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Enantioselective Adsorption of Chiral Amines on an Induced Helical Poly(bis(4-carboxyphenoxy)phosphazene): Chiral Filter Effect

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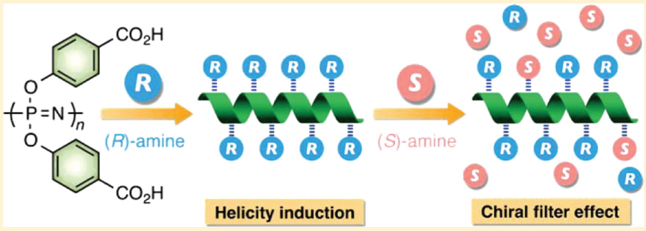
S *Supporting Information*

ABSTRACT: Optically inactive poly((bis(4-carboxyphenoxy)-phosphazene) (poly-**1**) showed a large optical rotation upon complexation with optically active (*R*)- or (*S*)-1-phenylethylamine (**2**) in DMSO after annealing the complex solution at 65 °C for ca. 2 h and maintained its optical activity in the presence of an equimolar amount of the opposite-handed **2**. The detailed analysis of the enantiomeric excess of **2** adsorbed on the poly-**1** revealed that the helical poly-**1** induced by (*R*)- or (*S*)-**2** most likely acts as a "*chiral filter*" to exclude one enantiomer from racemic **2**, resulting in the retention of its induced helical structure.



INTRODUCTION

Rodlike dynamic helical polymers with a controlled helix sense, such as polyisocyanates,[1] polysilanes,[2] polyisocyanides,[3] poly(carbodiimide)s,[4] and polyacetylenes,[5] show particularly interesting chiroptical properties, such as amplification of chirality,[1−6] memory effect,[7] chirality sensing,[8] chiral recognition,[9] and enantioselective catalysts for asymmetric synthesis[10] in covalent and noncovalent helical systems.[11]

We previously reported a unique preferred-handed helix induction in a poly(organophosphazene), poly(bis(4-carboxyphenoxy)phosphazene) (poly-**1**), and its memory of the helical chirality.[12] Poly-**1** is a soft, flexible polymer[13] with no stereogenic center and seems to be achiral, but it forms a helical conformation with an excess one-handedness in dimethyl sulfoxide (DMSO) in the presence of the optically active amine (*R*)-1-phenylethylamine ((*R*)-**2**). Upon heating the solution at 65 °C for ca. 2 h, the optical rotation showed a large negative value, the sign of which was opposite to that of (*R*)-**2** (Figure 1).[12] In contrast, the optical rotation of a model compound of poly-**1**, hexakis(4-carboxyphenoxy)cyclotriphosphazene (**CT**), hardly changed after annealing with (*R*)-**2**, and the sign and net specific rotation were the same as those of (*R*)-**2**. Interestingly, the optical activity of the poly-**1**−(*R*)-**2** solution was retained after the further addition of an equivalent amount of (*S*)-**2**.[12] These observations were ascribed to the memory of the induced helical conformation[7,14] of poly-**1** after the (*R*)-**2** complexed with poly-**1** was randomly replaced by (*S*)-**2** or that the helical poly-**1** induced by (*R*)-**2** may act as a "*chiral filter*" to exclude one enantiomer from the racemic amines (Figure 1).[7c]

The present study is concerned with the mechanism of this unexpected memory or chiral filter effect observed in poly-**1**. We then prepared poly-**1** with a different molecular weight (MW) (poly-**1L** and poly-**1H** for low and high MWs, respectively) (Figure 1) in order to investigate the effect of the MW on the helicity induction efficiency in poly-**1** and determined the enantiomeric excess (ee) values of **2** adsorbed on the induced helical poly-**1L** and poly-**1H**. Changes in the morphology of poly-**1L** and poly-**1H** in the presence and absence of **2** before and after annealing on the helicity induction in poly-**1** with (*R*)-**2** were also investigated by measuring the time-dependent changes in the atomic force microscopy (AFM) images of poly-**1H** on mica and the viscosity of the solutions of poly-**1L** and poly-**1H** with or without (*R*)-**2** in DMSO.

RESULTS AND DISCUSSION

Helicity Induction in Poly-1 and Chiral Filter Effect. Poly-**1L** and poly-**1H** were prepared according to the reported method developed by Allcock et al.[15] (Scheme 1 in Experimental Section). The number-average MW (M_n) and its molecular weight distribution (M_w/M_n; M_w is the weight-average molecular weight) of poly-**1L** and poly-**1H** were 1.1 × 10^5 and 1.06 and 3.2 × 10^6 and 1.18, respectively, as determined by size exclusion chromatography (SEC) as their ethyl esters. The degree of polymerization (DP) of poly-**1L** was also estimated to be 59 based on its ^{31}P NMR spectrum of the corresponding precursor polymer (Table 1).

As previously reported, poly-**1L** and poly-**1H** changed their specific rotation from a positive to a large negative value ($[\alpha]_D^{25}$ = −210° and −113°, respectively) after annealing the DMSO solutions containing (*R*)-**2** ([(*R*)-**2**]/[carboxy residues of poly-**1**] = 5) at 65 °C for ca. 2 h, the sign of which was opposite to that

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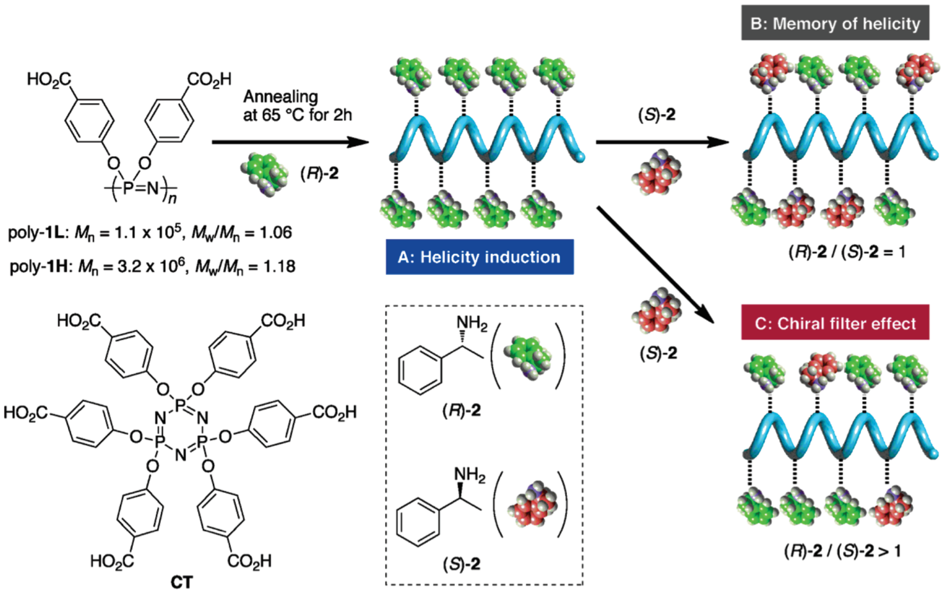
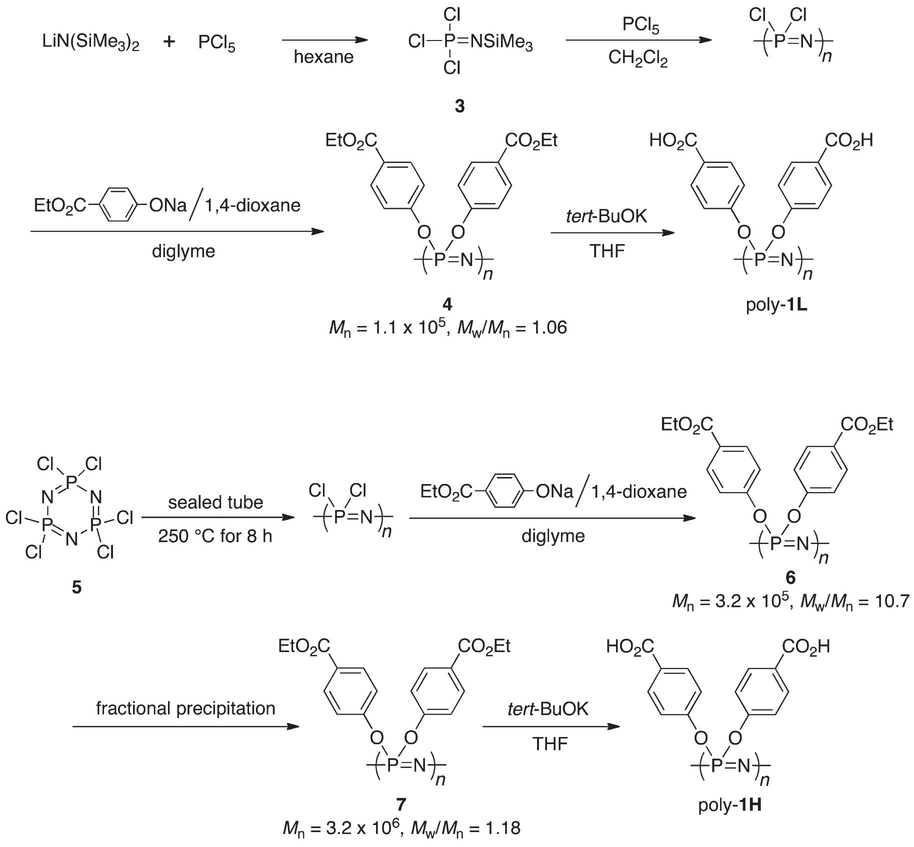


Figure 1. Structures of low (poly-**1L**) and high (poly-**1H**) molecular weight poly-**1**, **2**, and **CT**. Schematic illustration of helicity induction in optically inactive poly-**1** assisted by a chiral amine ((*R*)-**2**) (A) and subsequent macromolecular helicity memory (B). A preferred-handed helical conformation is induced in poly-**1** upon complexation with (*R*)-**2** after annealing at high temperature (A). The optical activity of poly-**1** is retained in the presence of an equimolar amount of (*S*)-**2** through "memory" of the macromolecular helicity (B) or by the "*chiral filter*" effect (C).

Scheme 1. Synthesis of Poly-1L and Poly-1H



of (*R*)-**2** ($[\alpha]_D^{25}$ + 33° in DMSO), whereas the specific rotation of the **CT**−(*R*)-**2** complex remained unchanged after annealing (Table 2).[12] The net specific rotations ($[\alpha]_D^{25}$) calculated by subtracting the specific rotations of **CT** from those of poly-**1L** and poly-**1H**, which reflect the rotational contribution derived from an induced helical conformation of the poly-**1** backbones, reached −327° and −230°, respectively. The higher MW poly-**1H** exhibited a rather lower specific rotation as compared to that of the low MW poly-**1L** probably because the poly-**1H** chains were significantly entangled with each other in solution even in the presence of (*R*)-**2**, which may hamper the efficient helicity induction into the poly-**1H** chains (see below).

The addition experiments of (*S*)-**2** ($[\alpha]_D^{25}$ +33° in DMSO) to the solutions of the annealed poly-**1L**− and poly-**1H**−(*R*)-**2** complexes were then performed. The poly-**1L**− and poly-**1H**−(*R*)-**2** solutions maintained their large negative specific rotations even after the addition of an equivalent amount of (*S*)-**2** (Table 3). Quite reasonably, the optical activity of the **CT**−(*R*)-**2** solution completely disappeared after the addition of an equivalent amount of (*S*)-**2** ([(*R*)-**2**]/[(*S*)-**2**] = 1) because **2** exists as a racemic mixture in the solution. There may be two possible mechanisms to explain this unusual phenomenon: One is the "*memory effect*",[7,12] which is the induced helical conformation of the poly-**1** with an excess one-handedness is memorized after the (*R*)-**2** complexed with poly-**1** could be randomly replaced by (*S*)-**2** (Figure 1B). Another is the "*chiral filter effect*",[7c] through which one enantiomer could be excluded for racemic amines assisted by the induced helical poly-**1**; in other words, the helical poly-**1** enantioselectively adsorbs one of the enantiomers of **2** (Figure 1C).

To gain concrete evidence for elucidating the mechanism, the amine **2** adsorbed on the poly-**1L** and poly-**1H** was recovered by precipitation of the polymer complexes in the poor solvent, toluene, followed by desorption of the bound **2** with aqueous 1 N HCl/methanol (1/10, v/v), and neutralization with sodium carbonate. The amine was almost quantitatively recovered and its ee was estimated by chiral HPLC analysis using a chiral column (Chiralcel OD or OD-H, Daicel) (Figure S1). Table 3 summarizes the results of the ee values of the bound **2** recovered from the helical poly-**1L** and poly-**1H**. Interestingly, the ee values of the recovered **2** were rich in *R* at 41% (poly-**1L**) and 32−34% (poly-**1H**). When the enantiomeric amine, (*S*)-**2**, was employed for the helicity induction followed by annealing at 65 °C for ca. 2 h, the bound **2** recovered from the helical poly-**1L** and poly-**1H** after the addition of an equimolar amount of (*S*)-**2** was rich in the *S*-enantiomer (ee = 40−42% (poly-**1L**) and 34−38% (poly-**1H**)). Apparently, the optical activity completely disappeared when the annealed poly-**1L**−(*R*)-**2** and poly-**1L**−(*S*)-**2** solutions were further annealed at 120 °C for 1 h after the addition of (*S*)-**2** and (*R*)-**2**, respectively, and the recovered **2** adsorbed on the poly-**1L** was totally racemic (ee = 0) (Table 3).

Table 1. Characteristics of Poly-1L and Poly-1H

polymer	$M_n \times 10^{-5}$ [a]	M_w/M_n [a]	DP[b]	av length (nm)[c]
poly-**1L**	1.1 (0.22)	1.06	59	
poly-**1H**[d]	32	1.18		61.4

[a] Determined as its ethyl esters by SEC (polystyrene standards) using tetrahydrofuran (THF) containing 0.1% tetra-*n*-butylammonium bromide as the eluent. Values in parentheses were calculated by ^{31}P NMR of the precursory polymer. [b] Calculated by ^{31}P NMR of the precursory polymer. [c] Estimated on the basis of an evaluation of ca. 400 individual polymer chains on mica by AFM. [d] After fractional precipitation using $CHCl_3$ as the solvent and *n*-hexane as the precipitant (see Experimental Section).

On the basis of these results, it can be concluded that the helical poly-**1** induced by the chiral amine **2** can indeed act as a *chiral filter*, thus exhibiting a chiral recognition ability, leading to the enantioselective adsorption of one of the enantiomers. In sharp contrast, when similar addition experiments were done for a typical dynamic helical polymer, poly(4-carboxyphenylacetylene), it did not show such a chiral filter effect. Instead, the polymer memorized its helical chirality induced by (*R*)-1-(1-naphthyl)ethylamine even after the addition of an equimolar amount of the opposite (*S*)-antipode. The bound chiral amines recovered from the induced helical poly(4-carboxyphenylacetylene) was racemic, while maintaining its preferred-handed helical conformation, indicating that the helical conformation of poly(4-carboxyphenylacetylene) with an excess handedness retained after the bound (*R*)-amine was randomly replaced by the opposite (*S*)-amine because the inversion of helicity of the polymer may be very slowly occurring after the fast exchange reaction.[7c]

Viscosity and Morphology Changes of Poly-1. Viscosity measurements were then conducted for the poly-**1L**− and poly-**1H**−(*R*)-**2** complexes in DMSO ([poly-**1**] = 5 mg/mL, [(*R*)-**2**]/[carboxy residues of poly-**1**] = 5) (Figure 2).[16] The viscosity of the poly-**1L**−(*R*)-**2** complex gradually increased with time before annealing (Figure 2A). However, once the solution was annealed at 65 °C for 2 h, the viscosity significantly decreased accompanying an increase in the specific rotation, while the viscosity and specific rotation values remained unchanged with time when the solution was annealed during the initial stage. These results indicate that poly-**1L** may intermolecularly interact to form a type of entangled aggregate before annealing (Figure 3A). However, once it was annealed in the presence of (*R*)-**2** during the initial stage (Figure 3C) or later (Figure 3E), the polymer may unravel to form an intramolecularly stable conformation, probably a preferred-handed helical conformation assisted by the chiral amine, thus showing a large negative optical rotation.[17] Once this happened, no entanglement may occur (Figure 3C,F) so that the viscosity and optical rotation did not change at all. A similar tendency in the viscosity change with time was observed for the poly-**1H**−(*R*)-**2** solution, although the viscosity gradually increased with time after annealing the solution (Figure 2B).[18]

AFM analyses of the poly-**1H** in the absence and presence of (*R*)-**2** on a freshly cleaved mica surface were also conducted to observe changes in the morphology of the polymer chains before and after annealing accompanied by viscosity and optical rotation

Table 2. Specific Rotations of Poly-1L, Poly-1H, and CT in the Presence of (*R*)-2 before and after Annealing at 65 °C for 2 h

	$[\alpha]_D^{25}$ (*c* 0.5, DMSO) (deg)				
	poly-**1L**[a]	poly-**1H**[a]	**CT**[a]	(poly-**1L**)−(**CT**)[b]	(poly-**1H**)−(**CT**)[b]
before annealing	+57	+10	+117	−60	−107
after annealing	−210	−113	+117	−327	−230

[a] Optical rotation was measured in DMSO ([(*R*)-**2**]/[carboxy residues of poly-**1** or **CT**] = 5) at 25 °C in a 5 cm quartz cell, and the specific rotation values were calculated on the basis of the concentrations (g/dL) of poly-**1** and **CT**. [b] Net rotations showing the rotational contribution derived from an induced helical conformation of poly-**1**.

Table 3. Results of Chiral Filter Experiments

		$[\alpha]_D^{20}$ (*c* 0.5, DMSO) (deg)[a]		% ee[c]	
run	poly-**1**−**2** complex	after annealing at 65 °C for 2 h	after addition of **2** with the opposite configuration[b]	UV	PM
1	poly-**1L**−(*R*)-**2**	−203	−282	41 (*R*-rich)	41 (*R*-rich)
2	poly-**1L**−(*R*)-**2**	−203	0[d]	0	0
3	poly-**1L**−(*S*)-**2**	+201	+284	40 (*S*-rich)	42 (*S*-rich)
4	poly-**1L**−(*S*)-**2**	+201	0[d]	0	0
5	poly-**1H**−(*R*)-**2**	−104	−189	34 (*R*-rich)	32 (*R*-rich)
6	poly-**1H**−(*S*)-**2**	+100	+191	34 (*S*-rich)	38 (*S*-rich)

[a] Measured in a 5 cm quartz cell. The specific rotation values were calculated on the basis of the concentrations (g/dL) of poly-**1**. [**2**]/[carboxy residues of poly-**1**] = 5. [b] An equimolar amount of (*R*)- or (*S*)-**2** was added after annealing. [c] Enantiomeric excess values of **2** adsorbed on poly-**1** estimated by HPLC using a chiral HPLC column (Chiralcel OD or Chiralcel OD-H) with UV and polarimeter (PM) detectors. [d] After annealing at 120 °C for 1 h.

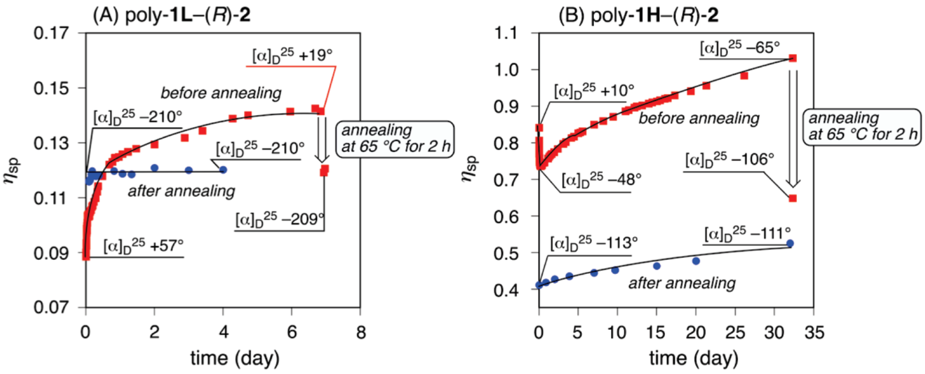


Figure 2. Plots of η_{sp} against time for poly-**1L** (A) and poly-**1H** (B) complexed with (*R*)-**2** ([poly-**1**] = 5 mg/mL, [(*R*)-**2**]/[carboxy residues of poly-**1**] = 5) before (red squares) and after (blue circles) annealing at 65 °C for 2 h in DMSO at 25 °C.

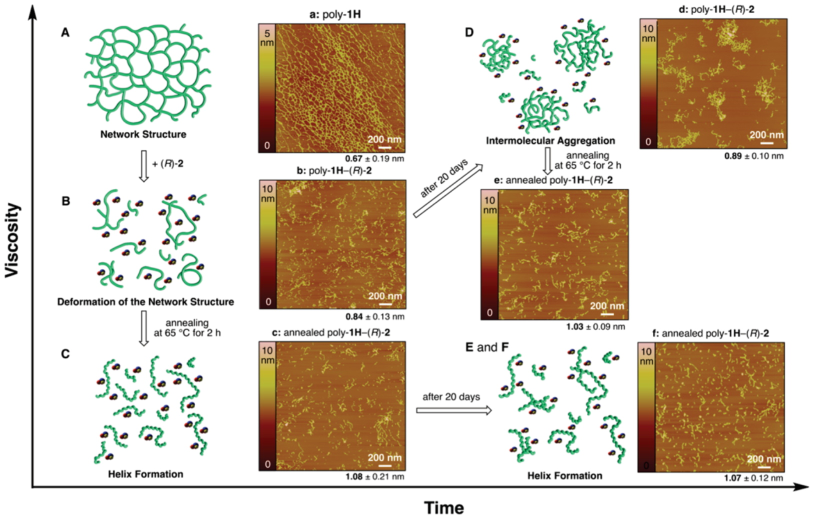


Figure 3. (A−F) Schematic models for the morphological changes in poly-**1H** chains in the absence (A) and presence of (*R*)-**2** before annealing (B) and those after annealing at 65 °C for 2 h (C, E, and F) in DMSO. The poly-**1H** chains complexed with (*R*)-**2** in B further entangled with time (D). The AFM images (a−f) correspond to the models (A−F); the original poly-**1H** (a), poly-**1H**−(*R*)-**2** complex just after the addition of (*R*)-**2** (b) and after the sample B was allowed to stand for 20 days (d) followed by annealing at 65 °C for 2 h (e). The sample B was annealed at 65 °C for 2 h (c) and then allowed to stand for 20 days (f). The average heights of the polymers are also shown below.

changes (Figure 3).[19] The AFM image of the original poly-**1H** suggests nanostructured network assemblies (a). Upon the addition of (*R*)-**2**, the entangled polymer chains tended to unravel, but it was not completed, showing bundle structures (b), resulting in the decreased viscosity. Annealing the solution at 65 °C for 2 h produced a further disentanglement, leading to molecularly dispersed poly-**1H** chains accompanied by a preferred-handed helicity induction in the polymer backbone, resulting in a large specific rotation, and this morphology remained for at least 20 days as directly visualized by AFM on mica (f). On the other hand, the poly-**1H**−(*R*)-**2** complex without annealing gradually re-entangled to form intermolecular aggregates over time, as shown in the AFM image after 20 days (d). However, annealing the solution (d) at 65 °C for 2 h instantly produced the unravelled polymer chains with a preferred-handed helical conformation (e), thus showing a similar AFM image as those of images c and f in Figure 2.[20] Thus, these AFM measurement results appeared to be in fairly good agreement with the viscosity changes of the poly-**1H** upon complexation with (*R*)-**2** and further annealing at 65 °C for 2 h.

In summary, we have found that an induced helical poly((bis-(4-carboxyphenoxy)phosphazene) (poly-**1**) assisted by an optically active amine after annealing the complex solution at 65 °C for ca. 2 h showed an unprecedented enantioselective adsorption ability toward racemic amines in DMSO and maintained its optical activity via exclusion of one enantiomer for the racemic ones. This unique *chiral filter* effect has never been observed for other dynamic helical polymers and may provide novel chiral materials for the resolution of racemic amines[8,9] through a conceptually new helical system.

■ EXPERIMENTAL SECTION

Materials. CH_2Cl_2 was treated with concentrated H_2SO_4, washed with 5% NaOH aqueous solution and water, and then dried over calcium hydride, distilled, and stored under nitrogen over calcium hydride. The dichloromethane was distilled again under high vacuum just before use. THF, diethyl ether, toluene, and benzene were dried over sodium benzophenone ketyl and distilled under nitrogen. $CHCl_3$ was dried over calcium hydride and distilled under nitrogen. Lithium bis-(trimethylsilyl)amide, anhydrous 2-methoxyethyl ether (diglyme), anhydrous 1,4-dioxane, and anhydrous DMSO were purchased from Aldrich and used as received. Ethyl 4-hydroxybenzoate, phosphorus pentachloride, anhydrous hexane, potassium *tert*-butoxide, and sodium hydride were obtained from Wako (Osaka, Japan), and tetra-*n*-butylammonium bromide was from Kishida (Osaka, Japan). (*R*)- and (*S*)-1-phenylethylamine ((*R*)- and (*S*)-2) (ee >98%) were kindly supplied from Yamakawa Chemical (Tokyo, Japan). Hexachlorocyclotriphosphazene (**5**) was obtained from Wako (Osaka, Japan) and purified by sublimation at 50 °C (0.1 mmHg), followed by recrystallization twice from hexane under a dry nitrogen atmosphere and resublimation at 50 °C (0.1 mmHg).

Poly-**1**s with a different molecular weight were prepared according to Scheme 1,[12,15] and detailed experimental procedures are described below.

Trichloro(trimethylsilyl)phosphoranimine (3). This compound was prepared according to the previously reported method from phosphorus pentachloride (PCl_5) and lithium bis(trimethylsilyl)amide (Scheme 1).[12,15] Yield: 30%. ^{1}H NMR ($CDCl_3$): δ 0.167 (d, CH_3, 9H). ^{31}P NMR ($CDCl_3$): δ −54.5.

Poly[bis(4-(ethoxycarbonyl)phenoxy)phosphazene] (Low Molecular Weight) (4). Cationic living polymerization of **3** was carried out using PCl_5 as a catalyst in a similar way previously reported[12,15] (Scheme 1). **3** (9.13 g, 0.041 mol) was placed in a 200 mL round-bottomed flask under nitrogen, and dry CH_2Cl_2 (87 mL) was added with a syringe. To this was added a solution of PCl_5 (8.2×10^{-4} mol) in CH_2Cl_2 at 30 °C. The feed ratio of monomer **3** to the initiator PCl_5 was 50. After 40 h at 30 °C, the complete consumption of **3** and the formation of poly-(dichlorophosphazene) were confirmed by ^{31}P NMR. CH_2Cl_2 was then evaporated, and toluene (49 mL) and 1,4-dioxane (70 mL) were added with a syringe. To this was added dropwise a suspension of the sodium salt of ethyl 4-hydroxybenzoate (0.10 mol) in 1,4-dioxane prepared from ethyl 4-hydroxybenzoate and sodium hydride. Dry diglyme (119 mL) was added, and then the mixture was kept under stirring at 115 °C for 18 h to remove toluene and 1,4-dioxane using a Dean−Stark trap. The reaction mixture was poured into a large amount of water, and the precipitate was collected by centrifugation. The product was purified by reprecipitation from THF to water twice and from THF to hexane twice and dried in vacuo at 60 °C for 2 h. Yield: 59%. ^{1}H NMR ($CDCl_3$): δ 1.29 (t, CH_3, 6H), 4.24 (q, CH_2, 4H), 6.59 (d, aromatic, 4H), 7.43 (d, aromatic, 4H). ^{31}P NMR ($CDCl_3$): δ −20.4. ^{13}C NMR ($CDCl_3$): δ 164.9, 153.8, 130.7, 126.0, 119.8, 60.9, 14.3. The molecular weight (M_n) and the distribution (M_w/M_n) of **4** were estimated to be 1.1×10^5 and 1.06, respectively, by SEC.

Poly[bis(4-(ethoxycarbonyl)phenoxy)phosphazene] (High Molecular Weight) (6). Ring-opening polymerization of **5** was carried out to obtain a high molecular weight polymer according to the reported method,[21] as shown in Scheme 1. **5** (25.1 g, 0.072 mol) was placed in a dry ampule, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation−flush procedure was repeated three times, the ampule was sealed under vacuum and then heated at 250 °C for 8 h. The resulting product was dissolved in dry benzene (200 mL) under a dry nitrogen atmosphere. After the solution was concentrated, the residue was poured into a large amount of hexane (200 mL). The solvent was removed by decantation, and the precipitate was dissolved in toluene (150 mL) and 1,4-dioxane (200 mL). To this was added dropwise a suspension of the sodium salt of ethyl 4-hydroxybenzoate (80.9 g, 0.43 mol) in 1,4-dioxane (600 mL). Dry diglyme (340 mL) was further added to the mixture, and the suspension solution was kept under stirring at 115 °C for 18 h to remove toluene and 1,4-dioxane using a Dean−Stark trap. The reaction mixture was then poured into a large amount of water, and the precipitate was collected by centrifugation and washed with water. The product was purified by reprecipitation from $CHCl_3$ to hexane twice and dried in vacuo at 60 °C for 2 h to give 9.8 g of **6** as a white solid in 36% yield. ^{1}H NMR ($CDCl_3$): δ 1.31 (t, CH_3, 6H), 4.22 (q, CH_2, 4H), 6.59 (d, aromatic, 4H), 7.41 (d, aromatic, 4H). ^{31}P NMR ($CDCl_3$): δ −21.0. The number-average molecular weight (M_n) and the distribution (M_w/M_n) of **6** were estimated to be 3.2×10^5 and 10.7, respectively, by SEC.

Fractional Precipitation of 6. The obtained high molecular weight polymer **6** was divided into several fractions by repeating the fractional precipitation using $CHCl_3$ as the solvent and hexane as the precipitant. To a $CHCl_3$ solution of **6** (10 mg/mL, 0.7 wt %) was added dropwise hexane slowly at room temperature under stirring until the solution became turbid. The mixture was then stirred at 55 °C for 1 h and allowed to cool down to room temperature slowly under stirring. After 2 h at room temperature, the precipitate was collected by centrifugation, washed with hexane, and dried in a vacuo at 50 °C for 2 h. This fractional precipitation procedure was repeated several times until the fractionated sample showed a narrow molecular weight distribution. The M_n and M_w/M_n of the final fractionated sample (**7**) were estimated to be 3.2×10^6 and 1.18, respectively, by SEC.

Poly-1L. Potassium *tert*-butoxide (64 g, 0.57 mol) was dissolved in THF (1.6 L), and the solution was cooled to 0 °C. To this were added dropwise a small amount of water (3.2 mL) and then **4** (8.0 g, 0.021 mol) in THF (320 mL). The reaction mixture was stirred at 0 °C for 1 h and then at room temperature for 40 h. The solution was poured onto 4 L of iced water and acidified with HCl(aq) to precipitate the poly-**1L**. Poly-**1L** was purified by washing with water and THF. Poly-**1H** was prepared from **7** in a similar way for the preparation of poly-**1L**.

Poly-1L. Yield: 55%. ^{1}H NMR (DMSO-d_6): δ 6.65 (d, aromatic, 4H), 7.43 (d, aromatic, 4H). ^{31}P NMR (DMSO-d_6): δ −20.9. ^{13}C NMR (DMSO-d_6): δ 165.7, 153.2, 130.4, 127.1, 119.5.

Poly-1H. Yield: 90%. ^{1}H NMR (DMSO-d_6): δ 6.65 (d, aromatic, 4H), 7.43 (d, aromatic, 4H). ^{31}P NMR (DMSO-d_6): δ −20.9.

Hexakis[4-(ethoxycarbonyl)phenoxy]cyclotriphosphazene. **5** (4.72 g, 0.014 mol) was placed in a 200 mL round-bottom flask under N_2, and 1,4-dioxane (50 mL) was added with a syringe. To this was added dropwise a suspension of the sodium salt of ethyl 4-hydroxybenzoate (39.5 g, 0.21 mol) in 1,4-dioxane, and the solution was stirred at 110 °C for 72 h. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The crude product thus obtained was purified by silica gel chromatography with ethyl acetate−hexane (1/1, v/v) as the eluent to give 11.4 g of the title product as a white powder in 74% yield. ^{1}H NMR ($CDCl_3$): δ 1.41 (t, CH_3, 18H), 4.38 (q, CH_2, 12H), 7.00 (d, aromatic, 12H), 7.88 (d, aromatic, 12H). ^{31}P NMR ($CDCl_3$): δ −7.57. ^{13}C NMR ($CDCl_3$): δ 165.3, 153.4, 131.1, 127.6, 120.4, 61.1, 14.4.

Hexakis(4-carboxyphenoxy)cyclotriphosphazene (CT). CT was prepared in a similar procedure for the preparation of poly-**1**. ^{1}H NMR (DMSO-d_6): δ 7.00 (d, aromatic, 12H), 7.84 (d, aromatic, 12H). ^{31}P NMR (DMSO-d_6): δ −8.60. ^{13}C NMR (DMSO-d_6): δ 165.9, 152.6, 131.0, 128.2, 120.3.

Instruments. Optical rotation was measured in a 5 cm quartz cell equipped with a temperature controller (EYELA NCB-2100) on a JASCO P-1030 polarimeter in dry DMSO. NMR spectra were taken on a Varian Mercury 300 spectrometer operating at 300 MHz for ^{1}H, 75 MHz for ^{13}C, and 121.5 MHz for ^{31}P with TMS (^{1}H and ^{13}C) and H_3PO_4 (^{31}P) as the internal and external standards, respectively. SEC measurements were performed with a JASCO PU-980 liquid chromatograph equipped with a UV (254 nm; UV-970) detector. A Tosoh TSKgel MultiporeH$_{XL}$-M GPC column (30 cm) was connected, and THF containing 0.1% tetra-*n*-butylammonium bromide was used as the eluent at a flow rate of 1.0 mL/min. The molecular weight calibration curve was obtained with standard polystyrenes (Tosoh). Optical purity measurements were performed by HPLC equipped with a UV (254 nm; JASCO UV-970) and a polarimeter (JASCO OR-1590) detector. A chiral column (Chiralcel OD or Chiralcel OD-H, Daicel, Tokyo, Japan; 25 × 0.46 (i.d.) cm) was connected, and hexane−2-propanol (50/1, v/v) was used as the eluent at a flow rate of 1.0 mL/min. IR spectra were recorded using a JASCO Fourier transform IR-620 spectrophotometer. Absorption spectra were taken on a JASCO V-570 spectrophotometer. Viscosities of DMSO solutions of poly-**1L** and poly-**1H** samples with or without (*R*)-**2** were measured by using conventional Ubbelohde-type capillary viscometers at 25 °C. The Huggins plots were used to determine the intrinsic viscosity [η]. AFM images were obtained in tapping mode using a Nanoscope IIIa microscope (Digital Instruments, Santa Barbara, CA). The AFM measurements were performed in air at ambient temperature using standard silicon cantilevers with a spring constant of ca. 40 N/m, a tip radius of 5−10 nm, and a resonance frequency of 220−300 kHz. All the images were collected with the maximum available number of pixels (512) in each direction. Scanning speed was at a line frequency of 1.0 Hz. The nanoscope image processing software was used for image analysis.

Viscosity Measurements. A typical experimental procedure is described below. Viscosities of poly-**1H** with or without (*R*)-**2** were measured in DMSO at 25 °C. A stock solution of poly-**1H** (10 mg/mL) was prepared in DMSO. A 3 mL aliquot of the stock solution was transferred to a conventional Ubbelohde-type capillary viscometer. The solution was diluted with 3 mL of DMSO, giving a 5 mg/mL solution of poly-**1H**. The initial viscosity was measured at 25 °C, and then 3 mL of DMSO was added to the viscometer with a transfer pipet, giving a 3.3 mg/mL solution of poly-**1H**. The viscosity was measured, and the above similar dilution procedure was repeated with 3 mL of DMSO (concentrations of poly-**1H** were 2.5 and 1.25 mg/mL), and viscosities were measured for each addition of DMSO.

The viscosity measurements of the nonannealed and annealed solutions of the poly-**1H**−(*R*)-**2** complex were performed as below. Stock solutions of poly-**1H** (10 mg/mL) and (*R*)-**2** in DMSO (0.31 and 0.16 M, respectively) were prepared. A 3 mL aliquot of the stock solution of poly-**1H** was transferred to a viscometer with a transfer pipet, and to this was added a 3 mL aliquot of the stock solution of (*R*)-**2** in DMSO (0.31 M) with a transfer pipet, giving a 5 mg/mL solution of poly-**1H**−(*R*)-**2** complex ([(*R*)-**2**] = 0.16 M). The initial viscosity was measured, and then a 3 mL aliquot of the stock solution of (*R*)-**2** (0.16 M) in DMSO was added to the viscometer with a transfer pipet, giving a 3.3 mg/mL solution of the poly-**1H**−(*R*)-**2** complex ([(*R*)-**2**] = 0.16 M). The viscosity was measured, and the above similar dilution procedure was repeated with the stock solution of (*R*)-**2** in DMSO (0.16 M) (concentrations of poly-**1H**−(*R*)-**2** complex were 2.5 and 1.25 mg/mL). To this was added a small amount of hydrochloric acid of the chiral amine ([(*R*)-**2**·HCl]/[carboxy residues of poly-**1H**] = 0.02), and the viscosity was measured.

Time-dependent viscosity and optical rotation changes of poly-**1H** and the poly-**1H**−(*R*)-**2** complex before and after annealing were conducted in DMSO at 25 °C ([poly-**1H**] = 5 mg/mL and [(*R*)-**2**]/[carboxy residues of poly-**1H**] = 5). The solution of the poly-**1H**−(*R*)-**2** complex was annealed at 65 °C after the sample had been allowed to stand for 32 days, and the same dilution procedure as described above was carried out in the viscosity measurements. For poly-**1L** and poly-**1L**−(*R*)-**2** complex before and after annealing, the viscosities were measured under the same conditions as mentioned above.

AFM Measurements. Stock solutions of poly-**1L** and poly-**1H** in DMSO (0.5 mg/mL) and 0.16 M DMSO solution of (*R*)-**2** before and after annealing were prepared. The stock solutions (5 μL) were deposited on the freshly cleaved mica substrates, the solutions were blown off simultaneously with a stream of nitrogen, and the substrates were dried in vacuo overnight before measurements. Polymer lengths were measured using the NIH Image program, developed at the National Institutes of Health (available on the Internet at http://rsb.info.nih.gov/nih-image/).

Chiral Filter Experiments. A typical experimental procedure is described below. A stock solution of the poly-**1L**−(*R*)-**2** complex ([poly-**1L**] = 5 mg/mL, [(*R*)-**2**]/[carboxy residues of poly-**1L**] = 5) was prepared, and the solution was annealed at 65 °C for 2 h and the optical rotation was measured at 20 °C. To this was added an equimolar amount of (*S*)-**2** ([(*S*)-**2**]/[carboxy residues of poly-**1L**] = 5), and the optical rotation of this solution was measured at 20 °C. The solution was poured into a large amount of toluene, and the precipitate was collected by centrifugation and washed with toluene. The recovered poly-**1L**−(*R*)-**2** complex was suspended in aqueous 1 N HCl/methanol (1/10, v/v), and the mixture was stirred at room temperature overnight. The supernatant separated by decantation was alkalized with aqueous 1 N NaOH, and the solvents were evaporated. The residue was then extracted with $CHCl_3$, the organic solvent was removed by evaporation under a nitrogen atmosphere, and the residue was diluted with a hexane−2-propanol mixture (50/1, v/v). Optical purity of **2** was estimated by HPLC using a chiral HPLC column (Chiralcel OD or Chiralcel OD-H, Daicel).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Chromatograms for the resolution of **2** enantioselectively adsorbed on helical poly-**1L** and poly-**1H**, AFM images of poly-**1L** and poly-**1L**−(*R*)-**2** complex before and after annealing at 65 °C for 2 h, and AFM images of poly-**1L** and poly-**1L**−(*R*)-**2** complex before and after annealing at 65 °C for 2 h on mica. This material is available free of charge via Internet at http://pubs.acs.org.

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(16) In the absence of **2**, poly-**1L** and poly-**1H** showed a linear relationship in the Huggins plots, and the intrinsic viscosities ($[\eta]$ (dL/g)) were 0.08 and 1.66, respectively.

(17) A possibility that poly-**1** is a dynamic helical polymer consisting of right- and left-handed helical segments separated by helical reversals[1,11] could not be completely excluded.

(18) The viscosities of the poly-**1L**− and poly-**1H**−(*R*)-**2** complexes significantly decreased upon the addition of a small amount of the hydrochloric acid salt of (*R*)-**2** ([(*R*)-**2**·HCl]/[carboxy residues of poly-**1**] = 0.02) independent of the annealing process, indicating that the polymers are a weak polyelectrolyte in DMSO in the presence of the chiral amine.

(19) Poly-**1L** chains were too short to observe the morphology changes by AFM (see Figure S2).

(20) On the basis of an evaluation of ca. 400 individual polymer chains separated from one another including those in Figure 3c, the number-average molecular length (L_n) and the length distribution (L_w/L_n) of poly-**1H** were estimated to be 61.4 nm and 1.6, respectively (Table 1).

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