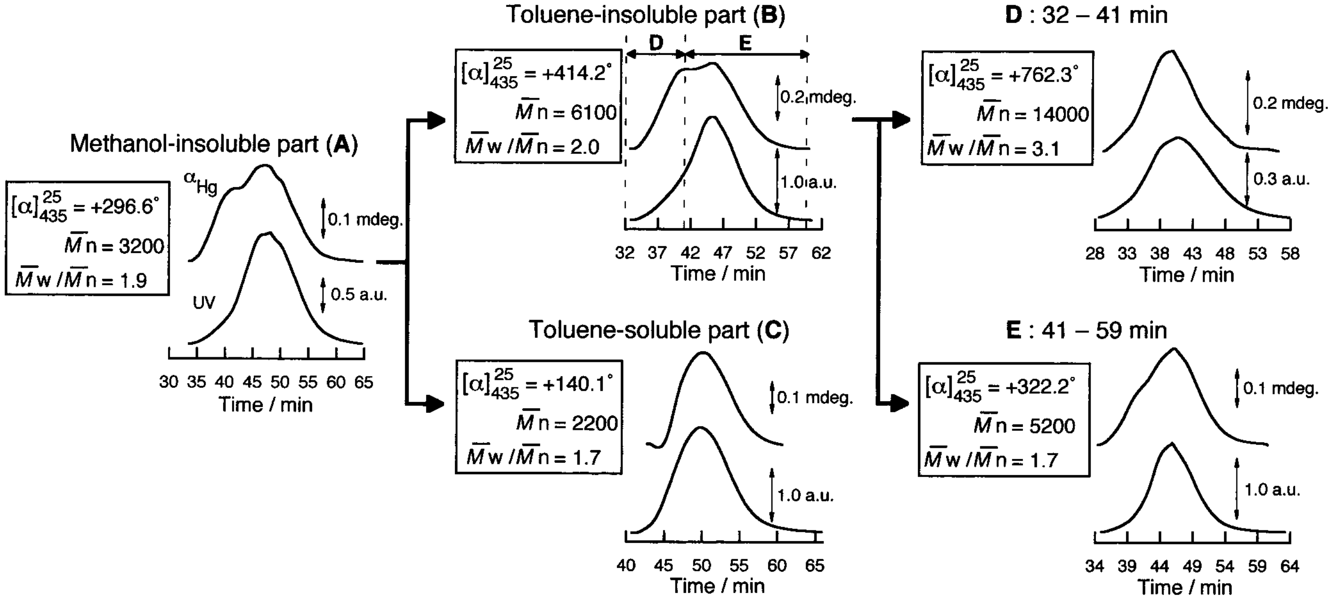


Figure 5. GPC curves monitored by ultraviolet (UV, bottom curve) and polarimetric (α_{Hg}, top curve) detector of poly(1-NMI) (run 8 in Table 1) during separation.

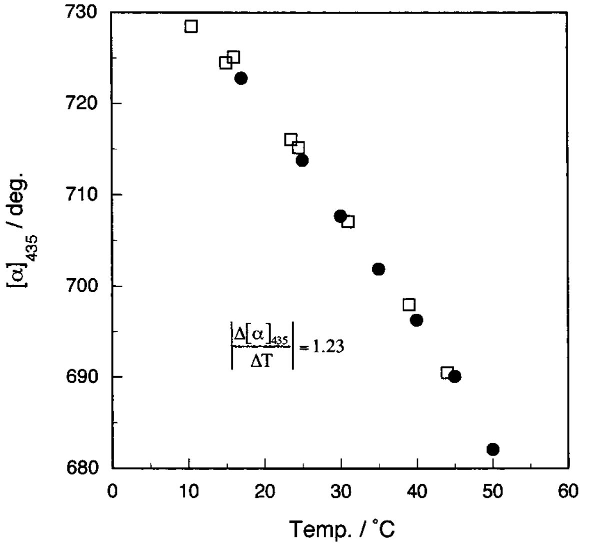


Figure 6. Change of the specific optical rotation of poly(1-NMI) ($[\alpha]_{435}^{25} = +718.6°$) on temperature (□, cooling; ●, heating).

to the toluene-insoluble and toluene-soluble part, respectively. The specific optical rotation of the toluene-insoluble part ($[\alpha]_{435}^{25} = +414.2°$, $\bar{M}_n = 6100$; Figure 5B) was larger than that of the toluene-soluble ones ($[\alpha]_{435}^{25} = 140.1°$, $\bar{M}_n = 2200$; Figure 5C). Since a α_{Hg} curve in chromatogram B still exhibited a shoulder shape in the high molecular weight range, the toluene-insoluble part was further separated into two fractions (32−41 min and 41−59 min) by GPC, as shown in Figure 5B. Chromatograms D and E were due to fractions of 32−41 and 41−59 min, respectively. In Figure 5D, the α_{Hg} curve almost corresponded to UV curve without a shoulder shape, suggesting that high molecular weight part exhibiting shoulder peak in the original poly(1-NMI) was separated. The specific optical rotation of the poly(1-NMI) of high molecular weight part (D) was +762.3° ($\bar{M}_n = 14\,000$, $[\alpha]_D^{25} = +324.4°$), which was the highest value in all poly(RMI) prepared so far. The low molecular weight part (E) of the poly(1-NMI) showed a specific optical rotation of +322.2° ($\bar{M}_n = 5200$). In all separations depicted in Figure 5, as the number-average molecular weights ($\bar{M}_n$) enlarged, the specific optical rotations increased. Interestingly, the optical activity of poly(1-NMI) formed with Et_2Zn−Bnbox in THF was dependent on molecular weights.

Poly(1-NMI) (run 9 in Table 1, $[\alpha]_{435}^{25} = +282.0°$) obtained by similar polymerization conditions to run 8 in Table 1 except for the polymerization scale was reprecipitated from THF−methanol (3/1, v/v) to separate into high and low molecular weight polymers. The specific optical rotation of the low molecular weight polymer (THF/methanol = 3/1-soluble part, $\bar{M}_n = 2500$) was +208.2°, and that of the high molecular weight polymer (THF/methanol = 3/1-insoluble part, $\bar{M}_n = 7400$) was +718.6°. Figure 6 displays the change in specific optical rotations of the high molecular weight part of the poly(1-NMI) on measurement temperature. Specific optical rotations of the poly(1-NMI) decreased with increasing measurement temperature. The poly(1-NMI) showed the highest temperature coefficient ($\Delta\ [\alpha]_{435}/\Delta T = 1.23$) in all poly(RMI) prepared so far,

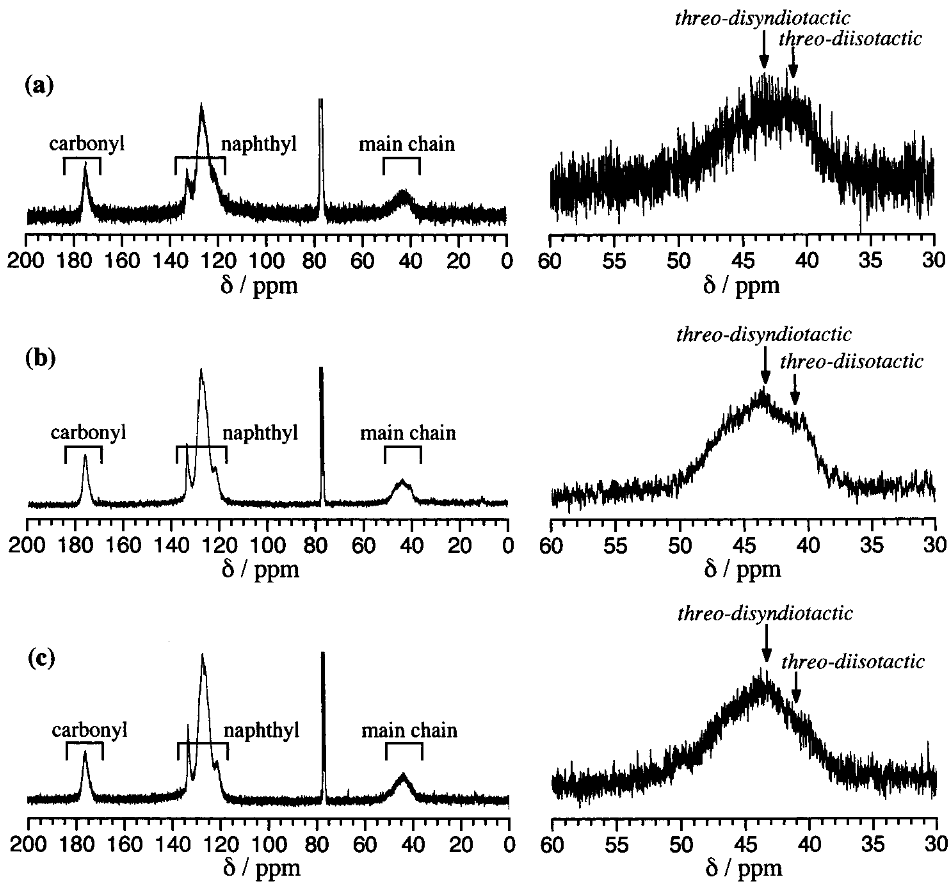


Figure 7. ^{13}C NMR spectra of poly(1-NMI): (a) THF/methanol = 3/1-insoluble part of run 9 in Table 1, $[\alpha]_{435}^{25} = +718.6°$; (b) THF/methanol = 3/1-soluble part of run 9 in Table 1, $[\alpha]_{435}^{25} = +208.2°$; (c) obtained with *n*-BuLi, run 2 in Table 1.

indicating that the high molecular weight part of the poly(1-NMI) has not only optical activity due to asymmetric carbons on the polymer main chain but also partial helical conformation formed by high continuity of (*S*,*S*)-configurations in *threo-diisotactic* structures.

To clarify the structure of the poly(1-NMI), ^{1}H and ^{13}C NMR were measured in $CDCl_3$. There was no difference in ^{1}H NMR spectra of the polymers. However, a different spectral pattern was observed in ^{13}C NMR spectra. The ^{13}C NMR spectra are shown in Figure 7. Parts a, b, and c of Figure 7 correspond to the poly(1-NMI) prepared with Et_2Zn−Bnbox (THF/methanol = 3/1-insoluble part of run 9 in Table 1, $[\alpha]_{435}^{25} = +718.6°$), with Et_2Zn−Bnbox (THF/methanol = 3/1-soluble part of run 9 in Table 1, $[\alpha]_{435}^{25} = +208.2°$), and *n*-BuLi (run 2 in Table 1), respectively. The low resolution of Figure 7a ($[\alpha]_{435}^{25} = +718.6°$) was caused by the poor solubility of the polymer. In Figure 7, there was no difference in the signals based on carbonyl and naphthyl groups among the polymers. However, the peaks around 41 ppm attributed to the main chain signals of optically active poly(1-NMI)s (Figure 7a,b) were definitely larger than those of optically inactive one (Figure 7c). In Figure 7, the peaks around 41 and 43 ppm were assigned to *threo-diisotactic* and *threo-disyndiotactic* structures, respectively, according to a previous paper reported by the authors.[10] That is, optically active poly(1-NMI) (Figure 7a,b) possesses more *threo-diisotactic* content than the optically inactive one (Figure 7c) in the main chains. On the other hand, it seems that the signal shape due to main chain carbons of highly optically active poly(1-NMI) (Figure 7a) was almost similar to that of optically active one (Figure 7b). But the relative intensity of *threo-diisotactic* signals around 41 ppm shown in Figure 7a was larger than that shown in Figure 7b. That is, the *threo-diisotactic* content of the highly optically active poly(1-NMI) (Figure 7a) was slightly larger than that of optically active one (Figure 7b). The difference of specific optical rotation between these optically active polymers may be ascribed to the *threo-diisotactic* content in the main chains. As the *threo-diisotactic* content increases, a succession of the same configurational pair, such as −(*S*, *S*)−(*S*, *S*)−(*S*, *S*)−(*S*, *S*)− or −(*R*,*R*)−(*R*,*R*)−(*R*,*R*)−(*R*,*R*)−, also enhances. Therefore, the highly optically active poly(1-NMI) contains successive −(*S*,*S*)−(*S*,*S*)− or −(*R*,*R*)−(*R*,*R*)− *threo-diisotactic* sequences, so that the polymer may form partial helical conformations.

Conclusions

(1) Asymmetric anionic polymerizations of 1-NMI were performed with Et_2Zn−Bnbox in detail to clarify the effect of polymerization conditions, such as molar ratio of [Bnbox] and [Et_2Zn], solvents, and temperatures, on optical activity of poly(1-NMI). Poly(1-NMI) obtained with the optimum conditions (conditions: initiator, [Bnbox]/[Et_2Zn] = 0.5; polymerization solvent, [toluene]/[toluene + THF] = 0.43; polymerization temperature, 0 °C) showed highly optical activity ($[\alpha]_{435}^{25} = +392.4°$).

(2) The high molecular weight part of poly(1-NMI) obtained with Et_2Zn−Bnbox in THF at room temperature for 72 h was separated by reprecipitation and GPC, and the part exhibited the highest specific optical rotation of +762.3° in all poly(RMI)s prepared so far.

(3) Poly(1-NMI) with the highest specific optical rotation ($[\alpha]_{435}^{25} = +718.6°$) showed the maximum temperature coefficient ($\Delta\ [\alpha]_{435}/\Delta T = 1.23$) in all poly(RMI)s. In addition, ^{13}C NMR spectra based on main-chain carbons revealed that the highly optically active polymer possesses more *threo-diisotactic* content than other polymers. On the basis of these results, the poly(1-NMI) may have optical activity due to partial helical conformation as well as asymmetric carbons on the polymer main chains.

Acknowledgment. This work was performed using facility of the Venture Business Laboratory, Yamaguchi University.

References and Notes

(1) Oishi, T.; Yamasaki, H.; Fujimoto, M. *Polym. J.* **1991**, *23*, 795.
(2) Onimura, K.; Tsutsumi, H.; Oishi, T. *Polym. Bull.* **1997**, *39*, 437.
(3) Onimura, K.; Tsutsumi, H.; Oishi, T. *Macromolecules* **1998**, *31*, 5971.
(4) Onimura, K.; Tsutsumi, H.; Oishi, T. *Chem. Lett.* **1998**, 791.
(5) Oishi, T.; Onimura, K.; Tanaka, K.; Horimoto, W.; Tsutsumi, H. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 473.
(6) Oishi, T.; Onimura, K.; Isobe, Y.; Yanagihara, H.; Tsutsumi, H. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 310.
(7) Zhou, H.; Onimura, K.; Tsutsumi, H.; Oishi, T. *Polym. J.* **2000**, *32*, 552.
(8) Isobe, Y.; Onimura, K.; Tsutsumi, H.; Oishi, T. *Polym. J.* **2000**, *32*, 1052.
(9) Cubbon, R. C. P. *Polymer* **1965**, *6*, 419.
(10) Isobe, Y.; Onimura, K.; Tsutsumi, H.; Oishi, T. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3556.
(11) Oishi, T.; Onimura, K.; Isobe, Y.; Tsutsumi, H. *Chem. Lett.* **1999**, 673.
(12) Reddy, P. Y.; Kondo, S.; Toru, T.; Ueno, Y. *J. Org. Chem.* **1997**, *62*, 2652.
(13) Reddy, P. Y.; Kondo, S.; Fujita, S.; Toru, T. *Synthesis* **1998**, 999.
(14) Abiko, A.; Masamune, S. *Tetrahedron Lett.* **1992**, *33*, 5517.
(15) Denmark, S. E.; Nakajima, N.; Nicaise, O. J.-C.; Faucher, A.-M.; Edwards, J. *J. Org. Chem.* **1995**, *60*, 4884.

MA010845A