

Stereochemistry in Anionic Polymerization of Styrene Derivatives Bearing Optically Active Amino Groups at *ortho*-Position

Hiroharu AJIRO, Shigeki HABAUE, and Yoshio OKAMOTO[†]

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University,
Furo-cho, Chikusa-ku, Nagoya 464–8603, Japan

(Received September 12, 2001; Accepted December 3, 2001)

ABSTRACT: Three *ortho*-substituted styrenes, 2-[(*S*)-2-(1-pyrrolidinylmethyl)-1-pyrrolidinylmethyl]styrene (**1**), 2-[(*S*)-2-(methoxymethyl)-1-pyrrolidinylmethyl]styrene (**2**), and 2-[(*S*)-2-(*N,N*-diethylaminomethyl)-1-pyrrolidinylmethyl]styrene (**3**), were synthesized, and the effects of the *ortho*-substituents on polymerizability and the stereoregularity and chiroptical property of the polymers obtained by anionic method were examined. The anionic polymerization of **1–3** with *n*-BuLi in toluene at 0°C gave optically active polymers in good yields. Although the polymer obtained from **2** with *n*-BuLi at 0°C showed a low stereoregularity, the anionic polymerization of **1** and **3** gave the polymers with a high stereoregularity, which was supported by ¹³C NMR analysis. The poly(**1**) and poly(**3**) are likely to have regular conformation. Enantioselective oxidative coupling of a naphthol derivative was carried out using poly(**1**)s as a chiral ligand to obtain a corresponding 2,2'-binaphthol derivative.

KEY WORDS 2-(Aminomethyl)styrene / Anionic Polymerization / Stereoregularity / Optically Active Polymer / Conformation / Enantioselective Oxidative Coupling / Chiral Ligand /

The synthesis of optically active polymers with a higher order structure, associated with a helical conformation, is one of the most attractive areas in polymer science. These polymers may show interesting chiroptical properties and chiral recognition function based on their chiral conformation.¹ For example, one-handed helical poly(triphenylmethyl methacrylate) [poly(TrMA)] possesses a high chiral recognition ability as a chiral stationary phase in high-performance liquid chromatography (HPLC) to resolve a wide range of racemates.²

Besides the polymethacrylate derivatives, various polymers, such as poly(dialkylsilane), poly(isocyanates), poly(isocyanides), poly(*N,N*-disubstituted acrylamide), and poly(chloral), are known to have a one-handed helical structure.¹ However, a helical structure has been speculated only for a few polystyrene derivatives.³

Isotactic polystyrene (iPS) is well known to have a 3₁ helical form consisting of a regular repetition of the conformation (tg) of the skeletal C–C bonds in a crystalline or gel state.⁴ Isotactic poly(*ortho*-methylstyrene) has a 4₁ helical conformation, while isotactic poly(*ortho*-fluorostyrene) exists as a 3₁ helical structure.⁵ The bulkiness of *ortho*-substituents strongly affects polymer conformation.

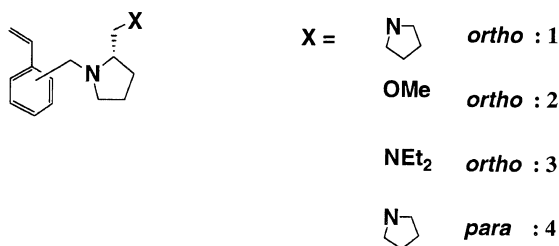
A polar substituent introduced at *ortho*-position of styrene may significantly influence the stereoregularity of the polymer through the intra- and intermolec-

ular coordination to a counter cation in anionic polymerization.^{6,7} For example, H. Yuki *et al.* reported the polymerization of *ortho*-methoxystyrene with *n*-BuLi in toluene at –78°C, which gave isotactic polymer due to the effect of the polar group at *ortho*-position. However, the polymerization at 0°C or higher temperature results in the low stereoregulation. The methoxy group at *ortho*-position may not be enough to control the stereoregularity in anionic polymerization. The proper design of *ortho*-substituted styrenes may provide the more efficient method for controlling the stereochemistry during anionic polymerization, and a stable helical structure due to the group at the *ortho*-position may be induced.

Recently, we reported that the anionic polymerization of the styrene derivative (**1**) bearing (*S*)-2-(1-pyrrolidinylmethyl)-1-pyrrolidinylmethyl group at *ortho*-position. This group has appropriate bulkiness and can strongly coordinate to a counter cation, which resulted in the formation of a stereoregular polymer with a regular conformation.⁸ Herein, we report a further investigation on the anionic polymerization of *ortho*-substituted styrenes leading to polymers with a higher order structure. In addition to **1**, two novel *ortho*-substituted styrenes, 2-[(*S*)-2-methoxymethyl-1-pyrrolidinylmethyl]styrene (**2**) and 2-[(*S*)-2-(*N,N*-diethylaminomethyl)-1-pyrrolidinylmethyl]styrene (**3**), were synthesized, and the effects of the *ortho*-substituents on their polymerizability and the stereoregularity of the obtained polymers were examined. The chiroptical properties of the obtained polymers and

[†]To whom correspondence should be addressed.

enantioselective oxidative couplings of a 2-naphthol derivative using poly(**1**) as a chiral ligand⁹ were discussed.



EXPERIMENTAL

Materials

The solvents, toluene and tetrahydrofuran (THF), used in polymerization were distilled from Na wire, and distilled again from *n*-BuLi for toluene and LiAlH₄ for THF under high vacuum just before use. *n*-BuLi was prepared from 1-chlorobutane and lithium powder in heptane under an atmosphere of argon. Monomers **1**–**4** were synthesized from *o*- or *p*-chloromethylstyrene and the corresponding amine using triethylamine in CH₂Cl₂.¹⁰

2-[(*S*)-2-Methoxymethyl-1-pyrrolidinylmethyl]styrene (**2**). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 1.57–1.75 (m, 3H, CH₂), 1.93 (m, 1H, CH₂), 2.20 (m, 1H, NCH₂), 2.73 (m, 1H, NCH₂), 2.86 (m, 1H, NCH), 3.31 (dd, 1H, *J* = 6.0 Hz and 9.2 Hz, CH₂O), 3.35 (s, 3H, OCH₃), 3.39 (d, 1H, *J* = 12.8 Hz, PhCH₂N), 3.41 (dd, 1H, *J* = 5.2 and 9.2 Hz, CH₂O), 4.19 (d, 1H, *J* = 12.8 Hz, PhCH₂N), 5.27 (dd, 1H, *J* = 1.6 and 11.0 Hz, =CH₂), 5.64 (dd, 1H, *J* = 1.6 and 17.6 Hz, =CH₂), 7.21–7.52 (m, 5H, aromatic and =CHPh). IR (neat, cm⁻¹) 2965, 2872, 2806, 1453, 1197, 1114, 909, 773. MS (FAB) *m/z* 232 ([M+H]⁺). [α]²⁵_D = -101°, [α]²⁵₃₆₅ = -424° (*c* = 0.3, CHCl₃).

2-[(*S*)-2-(*N,N*-Diethylaminomethyl)-1-pyrrolidinylmethyl]styrene (**3**). ¹H NMR (400 MHz, CDCl₃, δ, ppm): 1.00 (t, 6H, *J* = 7.2 Hz, CH₃), 1.60–1.73 (m, 3H, CH₂), 1.98 (m, 1H, CH₂), 2.14 (m, 1H, NCH₂), 2.34 (m, 1H, NCH₂), 2.47–2.60 (m, 6H, NCH₂ and NCH), 2.85 (m, 1H, NCH₂), 3.30 (d, 1H, *J* = 12.8 Hz, PhCH₂N), 4.24 (d, 1H, *J* = 12.8 Hz, PhCH₂N), 5.27 (dd, 1H, *J* = 1.2 and 11.0 Hz, =CH₂), 5.64 (dd, 1H, *J* = 1.2 and 17.4 Hz, =CH₂), 7.20–7.51 (m, 5H, aromatic and =CHPh). IR (neat, cm⁻¹) 2965, 2871, 2795, 1454, 1292, 908, 771. MS (FAB) *m/z* 273 ([M+H]⁺). [α]²⁵_D = -141°, [α]²⁵₃₆₅ = -557° (*c* = 0.3, CHCl₃).

Polymerization

Anionic polymerization was carried out in a glass ampoule equipped with a three-way-stopcock. Purified reagents were transferred to the ampoule using a syringe under dry nitrogen. The polymerization was initiated by adding a heptane solution of *n*-BuLi to a monomer solution (1.0 M, 1.5–2.0 mmol), and was terminated with a small amount of methanol. The polymers were precipitated in a large amount of methanol, then separated by centrifugation, and dried *in vacuo*.

Oxidative Coupling Reaction

Asymmetric oxidative coupling reaction of 2-hydroxy-3-naphthoic acid methyl ester with a Cu(I) catalyst under O₂ atmosphere was carried out according to the procedure reported by Nakajima *et al.*⁹ and the enantiomeric excess (ee) of an isolated product was determined by HPLC analysis using a chiral column, Chiralpak AD (Daicel) (eluent: hexane/isopropanol = 9/1).

Measurements

¹H and ¹³C NMR spectra were measured using a Varian Gemini-2000 (400 MHz for ¹H) or UNITY-INOVA-500 (500 MHz for ¹H) spectrometer in CDCl₃. Infrared (IR) spectra were recorded on a JASCO FT/IR-620 spectrometer. Mass spectra were taken on a JEOL LMS-AX505HA mass spectrometer. Optical rotation was measured on a JASCO DIP-181 or JASCO P-1030 polarimeter at 25°C. Circular dichroism (CD) spectra were obtained with a JASCO J-720L apparatus. The molecular weight of the polymer was determined by size-exclusion chromatographic analysis (SEC) on a Shodex System-21 SEC system equipped with a Shodex RI-71S, a Wyatt Technology DAWN DSP-F multiangle light-scattering (LS), and a JASCO OR-990 polarimetric detector at 40°C. Two commercial columns (Shodex KF-803 and KF-806L) were connected in series, and tetrahydrofuran (THF) was used as an eluent.

RESULTS AND DISCUSSION

The results of the radical and anionic polymerizations of **1**–**4** are summarized in Table I. We previously reported that the anionic polymerization of **1** with *n*-BuLi at 0°C proceeded in 44% yield, while the radical polymerization resulted in a low yield (Table I, entries 1 and 2).⁸ The novel monomers, **2** and **3**, were polymerized by anionic methods to investigate the effect of the optically active *ortho*-substituents on polymerizability and the stereoregularity and chiroptical property of the obtained polymers. Poly(**2**) and poly(**3**) were obtained in good yields as a methanol-insoluble fraction (Table I,

Table I. Anionic and Radical Polymerizations of Styrene Derivatives^a

Entry	Monomer	Solvent	Initiator	$\frac{[M]}{[I]}$	Temp. °C	Yield ^b %	M_n^c $\times 10^3$	M_w^c M_n	$[\alpha]_{365}^{25}$ ^d deg.
1 ^e	1	Toluene	AIBN	20	60	13 ^f	— ^g	— ^g	−283
2 ^e	1	Toluene	<i>n</i> -BuLi	20	0	44	92.8	1.30	−238 ^h
3	1	Toluene	<i>n</i> -BuLi	20	30	11	39.8	1.98	−203
4	1	Toluene	<i>n</i> -BuLi-TMEDA	20	0	63	398	1.30	−231
5	2	— ⁱ	AIBN	30	60	90 ^f	— ^g	— ^g	—
6	2	Toluene	<i>n</i> -BuLi	20	0	79 ^j	6.99 ^k	1.39 ^k	−165
7	2	Toluene	<i>n</i> -BuLi	10	0	55	6.41 ^k	1.53 ^k	−162
8	2	THF	<i>n</i> -BuLi	20	0	1	1.23 ^k	1.72 ^k	—
9	3	Toluene	<i>n</i> -BuLi	21	0	81	31.7	2.20	−408
10	4	Toluene	<i>n</i> -BuLi	30	0	28 ^l	483	1.92	−418

^a $[M] = 1.0$ M, time = 20 h. ^bMeOH-insoluble part. ^cDetermined by SEC in THF with LS. ^dIn chloroform at 25°C, $c = 0.3$. ^eRef. 8. ^fHexane-insoluble part. ^gNot determined. The obtained polymer was partially insoluble in common organic solvents. ^h $c = 0.8$. ⁱBulk. ^jTHF-soluble part: 26% yield. ^kDetected with RI. ^lAcetone-insoluble part.

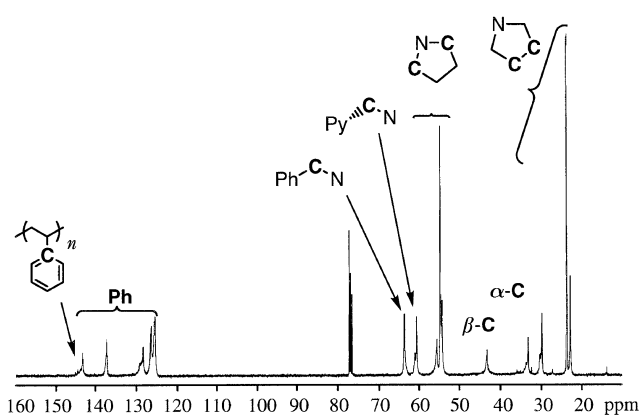


Figure 1. ¹³C NMR spectrum of poly(**1**) obtained with *n*-BuLi in toluene at 0°C (in CDCl₃ at 60°C).

entries 6, 7, and 9). The monomers were not observed in methanol-soluble parts. The polymer obtained from **2** with *n*-BuLi ($[2]/[n\text{-BuLi}] = 20$) was partially insoluble in common organic solvents, such as THF and CHCl₃, while poly(**3**) obtained with *n*-BuLi was totally soluble in these solvents.

Figure 1 shows the ¹³C NMR spectrum of poly(**1**) obtained by a typical anionic method (with *n*-BuLi in toluene at 0°C) and each peak is assigned as demonstrated in the figure. The expanded spectra of C-1 (phenyl) carbon in the polymers obtained with *n*-BuLi at 0°C are shown in Figure 2. The spectra of poly(**1**) and poly(**3**) ((a) and (c)) showed sharp patterns with small shoulder peaks, in contrast to those of poly(**2**), as well as poly(**4**) obtained with *n*-BuLi (Table I, entry 10) and the radically prepared poly(**1**) ((b), (d), and (e)), which demonstrated much broader peak patterns.

The anionic polymerization of **1** with the *n*-BuLi-*N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex at 0°C afforded a polymer in a good yield (Table I, entry 4), whereas that with *n*-BuLi at 30°C resulted in a low yield (Table I, entry 3). These polymers showed a sharp spectral pattern similar

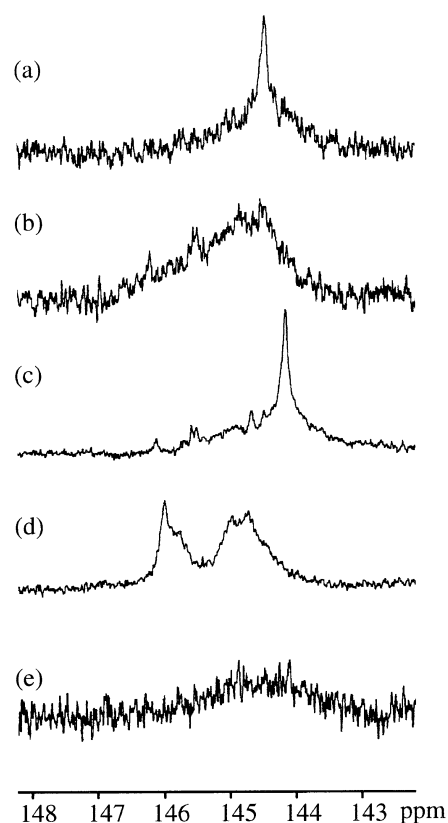


Figure 2. ¹³C NMR spectra of the C-1 (phenyl) carbon of poly(**1**) (a), poly(**2**) (b), poly(**3**) (c), poly(**4**) (d) obtained with *n*-BuLi at 0°C, and poly(**1**) (e) obtained with AIBN at 60°C.

to that of the polymer obtained with *n*-BuLi at 0°C (Figure 3). Therefore, anionically obtained poly(**1**) and poly(**3**) must have some high stereoregularity, although detailed tacticity are still unclear. The diamino groups at the *ortho*-position significantly influenced the stereoregularity of the polymers and the strong coordination power to the counter cation must be important during the anionic polymerization.

The specific rotation of poly(**1**)s prepared by the anionic method, $[\alpha]_{365}^{25} = -203$ – -238° (Table I, entries 2–4), was much smaller than those of the radically

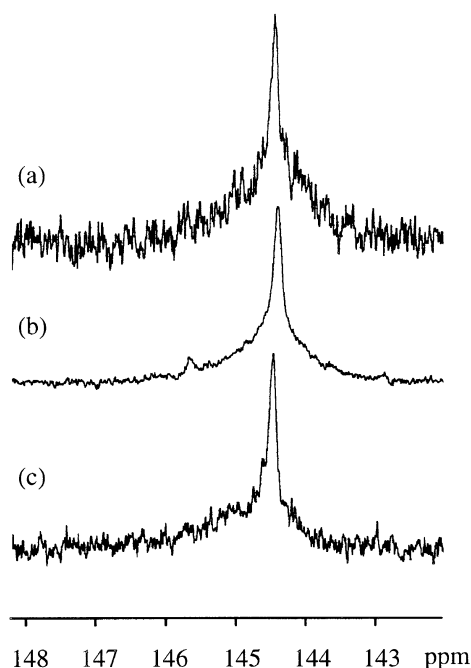


Figure 3. ^{13}C NMR spectra of the C-1 (phenyl) carbon of poly(**1**) obtained with *n*-BuLi at 0°C (a), with *n*-BuLi-TMEDA at 0°C (b), with *n*-BuLi at 30°C (c).

obtained poly(**1**) ($[\alpha]_{365}^{25} = -283^\circ$) (Table I, entry 1) and the corresponding model compound, (*S*)-1-(2-methylbenzyl)-2-(1-pyrrolidinylmethyl)pyrrolidine (**5**) ($[\alpha]_{365}^{25} = -352^\circ$), and the monomer **1** ($[\alpha]_{365}^{25} = -483^\circ$). On the other hand, its *para*-isomer, the monomer **4** ($[\alpha]_{365}^{25} = -395^\circ$), the corresponding model compound, (*S*)-1-(4-methylbenzyl)-2-(1-pyrrolidinylmethyl)pyrrolidine (**7**) ($[\alpha]_{365}^{25} = -411^\circ$), and the anionically obtained poly(**4**) using *n*-BuLi ($[\alpha]_{365}^{25} = -418^\circ$) (Table I, entry 10) showed similar specific rotation. In addition, the anionic polymerization of **2** gave the optically active polymers with a much smaller specific rotation, $[\alpha]_{365}^{25} = -162^\circ$ – -165° (Table I, entries 6 and 7), than those of the monomer **2** ($[\alpha]_{365}^{25} = -424^\circ$) and the corresponding model compound, (*S*)-1-(2-methylbenzyl)-2-methoxymethylpyrrolidine, (**6**) ($[\alpha]_{365}^{25} = -294^\circ$).¹¹ Poly(**3**) has a specific rotation, $[\alpha]_{365}^{25} = -408^\circ$ (Table I, entry 9), which was also much smaller than that of the monomer **3** ($[\alpha]_{365}^{25} = -557^\circ$). These results suggest that all the *ortho*-substituted polymers prepared by the anionic method may show some positive optical rotations associated with the main chain conformation

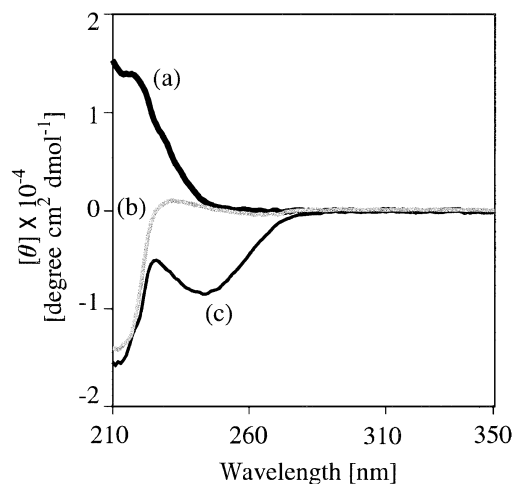
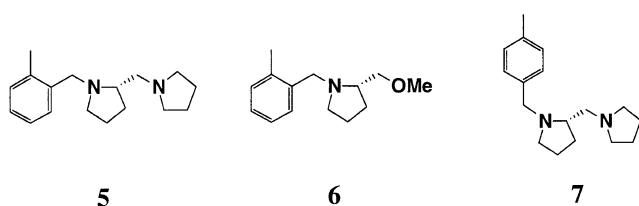


Figure 4. CD spectra of poly(**2**) obtained with *n*-BuLi (a), model compound **6** (b), and monomer **2** (c) (in THF).

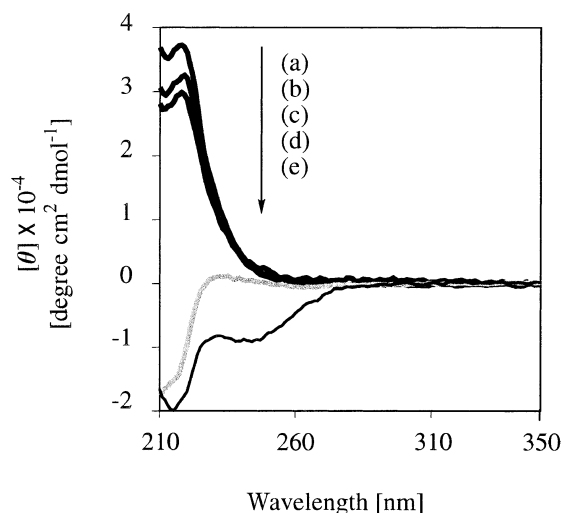


Figure 5. CD spectra of poly(**1**) obtained with *n*-BuLi at 0°C (a), *n*-BuLi-TMEDA at 0°C (b), *n*-BuLi at 30°C (c), model compound **5** (d), and monomer **1** (e) (in THF).

or configuration, in addition to the negative optical rotation due to the optically active side-chains. The chiroptical properties of the obtained polymers were investigated by CD spectroscopy.

Figure 4 shows the CD spectra of poly(**2**) (a), the model compound **6** (b), and the monomer **2** (c). Poly(**2**) exhibits a positive cotton effect around 210 nm, which is a characteristic feature of the polymer obtained by the anionic method, compared with the negative cotton effects of **2** and **6**. These results suggest that poly(**2**) may have a conformation which does not exist for **2** and **6**.

In Figure 5, the CD spectra of poly(**1**)s obtained with *n*-BuLi at 0°C (a), with *n*-BuLi-TMEDA at 0°C (b), and with *n*-BuLi at 30°C (c) are shown, together with the corresponding model compound **5** (d) and the monomer **1** (e).⁵ The polymers obtained by anionic method demonstrate a similar spectral pattern with a

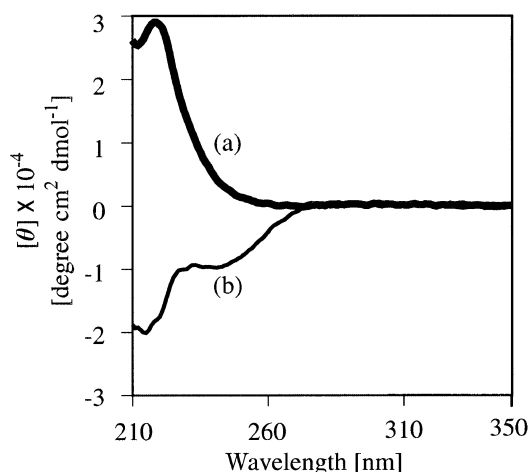


Figure 6. CD spectra of poly(3) (a) and monomer 3 (b) (in THF).

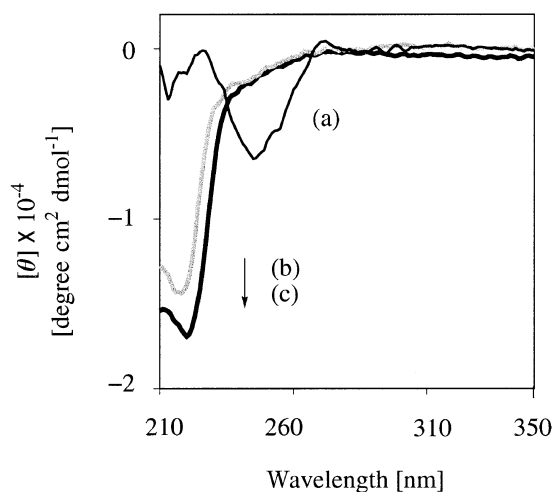


Figure 7. CD spectra of monomer 4 (a), model compound 7 (b), and poly(4) obtained with *n*-BuLi at 0°C (c) (in THF).

much stronger intensity than that of the poly(2) (Figure 4a). This may be ascribed to the fact that poly(1)s possess a higher stereoregularity than poly(2) by ^{13}C NMR analysis.

The CD spectra of 3 and poly(3) obtained with *n*-BuLi in toluene are depicted in Figure 6. The spectral pattern and peak intensity of the poly(3) are very similar to those of the poly(1) prepared under the same condition. The large positive cotton effects at 220 nm of poly(1)s and poly(3) may be caused by the higher order structure based on their high tacticity.

On the other hand, the CD spectrum (Figure 7c) of the anionically obtained poly(4), which is the *para*-isomer of poly(1), is similar to that of the corresponding model compound 7 (Figure 7b). This result indicates that the CD peak of the poly(4) is mainly due to the chiral pendant groups and not due to the main chain conformation. Therefore, these CD spectra (Figure 4–7) revealed that the anionically obtained polymers of *ortho* diaminomethyl styrene derivatives exhibit a quite

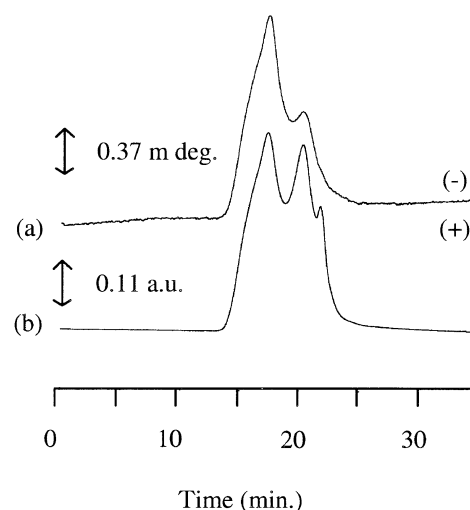


Figure 8. SEC traces of poly(2) obtained with *n*-BuLi at 0°C, monitored by polarimetric (a) and by UV (b) detectors (eluent: THF).

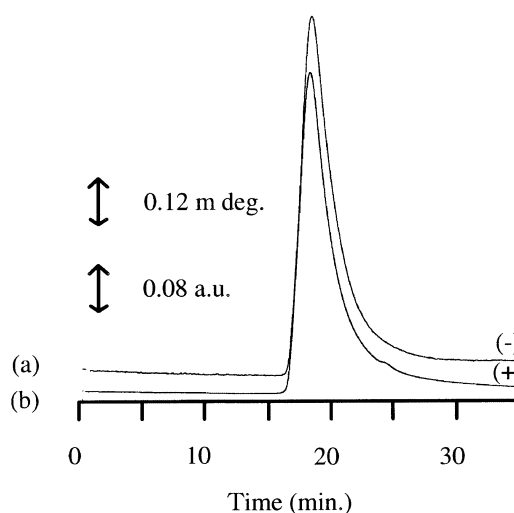
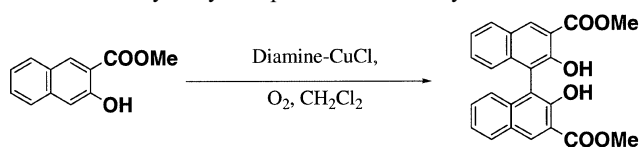


Figure 9. SEC traces of poly(1) obtained with *n*-BuLi at 0°C, monitored by polarimetric (a) and by UV (b) detectors (eluent: THF).

different cotton effect around 220 nm, probably due to the main chain conformation or configuration.

The SEC traces of poly(2) and poly(1) monitored with UV and polarimetric detectors are shown in Figures 8 and 9, respectively. Poly(2) consisted of several fractions of different molecular weights. The polarimetric detection indicates that the low molecular weight parts are less optically active than the higher molecular weight fraction. On the other hand, the SEC curve of poly(1) for the polarimetric detection is quite similar to that monitored by UV. In addition, the SEC analysis of the poly(3) showed almost the same results as those for the poly(1). These results indicate that the substituent of 2 may be less effective in controlling the stereochemistry during the anionic polymerization, and the optically active diamino groups at the *ortho*-position can more effectively generate a conformational

Table II. Enantioselective Oxidative Coupling of 2-Hydroxy-3-naphthoic Acid Methyl Ester^a

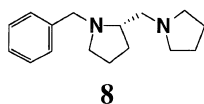
Entry	Chiral Diamine	Time h	Yield ^b	ee ^c
			%	%
1	8	24	34	25(<i>S</i>)
2	poly(4)	24	20	25(<i>S</i>)
3	poly(1) ^d	36	72	36(<i>S</i>)
4	poly(1) ^e	24	89	38(<i>S</i>)

^aDiamine (0.08 equiv.) and CuCl (0.08 equiv.) were used.

^bIsolated yields of purified product. ^cDetermined by chiral HPLC analysis. ^dRadically obtained poly(**1**) was used (Table I, entry 1). ^eAnionically obtained poly(**1**) was used (Table I, entry 2).

chirality in the main chain.

The obtained optically active polymers were applied as chiral ligands for a catalyst in an asymmetric reaction. The results of the enantioselective oxidative coupling of 2-hydroxy-3-naphthoic acid methyl ester in the presence of these polymers are listed in Table II.⁹ The reaction with (*S*)-1-benzyl-2-(1-pyrrolidinylmethyl)pyrrolidine (**8**) as a model ligand (Table II, entry 1) resulted in a low yield with 25% ee(*S*). The improvement for the activity and the enantioselectivity was not observed in the reaction using poly(**4**) as a ligand (Table II, entry 2). However, the binaphthol derivative with a higher enantioselectivity was produced with the anionically and radically obtained poly(**1**)s in better yields. Therefore, the polystyrenes with the optically active pendant groups at the *ortho*-position can be utilized as an effective polymeric ligands for this reaction, although a clear effect of main chain tacticity on the enantioselectivity was not observed.



CONCLUSIONS

The anionic polymerization of styrene derivatives bearing optically active diamino groups at *ortho*-position (**1** and **3**) gave the polymers with a higher stereoregularity, and these polymers showed different chiroptical properties, compared with the corresponding model compounds and the radically obtained polymer. This must be due to the conformation based on the stereoregular main chain.

Acknowledgments. This work was partially supported by a Grant-in-Aid for Scientific Research (No. 11450355) from the Ministry of Education, Culture, Sports, Science and Technology.

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- 6:** ¹H NMR (400 MHz, CDCl₃, δ, ppm): 1.58–1.73 (m, 3H, CH₂), 1.94 (m, 1H, CH₂), 2.19 (m, 1H, NCH₂), 2.37 (s, 3H, CH₃Ph), 2.72 (m, 1H, NCH₂), 2.88 (m, 1H, NCH), 3.33 (s, 3H, OCH₃), 3.29–3.44 (m, 3H, PhCH₂N, and CH₂O), 4.11 (d, 1H, *J* = 13.2 Hz, CH₂O), 7.10–7.29 (m, 4H, aromatic). IR (neat, cm⁻¹) 2962, 2872, 2807, 1699, 1604, 1460, 1196, 1111, 743. MS (FAB) *m/z* 220 ([M+H]⁺).