

Asymmetric anionic polymerization of *n*-diphenylmethylitaconimide with chiral ligand-organometal complex

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Summary

Asymmetric anionic polymerizations of achiral *N*-diphenylmethylitaconimide (DPII) were performed with chiral ligand – organometal complexes in toluene. The obtained poly(DPII)s exhibited molecular weights of 1.5×10^3 to 6.3×10^3 and specific rotation ($[\alpha]_{435}^{25}$) between $+7.5$ to -18.4° (THF). The chirality of polymer was significantly affected by the organometals and chiral ligands. The poly(DPII) obtained with (*4S*)-2,2'-(1-ethylpropylidene)bis(4-benzyl-4,5-dihydrooxazole) (Bnbox) / *n*-butyllithium (*n*-BuLi) exhibited the highest specific rotation (-18.4°). The optical activities of the poly(DPII)s were attributed to configurational chirality of the main chain more than conformational chirality, judged from NMR, circular dichroism (CD) and GPC analyses using UV and polarimetric detectors.

Introduction

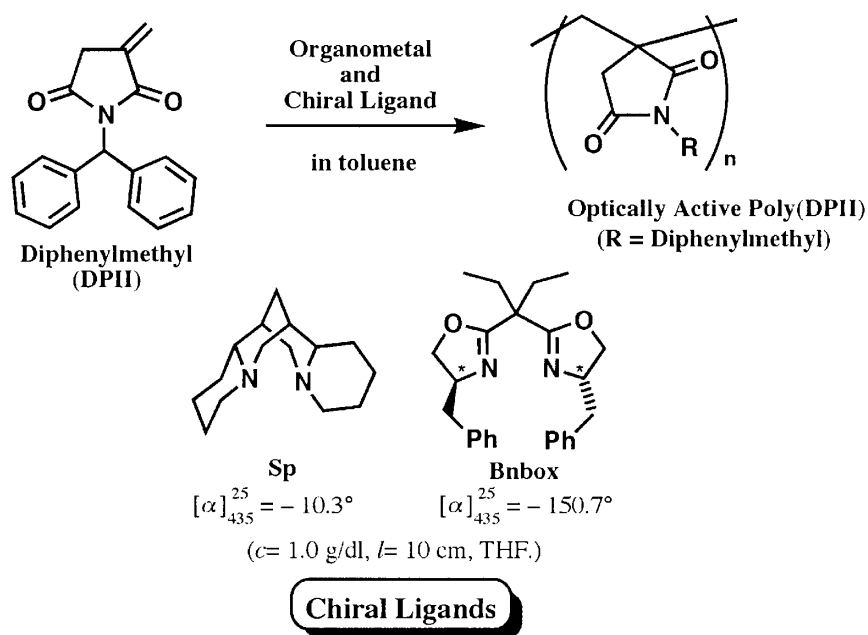
Chiral synthetic polymers are particularly interesting because of their applications as chiral stationary phases for high performance liquid chromatography (HPLC), polymeric reagents and catalysts [1,2]. Considerable attention has been focused on the syntheses of optically active polymers with chirality in the main chain [3]. From this point of view, recently, the authors have investigated the synthesis of optically active polymers, i.e., poly(*N*-substituted maleimide; RMI) with chirality in the main chain [4].

On the other hand, there have been a number of papers on the syntheses of one-handed helical polymers by asymmetric polymerizations [5]. Generally, chiral polymers with conformational chirality tend to exhibit much higher specific rotations than optically active polymers with chirality in the main chain, and the specific optical rotations have reached into the thousands of degrees for some systems. Some of these polymers have also been useful as chromatographic supports [6].

N-Substituted itaconimide (RII) is a 1,1-disubstituted ethylene type monomers with a five membered cyclic imide structure, and an exocyclic double bond. Thus, the chirality of the polymers obtained from asymmetric polymerizations of RII is

expected to be attributed to conformational chirality based on structures of the main chain because of bulkiness of five membered-cyclic imide, as well as bulky methacrylate reported previously. [3,7] In the case of poly(RII), there could be a possibility of exhibiting optical activity even though poly(RII) contains a little bulky *N*-substituent because a five membered cyclic imide group may have bulkiness enough to maintain preferential conformation of the polymer main chain by itself. Radical polymerizations and copolymerizations of RII have been accomplished so far [7,8]. Anionic polymerizations of RII (R=*n*-butyl, 4-methylphenyl, 2-ethylphenyl, 2,6-diethylphenyl) with *sec*-butyllithium at -78°C were briefly reported in some of these papers [8]. However, there have been no articles on the asymmetric anionic polymerizations of RII.

This paper describes asymmetric anionic polymerizations of diphenylmethylnitaconimide (DPII) with several chiral ligand/organometal complexes, as shown in Scheme 1. All of the obtained polymers showed optical activity, but specific rotations and molecular weights of the polymers were relatively low, compared with poly(RMI)s. The chiroptical properties of the polymers were investigated by NMR, circular dichroism (CD), and GPC analysis with both UV and polarimetric detectors.



Scheme 1. Asymmetric anionic polymerization of chiral ligand/organometal complexes

Experimental

Monomers

DPII was prepared from itaconic anhydride and diphenylmethylamine by a method of maleimide synthesis reported lately [9]. *N*-diphenylmethylnitaconimide (DPII) mp

119-120°C, $^1\text{H-NMR}$ (CDCl_3) δ : 3.37 (2H t, $J= 2.31$ Hz, C- $\text{CH}_2\text{-C=O}$), 5.63 (1H, dd, $J= 1.98, 2.31$ Hz, $\text{CH}_2\text{=C-}$), 6.34 (1H, dd, $J= 1.98, 2.31$ Hz, $\text{CH}_2\text{=C-}$), 6.64 (1H, s, CH), 7.20-7.32 (10H, m, phenyl).

Reagents and Solvents

Commercially available *n*-butyllithium (*n*-BuLi) and diethylzinc (Et_2Zn) were used without further purification. Azobisisobutyronitrile (AIBN) was purified by usual methods. (-)-Sparteine (Sp) was purchased and purified by distillation just before use. (4*S*)-2,2'-(1-Ethylpropylidene)bis(4-benzyl-4,5-dihydrooxazole) (Bnbox: $[\alpha]_{435}^{25} = -150.7^\circ$) was synthesized by the published procedure [10].

Polymerization

Anionic homopolymerizations of DPII were carried out in toluene under dry nitrogen atmosphere. A chiral ligand and organometal were mixed at 0 °C just before use. An initiator solution was added to the monomer solution cooled to 0, -40, -73 and -94 °C. The reaction was terminated by the addition of a few drops of methanol. The polymer was precipitated in excess methanol containing a small amount of hydrochloric acid, separated by filtration, and purified by re-precipitation from THF-methanol three times.

Measurements

Gel permeation chromatography (GPC) measurement of polymers was accomplished on a LC-10AS (Shimadzu) equipped with a UV detector SPD-A (Shimadzu) and on a polarimetric detector OR-990 (Japan Spectroscopic Co.) using THF as eluent at 50 °C. Four GPC columns HSG-10, 15, 20, 40H (Shimadzu) were connected in series, and molecular weight was calibrated with standard polystyrene. Hg-line specific optical rotations were measured with a JASCO DIP-140 at 25 °C. Circular dichroism (CD) spectra were obtained using a JASCO J-20C. Ultraviolet (UV) spectra were obtained with a Shimadzu UV 2200 spectrophotometer. ^1H and ^{13}C NMR spectra of polymers were measured in chloroform-*d* at room temperature in the presence of tetramethylsilane (TMS) as an internal standard using a JEOL EX-270 (^1H , 270 MHz, ^{13}C , 68.7 MHz) spectrometer.

Results and Discussion

Asymmetric Polymerization of RII

Asymmetric anionic polymerizations of achiral DPII were performed with chiral ligand / organometal complexes in toluene, as shown in Scheme 1. All the polymers had optical activity, which was influenced by organometals and chiral ligands. Table 1 shows the results of the asymmetric polymerizations of DPII. The polymerization of DPII with organolithium offered poly(DPII) in relatively high yield even at low temperatures (-40 to -94°C; runs 2, 3, 5, 6, 9, 10, 12, and 13 in Table 1). In using Et_2Zn , yields were low (runs 7, 14 in Table 1). Poly(DPII)s obtained with Bnbox/organolithium at -73 and -40 °C exhibited higher molecular weights than those obtained with other systems shown in Table 1. The molecular weights of the polymers were higher than that (2.8×10^3) obtained from the polymerization of DPII with radical initiator (run 15 in Table 1). Poly(DPII) obtained with Bnbox/*n*-BuLi possessed the highest specific rotation of -18.4° in poly(DPII)s obtained with other

systems. Poly(DPII) obtained with Sp/organolithium and Bnbox/organolithium tended to show *dextro*-rotation and *levo*-rotation, respectively.

Table 1. Anionic and Radical Polymerizations of DPII

Run	Monomer (mol/L)	Initiator (mol%)	Ligand ^a	Solvent ^b (mL)	Polym. time (h)	Polym. temp. (°C)	Yield ^c (%)	\overline{M}_n^d x10 ³	$\overline{M}_w / \overline{M}_n^d$	$[\alpha]_{435}^{25}$ (deg.)
1	DPII (0.18)	<i>n</i> -BuLi (10)	Sp	Tol. (10)	24	0	71.0	2.9	2.0	7.5
2	DPII (0.18)	<i>n</i> -BuLi (10)	Sp	Tol. (10)	72	-40	84.6	4.3	1.2	6.9
3	DPII (0.18)	<i>n</i> -BuLi (10)	Sp	Tol. (10)	48	-94	76.9	1.9	1.2	4.2
4	DPII (0.18)	FILi (10)	Sp	Tol. (10)	24	0	85.0	2.8	1.5	4.3
5	DPII (0.18)	FILi (10)	Sp	Tol. (10)	72	-40	85.9	2.4	1.5	6.7
6	DPII (0.18)	FILi (10)	Sp	Tol. (10)	48	-94	76.7	2.0	1.3	6.2
7	DPII (0.18)	Et ₂ Zn (10)	Sp	Tol. (10)	48	0	7.9	1.4	1.3	-1.8 ^f
8	DPII (0.18)	<i>n</i> -BuLi (10)	Bnbox	Tol. (10)	48	0	88.4	4.7	2.1	-1.5
9	DPII (0.18)	<i>n</i> -BuLi (10)	Bnbox	Tol. (10)	96	-40	38.6	1.7	1.2	-18.4
10	DPII (0.18)	<i>n</i> -BuLi (10)	Bnbox	Tol. (10)	48	-73	89.0	6.3	2.2	1.6
11	DPII (0.18)	FILi (10)	Bnbox	Tol. (10)	48	0	78.9	2.2	1.6	-3.3
12	DPII (0.18)	FILi (10)	Bnbox	Tol. (10)	24	-40	84.3	6.3	1.2	-3.8
13	DPII (0.18)	FILi (10)	Bnbox	Tol. (10)	48	-73	89.6	4.0	1.8	-4.5
14	DPII (0.18)	Et ₂ Zn (10)	Bnbox	Tol. (10)	96	-40	4.4	1.5	1.3	4.3
15	DPII (0.60)	AIBN (1)	-	THF (3)	24	60	91.4	2.8	1.5	-

^a [Initiator]/[Ligand] = 1.0/1.2 ^b Tol.; toluene, THF; tetrahydrofuran. ^c MeOH-insoluble part. ^d By GPC.

^e *c* = 1.0 g/dL,

l = 10 cm, THF. ^f *c* = 0.4 g/dL, *l* = 5 cm, THF. ^g *c* = 0.1 g/dL, *l* = 5 cm, THF.

The polymerization of RII forms 3 types of structures (*isotactic*, *syndiotactic* and *heterotactic*) for poly(RII), as shown in Scheme 2. Chiroptical properties of poly(RII) could be attributed to *isotactic* structure, which arises from a chirality caused only by helicity.

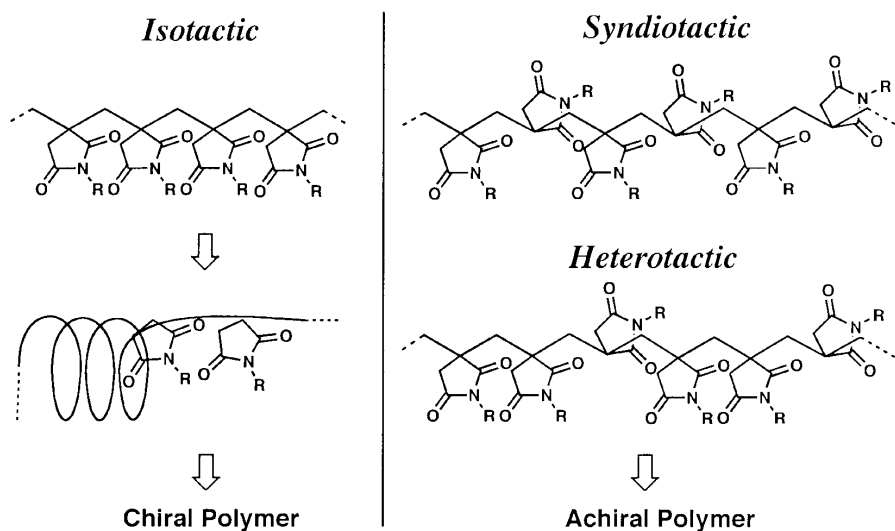


Figure 1 shows ^1H NMR spectra of DPII and poly(DPII) (run 9 in Table 1). Peaks at 5.63 ppm and 6.34 ppm assigned to *exo* vinyl groups disappeared after polymerization, suggesting that the polymerization completely proceeded at *exo* vinyl group.

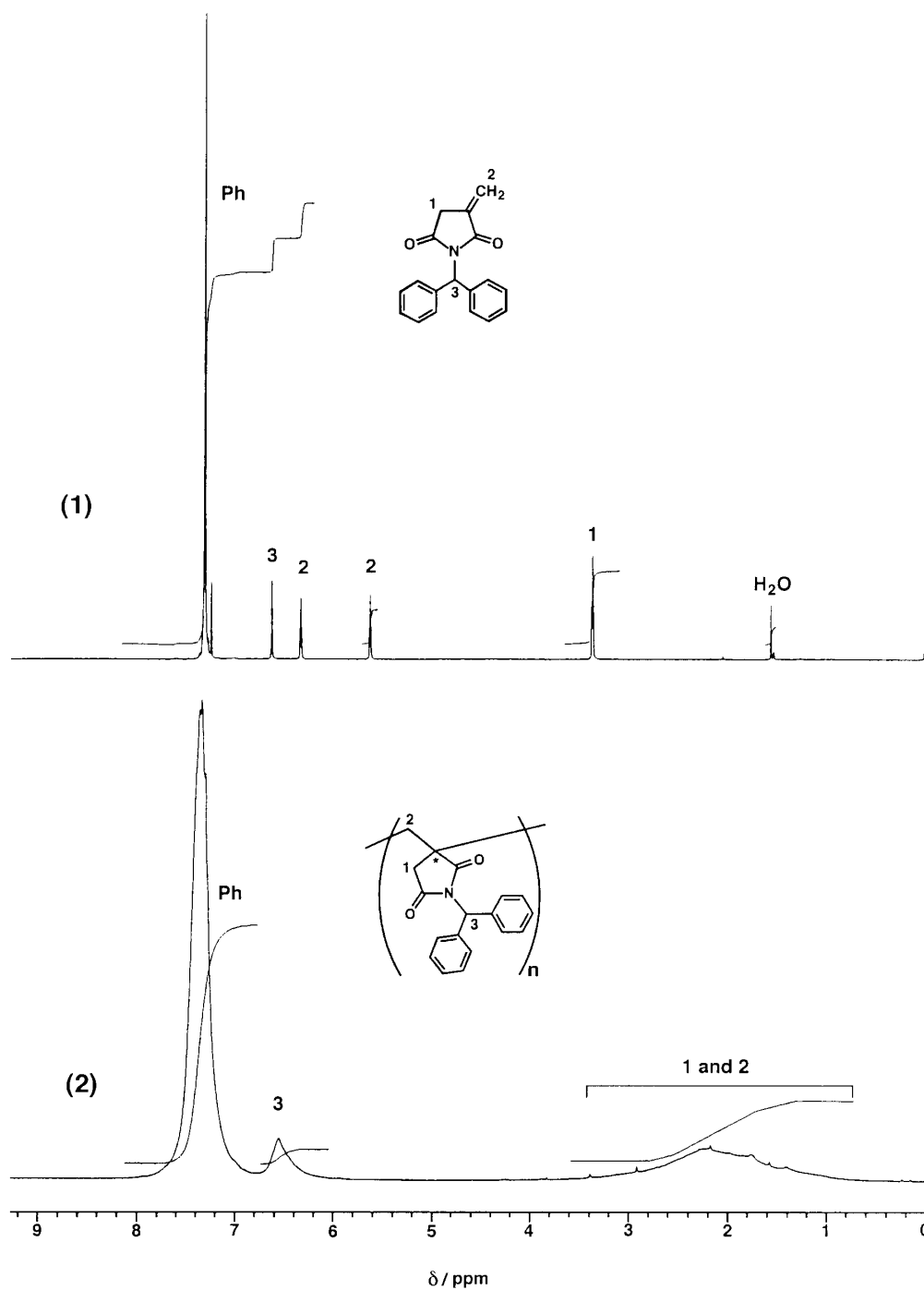


Figure 1. ^1H NMR spectra for (1) DPII and (2) poly(DPII) obtained with Bnbox/*n*-BuLi at -40 $^\circ\text{C}$ (run 9).

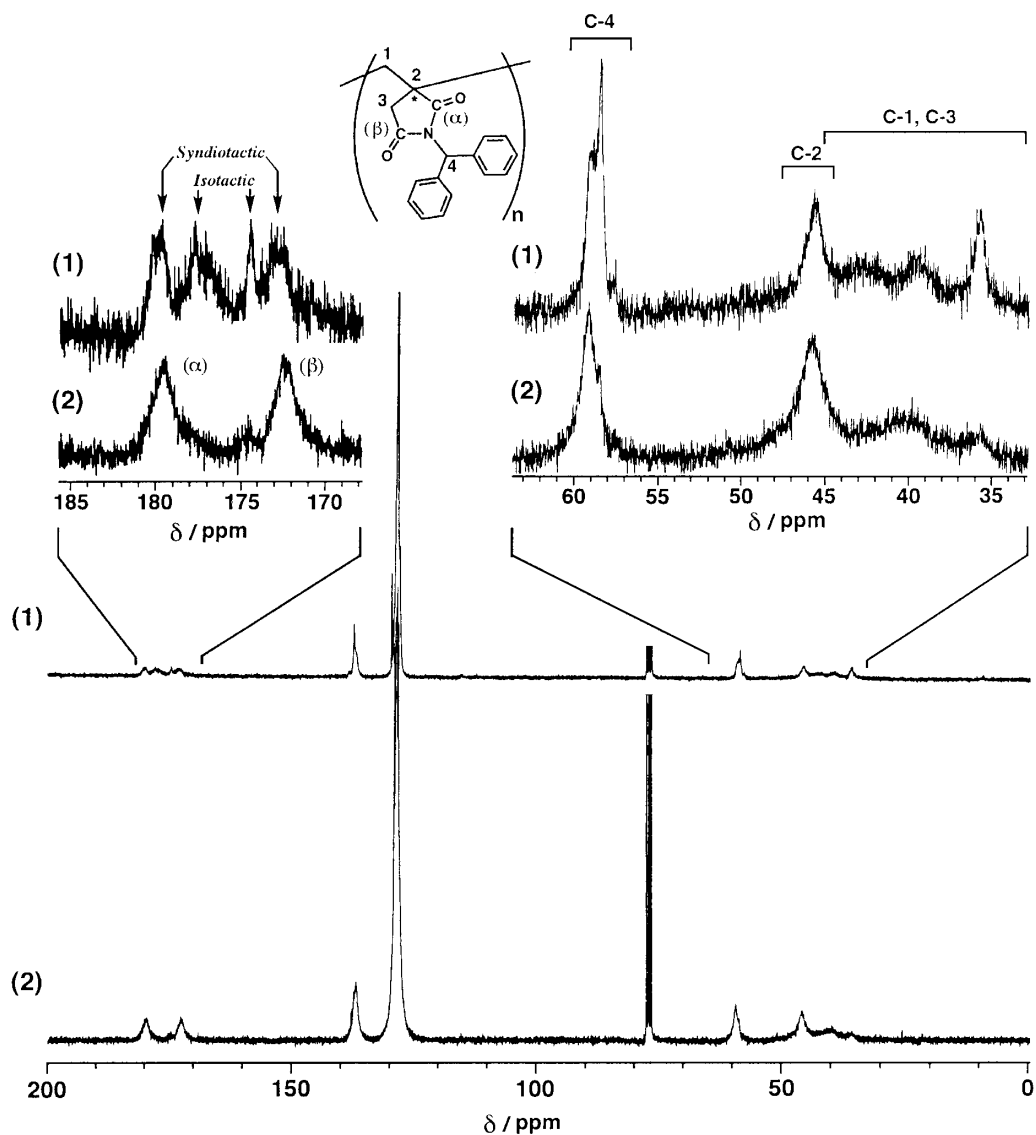


Figure 2. Expanded ^{13}C NMR spectra for poly(DPII) obtained with (1) Bnbox/*n*-BuLi at $-40\text{ }^{\circ}\text{C}$ (run 9) and (2) radical (run 15).

Figure 2 depicts ^{13}C NMR spectra of two samples poly(DPII), one obtained with Bnbox/*n*-BuLi complex (1) (run 9 in Table 1) and the other with AIBN (2) (run 15 in Table 1). The poly(DPII) obtained with AIBN showed two broad peaks (172.5, 179.5 ppm) assigned to carbonyl groups (α and β) in imide ring due to *syndiotactic* structure, according to the ^{13}C NMR data for poly(*n*-butylitaconimide) (poly(*n*-BuII)) [8]. They described that predominantly *isotactic* and *syndiotactic* poly(*n*-BuII) were produced in the anionic and radical polymerizations, respectively. On the other hand, the poly(DPII) obtained with Bnbox/*n*-BuLi exhibited new peaks at about 36 ppm, 174 ppm and 176–178 ppm. Because the polymer manifested chirality (-18.4°), the

polymer should contain *isotactic* structure in the main chain. Thus the peaks at 174 ppm and 176–178 ppm could be assigned to carbonyl carbons in imide ring due to *isotactic* structures. Consequently, poly(RII)s obtained with the chiral ligand/organometal complex could contain both *isotactic*, *syndiotactic* and/or *heterotactic* structures, as shown in Scheme 2. But we have not yet quantified the tacticity of poly(DPII)s because of the poor resolution of the peaks.

Chiroptical property and structure of the polymers

The obtained poly(DPII)s were optically active, and the chiroptical properties of the polymers were significantly affected by organometals and chiral ligands. Typical CD and UV spectra for poly(DPII)s and chiral ligand Bnbox are shown in Figure 3. Poly(DPII) revealed quite different CD peaks from the chiral ligand of Bnbox, suggesting that chirality of the polymers are attributed to not the chiral ligand but configurational and/or conformational chirality of the polymer main chain. In use of chiral ligand Bnbox/organometal system, poly(DPII) obtained with Bnbox/*n*-BuLi at -40 °C showed the highest *levo*-specific rotation of -18.4°. The stereoregularity of poly(DPII) obtained with Bnbox/*n*-BuLi at -40 °C was higher than that at 0 °C. To obtain more detailed information about relationship between molecular weights and chirality of the polymer, GPC analysis was performed using UV and polarimetric detectors.

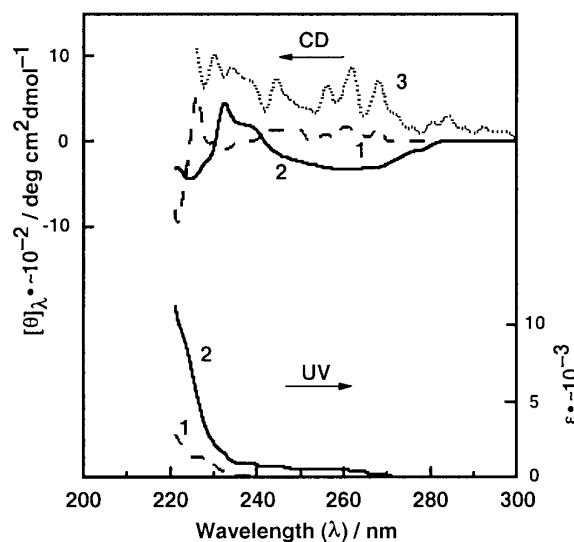


Figure 3. CD and UV spectra for poly(DPII) obtained with Bnbox/*n*-BuLi at (1) 0°C (2) -40°C and (3) ligand Bnbox.

Figure 4 depicts GPC chromatogram of poly(DPII) obtained with Bnbox/*n*-BuLi monitored by polarimetric detector (α_{Hg}) (top curve) and UV detector (bottom curve). The GPC curve by polarimetric detector in the range of low molecular weight part exhibited a shoulder curve. But the GPC curve by UV detector at the range of low molecular weight part exhibited no shoulder curves. This indicates that the chiroptical property of low molecular weight part is higher than that of high molecular

weight part. The chiroptical property of oligomer was due to configurational chirality of the main chain. The GPC curve by UV detector fully corresponded to one by polarimetric detector in the range of high molecular weight part, suggesting that chirality of the polymer was attributed to not chiral carbons of the main chain-ends but chiral stereogenicity of the whole main chain.

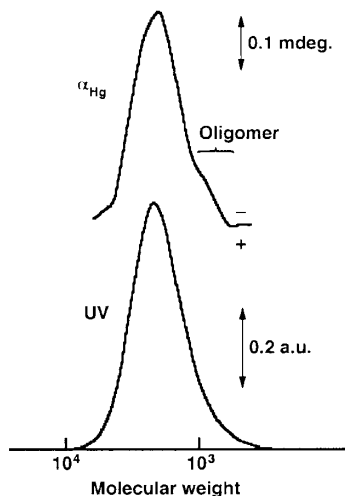


Figure 4. GPC curves for poly(DPII) obtained with Bnbox/*n*-BuLi in toluene. The top chromatogram was obtained by polarimetric detection (α_{Hg}) and the bottom by UV detection (254 nm).

Effect of temperature on the specific rotation of poly(DPII) is shown in Figure 5. The absolute value of specific rotation gradually decreased with increasing temperatures. The temperature coefficient constant of the specific rotation was very low ($|\Delta[\alpha]/\Delta T| = 0.05$).

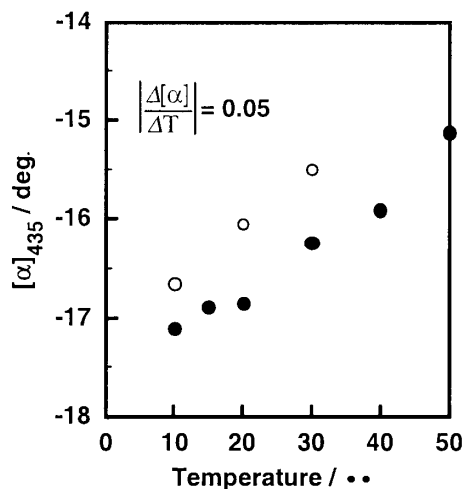


Figure 5. Effect of temperature on specific rotation of poly(DPII) obtained with Bnbox/*n*-BuLi in toluene: (E) cooling and (J) heating.

It seems that the poly(DPII) contains few helical conformations. If the polymers contained helical structures, the values of the specific rotation should remarkably vary with temperatures. Chiroptical properties of poly(DPII) were attributed to more configurational chirality than conformational one of the main.

Conclusions

- (1) Asymmetric homopolymerizations of achiral *N*-diphenylmethylytaconimide (DPII) were carried out to obtain optically active polymers, using chiral ligand / organometal complexes.
- (2) The polymerizations with chiral ligand/organolithium afforded poly(DPII)s in higher yields than those with chiral ligand/Et₂Zn.
- (3) The obtained polymers were all optically active, but the specific rotations of the polymers were relatively low. Poly(DPII) obtained with Bnbox/*n*-BuLi possessed much higher specific rotation of -18.4° than poly(DPII)s obtained with other systems.
- (4) Optical activity of poly(DPII) was attributed to rather configurational chirality than conformational one of the main chain, judging from CD, NMR spectra and GPC curves.

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