Anionic Polymerization of Novel Styrene Derivatives Bearing Various Amino Groups at *ortho*-Position

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ABSTRACT: The novel styrene derivatives bearing various amino groups at *ortho*-position, 2-(1-indoliny)lmethylstyrene (**2**), 2-(9-carbazolyl)methylstyrene (**3**), 2-(*N,N*-diphenylamino)methylstyrene (**4**), 2-(*N*-3-methoxyphenyl-*N*-phenylamino)methylstyrene (**5**), and 2-(*N*-3-methylphenyl-*N*-phenylamino)methylstyrene (**6**), were synthesized and polymerized with radical and anionic initiations. As the bulkiness of the substituents at the *ortho*-position increased, the polymerizabilities of these monomers during the radical and anionic methods significantly decreased. The anionic polymerization of **4–6** with the *n*-butyllithium (–)-sparteine complex in toluene at 0 °C afforded the optically active polymers ($[\alpha]_{365}^{25} +48^\circ$ to $+22^\circ$), whereas no optical activity was observed for the polymers of **2** and **3** obtained under the same conditions. The optically active polymers likely have a chiral helical conformation which is related to a high stereoregularity.

KEY WORDS 2-(Aminomethyl)styrene / Anionic Polymerization / Stereoregularity / Optically Active Polymer /

In the syntheses of vinyl polymers, the substituents on the monomers are very important for not only introducing functionality but also controlling the reactivities of the monomers and stereostructures during the polymerization. The *ortho*-substituents on the styrene derivatives significantly influence both the polymerizability and the structure of the obtained polymers due to the position very close to the growing chain end during the polymerization. Some *ortho*-substituted styrene derivatives have been reported.¹ For example, Natta *et al.* reported the polymerizabilities of various styrene derivatives substituted at the *ortho*-, *meta*-, and *para*-positions by methyl or other groups.² The anionic polymerization of *ortho*- and *para*-methoxystyrenes was studied by Geerts *et al.*, clarifying the fact that the favorably located at the *ortho*-methoxy group of a terminal unit induces the instantaneous initiation reaction, while the initiation of *para*-methoxystyrene was slow.³ Yuki *et al.* also investigated the stereospecific anionic polymerization of *ortho*-methoxystyrene.⁴

The proper bulky substituent on the side chain may play an important role in the formation of a higher order structure. Poly(triphenylmethyl methacrylate) with a high isotacticity, for example, can maintain the helical structure by the bulky triphenylmethyl groups, which is stable even in solution.⁵ On the other hand, it is well known that isotactic polystyrene has a 3_1 helical conformation in a crystalline or gel state.² However, few studies have been reported concerning the polystyrene derivatives with a stable helical con-

formation in solution. Ortiz and Khan reported that the optically active poly(3-methyl-4-vinylpyridine) was prepared using chiral lithium amide derivatives as an anionic initiator,⁶ but the specific rotation slowly disappeared at room temperature in solution.

Recently, we reported that the anionic polymerization of a styrene derivative (**1**) bearing the optically active diamine at *ortho*-position produced a polymer with a high stereoregularity and a stable regular conformation based on the stereoregular backbone structure.⁷ The amino group at the *ortho*-position appears to coordinate to the counter cation and control the stereochemistry during the polymerization.

In the present study, we synthesized the novel styrene derivatives bearing achiral and bulky amino groups at the *ortho*-position, 2-(1-indoliny)lmethylstyrene (**2**), 2-(9-carbazolyl)methylstyrene (**3**), 2-(*N,N*-diphenylamino)methylstyrene (**4**), 2-(*N*-3-methoxyphenyl-*N*-phenylamino)methylstyrene (**5**), and 2-(*N*-3-methylphenyl-*N*-phenylamino)methylstyrene (**6**), and investigated the effect of the *ortho*-substituents on the polymerizabilities and stereocontrol during the radical and anionic polymerizations. The chiropti-

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cal properties of the polymers obtained by the asymmetric anionic polymerization with the chiral complex of *n*-butyllithium (*n*-BuLi) and (–)-sparteine ((–)-Sp) were also discussed.

EXPERIMENTAL

Materials

α,α' -Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. (–)-Sp and 2,3-dimethoxy-1,4-bis(dimethylamino)butane ((–)- and (+)-DDB) were purified by distillation. Toluene used for the polymerization was distilled from Na wire, and distilled again from *n*-BuLi under high vacuum just before use. *n*-BuLi was prepared from 1-chlorobutane and lithium powder in heptane under an atmosphere of argon.

Syntheses of Monomers 2–6

Monomers **2–6** were synthesized from *ortho*-chloromethylstyrene and the corresponding amines using NaH in a mixture of THF and DMF at r.t. or 40 °C. The obtained **2–6** were purified by column chromatography (SiO₂, hexane/ethyl acetate = 5/1) for **2**, **5**, and **6**, or recrystallization for **3** and **4**.

2-(1-Indolyl)methylstyrene (2): Yield 91%. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 2.94 (t, 2H, J = 8.4 Hz, ArCH₂), 3.25 (t, 2H, J = 8.4 Hz, CH₂NAr), 4.25 (s, 2H, NCH₂Ar), 5.30 (dd, 1H, J = 1.6 and 11.2 Hz, =CH₂), 5.67 (dd, 1H, J = 1.6 and 17.4 Hz, =CH₂), 6.53 (d, 1H, J = 8.0 Hz, Ar), 7.05–7.55 (m, 9H, Ar and =CH). IR (neat, cm^{–1}) 2822, 1606, 1488, 1268, 915, 771, 746. MS (FAB) m/z 235 ([M]⁺).

2-(9-Carbazolyl)methylstyrene (3): Yield 56%. Recrystallized from hexane/diethyl ether = 4/1; mp 126.4–126.9 °C. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 5.46 (dd, 1H, J = 1.2 and 7.2 Hz, =CH₂), 5.55 (s, 2H, ArCH₂N), 5.76 (dd, 1H, J = 1.2 and 17.4 Hz, =CH₂), 6.50 (d, 1H, J = 8.0 Hz, Ar), 6.98 (m, 1H, Ar), 7.12–7.55 (m, 10H, Ar and =CH), 8.14

(m, 2H, Ar). IR (KBr, cm^{–1}) 3054, 1626, 1598, 1485, 1326, 750, 722. MS (FAB) m/z 284 ([M+H]⁺).

2-(*N,N*-Diphenylamino)methylstyrene (4): Yield 51%. Recrystallized from hexane/chloroform = 30/1; mp 104.3–105.1 °C. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 5.01 (s, 2H, ArCH₂N), 5.34 (dd, 1H, J = 1.6 and 11.0 Hz, =CH₂), 5.65 (dd, 1H, J = 1.6 and 17.2 Hz, =CH₂), 6.91–7.24 (m, 13H, Ar and =CH), 7.38 (m, 1H, Ar), 7.47 (m, 1H, Ar). IR (KBr, cm^{–1}) 3066, 1586, 1495, 1229, 747, 726, 696. MS (FAB) m/z 286 ([M+H]⁺).

2-(*N*-3-Methoxyphenyl-*N*-phenylamino)methylstyrene (5): Yield 75%. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.69 (s, 3H, CH₃O), 5.00 (s, 2H, ArCH₂N), 5.33 (dd, 1H, J = 1.6 and 11.0 Hz, =CH₂), 5.64 (dd, 1H, J = 1.6 and 17.2 Hz, =CH₂), 6.46 (m, 1H, Ar), 6.57 (m, 2H, Ar), 6.91–7.25 (m, 9H, Ar and =CH), 7.38 (m, 1H, Ar), 7.46 (m, 1H, Ar). IR (neat, cm^{–1}) 3025, 1591, 1494, 1165, 1077, 754, 693. MS (FAB) m/z 316 ([M+H]⁺).

2-(*N*-3-Methylphenyl-*N*-phenylamino)methylstyrene (6): Yield 60%. ¹H NMR (400 MHz, CDCl₃, δ , ppm): 2.24 (s, 3H, CH₃), 5.00 (s, 2H, ArCH₂N), 5.31 (dd, 1H, J = 1.2 and 11.0 Hz, =CH₂), 5.63 (dd, 1H, J = 1.2 and 17.4 Hz, =CH₂), 6.74–7.19 (m, 12H, Ar and =CH), 7.39 (m, 1H, Ar), 7.45 (m, 1H, Ar). IR (neat, cm^{–1}) 3060, 1595, 1496, 1454, 1264, 1239, 770. MS (FAB) m/z 300 ([M+H]⁺).

Polymerization

Anionic polymerization was carried out in a glass ampule equipped with a three-way stopcock. The polymerization was initiated by adding a heptane solution of *n*-BuLi or a mixture of *n*-BuLi solution and a chiral diamine (1:1.2) to a monomer solution (1.0 M, 1.6–2.0 mmol) under dry nitrogen, and was later 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*.

Measurements

The 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 using a JASCO P-1010 or JASCO P-1030 polarimeter at 25 °C. The UV spectra were measured on a JASCO Ubest-55 spectrophotometer. The Circular dichroism (CD) spectra were obtained using a JASCO J-720L apparatus. The molecular weight of the polymer was determined by a vapor pressure osmometer (VPO, Gonotec Osmomat 070)

and size-exclusion chromatographic analysis (SEC) using a Shodex System-21 SEC system equipped with Shodex UV-41, Shodex RI-71S, JASCO OR-990 polarimetric detector, and a Wyatt Technology DAWN DSP-F multiangle light scattering (LS) detector at 40 °C. Two commercial columns (Shodex KF-803 and KF-806L) were connected in series, and tetrahydrofuran (THF) was used as the eluent.

RESULTS AND DISCUSSION

The radical polymerization of **2–6** with α, α' -azobisisobutyronitrile (AIBN) in toluene at 60 °C was performed, and the results are listed in Table I together

Table I. Radical Polymerization of **2–8** with AIBN^a

Entry	Monomer	Conc. mol/L	Time h	Yield ^b %	M_n^c $\times 10^3$	M_w^c M_n
1 ^d	7	— ^e	24	59	26	1.9
2 ^d	8	— ^e	20	89	— ^f	— ^f
3	2	2.2	20	78	28	2.8
4	3	0.8	20	43	5.6	1.9
5	4	0.8	20	9	2.6	1.1
6	4	1.7	20	13	3.1	1.1
7	5	1.7	24	16	3.3	1.2
8	6	1.7	20	7	3.9	1.1

^aSolvent = toluene, temp. = 60 °C, [monomer]/[initiator] = 40. ^bHexane-insoluble part. ^cDetermined by SEC in THF with RI or UV (polystyrene standard). ^dRef 7. ^eIn bulk. ^fThe obtained polymer was insoluble in common organic solvents.

with those of 2-(*N,N*-dimethylamino)methylstyrene (**7**)⁷ and 2-(1-pyrrolidinyl)methylstyrene (**8**)⁷ for comparison. The polymerization of **8** in bulk gave an insoluble polymer in common organic solvents, such as THF and CHCl₃, with a good yield, although the detailed structure is unclear. The substituent at the *ortho*-position of styrene significantly affected the polymer yield and the number average molecular weight (M_n), and polymerizabilities clearly decreased with an increase in the bulkiness of the substituents. The monomers **4–6** possessing the diphenylaminomethyl group afforded the polymers in much lower yields (7–16%) with an M_n value around 3000–4000.

The results of the anionic polymerization of **2–8** with *n*-BuLi or the complexes of *n*-BuLi with the optically active diamines (–)-Sp and (–)- or (+)-DDB in toluene are summarized in Table II. The typical red color due to a benzyl anion was observed in all cases during the polymerization. The obtained polymers were fully soluble in THF and CHCl₃. As previously reported, the polymerization of **8** with *n*-BuLi in toluene at 0 °C quantitatively proceeded, although the

Table II. Anionic Polymerization of **2–8**^a

Entry	Monomer	Initiator	$\frac{[Monomer]}{[Initiator]}$	Temp. °C	Yield ^b %	M_n^c $\times 10^3$	M_w^c M_n	$[\alpha]_{365}^{25d}$ deg
1 ^e	7	<i>n</i> -BuLi	20	0	0	—	—	—
2 ^e	7	<i>n</i> -BuLi	20	30	25	3.5	1.1	—
3 ^e	8	<i>n</i> -BuLi	20	0	78 ^f	5.0	1.7	—
4	2	<i>n</i> -BuLi	20	0	95	32	2.1	—
5	2	<i>n</i> -BuLi	20	–78	0	—	—	—
6	3	<i>n</i> -BuLi	20	0	41	4.4	1.4	—
7	4	<i>n</i> -BuLi	20	0	26	4.9(6.1) ^g	1.3	—
8	5	<i>n</i> -BuLi	10	0	23	2.9	1.4	—
9	6	<i>n</i> -BuLi	20	0	12	2.2	1.7	—
10	2	<i>n</i> -BuLi-(+)-DDB	20	0	97	9.1	1.5	~0
11	3	<i>n</i> -BuLi-(–)-DDB	20	0	78	7.7	1.5	~0
12	3	<i>n</i> -BuLi-(–)-Sp	20	0	14	2.9	1.5	~0
13	4	<i>n</i> -BuLi-(–)-DDB	20	0	56	13(32) ^h	3.3	~0
14	4	<i>n</i> -BuLi-(–)-Sp	20	0	20	3.6	1.1	+39 ⁱ
15	5	<i>n</i> -BuLi-(–)-Sp	10	0	46	3.7	1.1	+48
16	5	<i>n</i> -BuLi-(–)-Sp	10	30	22	2.3	1.3	+17
17 ^j	5	<i>n</i> -BuLi-(–)-Sp	30	0	16	3.3	1.1	+37
18	6	<i>n</i> -BuLi-(–)-Sp	20	0	16	2.0	1.4	+22

^aSolvent = toluene, time = 20 h, [monomer] = 1.0 mol/L. ^bMeOH-insoluble part. ^cDetermined by SEC with RI or UV in THF (polystyrene standard). ^dIn CHCl₃, c = 0.30–0.38. ^eRef 7. ^fConversion > 99%. ^gDetermined by VPO. ^hDetermined by GPC with LS. ⁱ $[\alpha]_{365}^{25} = +10$. ^jTime = 100 h.

polymerization of **7** did not afford a methanol-insoluble polymer at the same temperature (Table II, entries 1–3) probably due to the bulkiness of the *ortho*-substituents.⁷ The polymerization of **2** with *n*-BuLi at 0 °C produced to give the polymer in a good yield (entry 4), suggesting that the indolinyll group is less hindered and provides a polymer under these conditions. However, the polymerization hardly proceeded at a lower temperature (entry 5). In contrast, the bulkiness of the substituents of **3–6**, significantly influenced the anionic polymerizability, which was rather similar to that of the radical polymerization shown in Table I, and the polymer yields for **3–6** were much lower than those for **2** and **8**.

On the other hand, the polymerization using the *n*-BuLi- (–)- or (+)-DDB complex as an initiator afforded poly(**3**) and poly(**4**) in improved yields, 78% and 56%, with a molecular weight, $M_n = 7700$ and 13000, respectively (entries 11 and 13), while these polymers showed almost no optical activity. The polymerizations of **3–6** with (–)-Sp as a chiral diamine in toluene at 0 °C resulted in lower yields than those of the polymerization with a DDB ligand. Interestingly, poly(**4**), poly(**5**), and poly(**6**), bearing *N,N*-diphenyl-amino groups as the substituent, obtained with the *n*-BuLi-(–)-Sp system, showed a positive specific rotation ($[\alpha]_{365}^{25} +22^\circ$ to $+48^\circ$, in CHCl_3) (entries 14, 15, 17, and 18), although poly(**3**) had almost no optical rotatory power (entry 12). During the asymmetric polymerization of **5** with (–)-Sp at a higher temperature (30 °C), the specific rotation of the obtained polymer decreased to $+17^\circ$ (entry 16). Therefore, the polymerization conditions and the bulkiness of the *ortho*-substituent are very important for introducing the chirality to the polymer.

Figure 1 shows the ^1H NMR spectra of **4** and poly(**4**) obtained with *n*-BuLi (Table II, entry 7). Each peak is assigned as shown in the figures, and a broad peak pattern was observed for the polymer. Figure 2 depicts the ^{13}C NMR spectra of the monomer and the polymer of **4**. The tacticity of the polystyrene derivatives is often estimated from the spectral pattern of the C-1 (phenyl) carbon,⁸ whose spectra of poly(**4**), poly(**5**), and poly(**6**) obtained under various conditions by the anionic methods are shown in Figure 3. Very different spectral patterns were observed between poly(**4**)s obtained without and with (–)-Sp (a–c), indicating that the tacticities of these polymers are different from one another and are significantly affected by the anionic initiators. In addition, a similar spectral pattern with relatively sharp peaks was observed for the polymers prepared with the complex of *n*-BuLi and (–)-Sp (c–e). Therefore, the polymers prepared with (–)-Sp must have some stereoregular structure in the main chain, although the detailed as-

Figure 1. ^1H NMR spectra of **4** (in CDCl_3 at room temperature, 400 MHz) (a) and poly(**4**) obtained with *n*-BuLi (in CDCl_3 at 60 °C, 500 MHz) (b).

Figure 2. ^{13}C NMR spectra of **4** (in CDCl_3 at room temperature, 100 MHz) (a) and poly(**4**) obtained with *n*-BuLi-(–)-DDB (in CDCl_3 at 60 °C, 125 MHz) (b).

signment of the tacticities is unclear.

The SEC traces of the optically active poly(**5**) obtained with the (–)-Sp complex (Table II, entry 15) monitored with UV and polarimetric detectors are shown in Figure 4. The SEC curve of poly(**5**) for

Figure 3. ^{13}C NMR spectra of the C-1 (phenyl) carbon of poly(**4**)s obtained with *n*-BuLi (a), with *n*-BuLi(–)-DDB (b), with *n*-BuLi(–)-Sp (c), poly(**5**) obtained with *n*-BuLi(–)-Sp (d), and poly(**6**) obtained with *n*-BuLi(–)-Sp (e) (in CDCl_3 at 60°C , 125 MHz).

Figure 4. SEC traces of poly(**5**) obtained with *n*-BuLi(–)-Sp at 0°C , monitored by UV (a) and by polarimetric (b) detectors (A series of SEC columns, Shodex KF-803, KF-806L, and Tosoh TSKgel G2000H_{XL}, was used).

the polarimetric detection is almost coincident with that monitored by UV. The SEC analyses for the optically active poly(**4**) and poly(**6**) also showed similar results. These suggest that the anionically prepared poly(**4**)–poly(**6**) with *n*-BuLi(–)-Sp may have a stable chiral conformation, probably a helical conforma-

Figure 5. UV and CD spectra of poly(**3**) (a), poly(**5**) (b), and poly(**6**) (c), obtained with *n*-BuLi(–)-Sp (in THF).

Figure 6. The polts of specific rotations of poly(**5**) during the heating in toluene at 100°C .

tion, based on the stereoregular backbone structure.

Figure 5 shows the CD spectra in THF of the polymers obtained from **5** and **6** with (–)-Sp (Table II, entries 15 and 18). A weak cotton effect was observed around 290 nm for these polymers, while no significant absorption was observed for poly(**3**) prepared with (–)-Sp.

The changes of the specific rotation during the heating of poly(**5**) (Table II, entry 15) in toluene at 100°C are plotted in Figure 6. For the first 20 h, the specific rotation rapidly decreased and the $[\alpha]_{365}^{25}$ value changed from $+59^\circ$ to $+30^\circ$ (in toluene) after about 70 h, and the recovered polymer after 168 h showed a specific rotation, $[\alpha]_{365}^{25} +28^\circ$ (in CHCl_3) and molecular weight, $M_n = 2800$. These results imply that the higher order structure of poly(**5**) formed during the asymmetric anionic polymerization was partially lost by heating.

CONCLUSIONS

Novel styrene derivatives bearing bulky amino groups at *ortho*-position, such as **4**, **5**, and **6** were synthesized, and the bulkiness of the *ortho*-substituents of these monomers significantly influenced the polymerizabilities and the stereostructure of the polymers. The asymmetric anionic polymerization with *n*-BuLi-(–)-Sp afforded optically active polymers, whose chirality may be due to a chiral conformation, probably a helical structure, based on the stereoregular main chain structure.

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