Macromolecules

ARTICLE

pubs.acs.org/Macromolecules

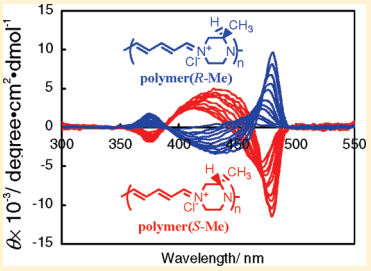
Ionic Helical Polymers with Expanded π-Conjugation System Derived from Through-Space Interaction in Piperazinium Ring and Their Spontaneous Dynamic Conformational Changes

Isao Yamaguchi,* Sachiko Jonai, and Yukari Matsuda

Department of Material Science, Faculty of Science and Engineering, Shimane University, 1060 Nishikawatsu, Matsue 690-8504, Japan

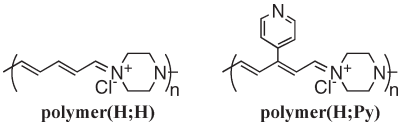
Supporting Information

ABSTRACT: Reactions of *N*-(2,4-dinitrophenyl)-4-arylpyridinium chlorides (aryl = H and 4-pyridiyl (Py)) with *R*-(−)- or *S*-(+)-2-methylpiperazines caused ring-opening of the pyridinium ring and yielded ionic polymers that consisted of 5-(2-methylpiperazinium)-3-aryl-penta-2,4-dienylideneammonium chloride units, namely, polymer(*R*-M;H), polymer(*S*-Me;H), polymer(*R*-Me;Py), and polymer(*S*-Me;Py). Reactions of achiral polymer(Me;H) with *R*-(−)- or *S*-(+)-1,1′-binaphthyl-2,2′-diyl sodium phosphates caused an anion exchange that yielded polymers with chiral phosphate anions. CD measurements revealed that polymer(*R*-Me;H) and polymer(*S*-Me;H) as well as polymer(*R*-Me;Py) and polymer(*S*-Me;Py) formed opposite helical conformations; therefore, it is clear that the helical conformation can be controlled by varying the substituent on the piperazinium ring. In addition, CD measurements of achiral polymer(Me;H) in the presence of *R*-(−)- or *S*-(+)-1,1′-binaphthyl-2,2′-diyl sodium phosphates revealed that the chiral anions incorporated by the anion exchange reaction in solution induced helical conformations in the polymer backbone. The helical conformations disappeared as the 2-methylpiperazinium rings in the polymers converted from the boat to the chair form via a half-chair intermediate, and this conformational change was accompanied by a decrease in the amount of π-conjugation length. These spontaneous, dynamic changes in a polymer's helical conformation occurred without using external stimuli. These changes affected the viscosity and the electrochemical properties of the polymer solutions; the η_{sp}/c value of the polymers in methanol decreased with time, and electrochemical oxidation peaks of the polymers shifted to higher potentials when the polymer solution was left standing in air.



INTRODUCTION

π-Conjugated polymer main chains generally consist of aromatic rings and unsaturated bonds that are required to build the expanded π-conjugation system. The existence of aliphatic cycles in the polymer main chain usually prevents the expansion of the π-conjugation system along the polymer chain. Recently, we reported the synthesis of water-soluble ionic π-conjugated polymers, polymer(H;H) and polymer(H;Py), from ring-opening reactions of the pyridinium ring of *N*-(2,4-dinitrophenyl)-4-arylpyridinium chloride (aryl = H: **1**; aryl = 4-pyridyl (Py): **2**) with piperazine.[1]

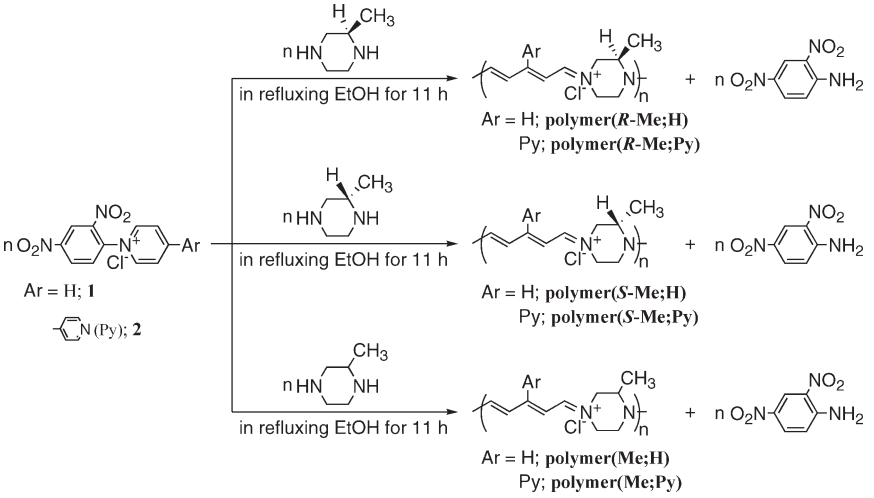


The polymers comprise aliphatic piperazinium rings linked by π-conjugated 3-aryl-penta-2,4-dienylideneammonium chloride units. The expanded π-conjugated system along the polymer chain is derived from the through-space interaction between the orbitals of electrons on the nitrogen atoms of the piperazinium ring and π-conjugation decreases with the conversion of the piperazinium rings from the boat to the chair form.

Helical π-conjugated polymers have been attracting attention because of their chiral structure, which is common in naturally occurring polymers, and because of their interesting chirooptical properties such as polarized photoluminescence and electroluminescence.[2] Monosubstituted *cis*-poly(acetylene) derivatives (PAs) prepared with Rh catalysts are the most commonly studied helical π-conjugated polymers.[3] Control of the helical conformation of PAs is important for controlling their optical properties and enantioselectivities, and this control can be achieved by varying temperature and solvent and by the addition of chiral species in solution.[3] In the case of PAs with photoisomerizable azobenzene side groups, the helical conformation of the PAs changes when the azobenzene group is photoisomerized.[4] To the best of our knowledge, however, there have been no reported examples of helical polymers in which the main chains have isomerizable groups. Such a polymer is expected to have a dynamic change of the helical conformation upon isomerization. In this study, cationic π-conjugated polymers containing convertible chiral piperazinium rings in the main chain were synthesized by the reaction of **1** and **2** with (*R*)-(−)- or (*S*)-(+)-2-methylpiperazines. Corresponding achiral polymers were synthesized by the reaction of **1** and **2** with 2-methylpiperazine. Helical conformation

Received: December 16, 2010
Revised: January 26, 2011
Published: February 11, 2011

Scheme 1. Synthesis of Polymers with 2-Methylpiperazinium Rings



was induced in the achiral polymer backbone by incorporation of chiral anions through ion exchange reactions with *R*-(−)- or *S*-(+)-1,1′-binaphthyl-2,2′-diyl sodium phosphates. Understanding how the helical conformation changes with the conversion of the chiral and achiral 2-methylpiperazinium rings and also how conformational changes affect chemical properties will provide useful information for the development of new functional materials. In addition, these cationic, water-soluble, π-conjugated helical polymers are expected to be useful as biosensing materials that target anionic biomolecules such as DNA and proteins.

Herein, we report the synthesis of these helical polymers and the changes in their conformations and chemical properties with the conversion of the (*R*)-(−)- or (*S*)-(+)-2-methylpiperazinium ring. Conformational changes, resulting from the conversion of the 2-methylpiperazinium ring, for both the chiral and the achiral polymers are compared.

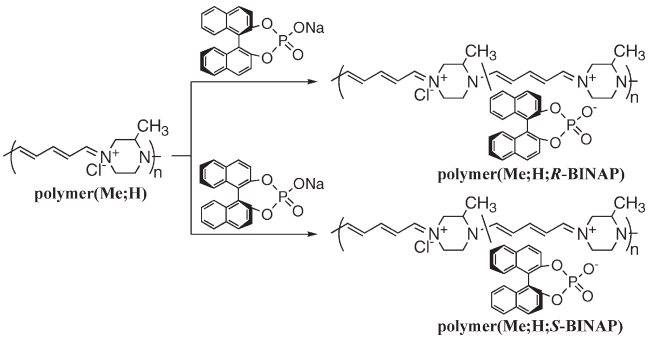
RESULTS AND DISCUSSION

Synthesis. The reactions of (*R*)-(−)-2-methylpiperazine, (*S*)-(+)-2-methylpiperazine, and 2-methylpiperazine with **1** in refluxing ethanol caused ring-opening of the pyridinium ring to afford polymer(*R*-Me;H), polymer(*S*-Me;H), and polymer(Me;H) in 83%, 72%, and 82% yields, respectively, while the reactions of the same with **2** afforded polymer(*R*-Me;Py), polymer(*S*-Me;Py), and polymer(Me;Py) in 83%, 92%, and 85% yields, respectively (Scheme 1).

The reactions of achiral or rasemic polymer(Me;H) with *R*-(−)- or *S*-(+)-1,1′-binaphthyl-2,2′-diyl sodium phosphates (*R*- or *S*-BINAP-PO_4Na) in a 1:1 molar ratio caused anion exchange between Cl^- and BINAP-PO_4^- to yield polymer(Me;H;*R*-BINAP) or polymer(Me;H;*S*-BINAP), respectively (Scheme 2). The peak integral of the ^{1}H NMR spectra suggested that the molar ratio of Cl^- and *R*-BINAP-PO_4^- in polymer(Me;H;*R*-BINAP) was 0.25:0.75, and the molar ratio of Cl^- and *S*-BINAP-PO_4^- in polymer(Me;H;*S*-BINAP) was 0.14:0.84.

The polymers thus obtained were completely soluble in MeOH and water and were partly soluble in dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF). The number-average molecular weights (M_n's) and weight-average molecular weights (M_w's), determined by GPC, are summarized in Table 1.

Scheme 2. Anion Exchange Reaction



The somewhat low M_w values of the polymers are apparently because of the low solubility of the polymers in the eluent.

Figure 1 shows ^{1}H NMR spectra of polymer(*R*-Me;H) and polymer(*R*-Me;Py) in CD_3OD, measured immediately after the preparation of the solutions. The peak assignments are shown in the figure. The ^{1}H NMR spectra of the CD_3OD solution of polymer(*R*-Me;H), polymer(*S*-Me;H), and polymer(Me;H) were similar, and each spectrum showed three signals, at approximately δ 7.8, 7.7, and 6.2 in a 1:2:2 integral ratio, arising from the protons in the penta-2,4-dienylideneammonium group. While the ^{1}H NMR spectra of the CD_3OD solution of polymer(*R*-Me;Py), polymer(*S*-Me;Py), and polymer(Me;Py) showed two signals, at approximately δ 7.1 and 6.4 in a 1:1 integral ratio, arising from the protons in the penta-2,4-dienylideneammonium group. These observations suggest that the π-electrons are delocalized along the penta-2,4-dienylideneammonium group. The ^{13}C NMR data also support this view, showing three signals arising from the penta-2,4-dienylideneammonium group. The signal due to the terminal groups of the polymers was not observed in the ^{1}H NMR spectra.

UV−vis Spectra. The UV−vis data of polymers are summarized in Table 1. The freshly prepared MeOH solutions of the polymers with a pyridyl group showed absorption maxima at longer wavelengths than those without a pyridyl group. These

Table 1. Synthesis Results and Optical and Electrochemical Properties

product	yield, %	η_{sp}/c,[a] g^{-1} dL	M_w (M_w/M_n)[b]	absorption, nm	rate constant[f] $k \times 10^{-5}$, s^{-1}	rate constant[f] $k' \times 10^{-5}$, s^{-1}	E_a,[g] V
polymer(*R*-Me;H)	83	0.68	7610 (1.5)	482 (5.12),[c] 446,[d] 422[e]	10	2.9	0.66
polymer(*S*-Me;H)	72	0.58	6380 (1.2)	481 (5.21),[c] 442,[d] 425[e]	10	2.9	0.65
polymer(Me;H)	82	0.67	7640 (1.3)	482 (5.07),[c] 444,[d] 426[e]	7.2	5.2	0.65
polymer(*R*-Me;Py)	83	0.15	4820 (1.4)	505 (4.68),[c] 477,[d] 445[e]	12	3.1	0.85
polymer(*S*-Me;Py)	92	0.14	4600 (1.4)	503 (4.66),[c] 476,[d] 448[e]	12	3.1	0.85
polymer(Me;Py)	85	0.21	5350 (1.4)	502 (4.65),[c] 475,[d] 448[e]	3.0	2.3	0.84

[a] Measured at the concentration of 0.1 g dL^{-1} in MeOH at 30 °C. [b] Determined by GPC (eluent = DMF containing 0.006 M LiBr vs polystyrene standards). DMF soluble parts (~60%) of polymers. [c] Measured immediately after preparation of the solutions. log ε (M^{-1} cm^{-1}) values based on repeating unit are shown in parentheses. [d] Absorption due to product having piperazinium rings in the half-chair form. [e] Absorption due to product having piperazinium rings in the chair form. [f] k and k' values are rate constants of conversion of the piperazinium ring from the boat form to the half-chair form and from the half-chair form to the chair form at 30 °C, respectively. [g] Peak potential measured by cyclic voltammetry in DMSO solution of $[Et_4N]BF_4$ (0.10 M).

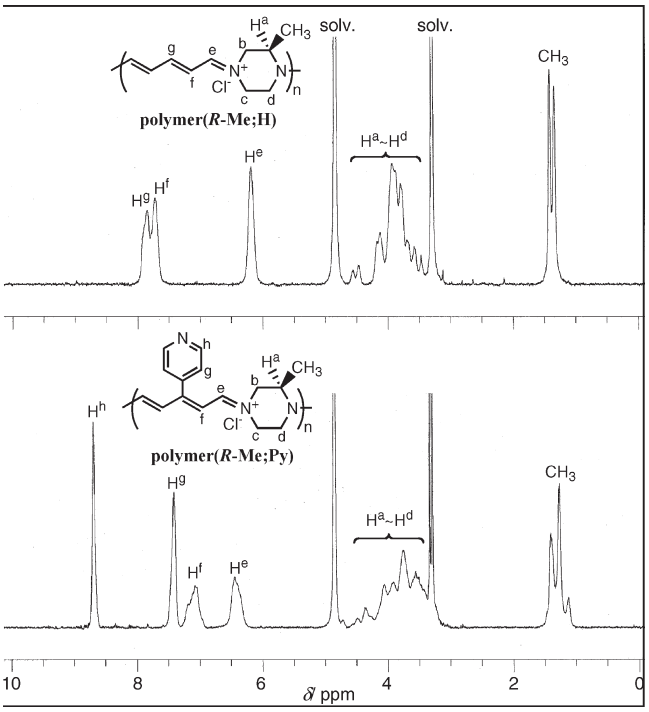


Figure 1. ^{1}H NMR spectra of polymer(*R*-Me;H) and polymer(*R*-Me;Py) in CD_3OD, measured immediately after the preparation of the solutions.

observations suggest that the π-conjugation system of the polymers is expanded to the pyridyl group.

The absorption wavelengths of the freshly prepared MeOH solution of polymer(*R*-Me;H) and polymer(*R*-Me;Py) vary with the amount of time they are allowed to stand at 30 °C in air, as shown in Figure 2. The changes in wavelengths correspond to the two-step conversion of the 2-methylpiperazinium ring from the boat to the chair form via a half-chair intermediate, as illustrated in Scheme 3. Similar spectral changes were observed in the UV−vis spectra of other polymers. We proposed a possible reaction mechanism for the predominant formation of the piperazinium ring with the thermodynamically unstable boat form in the polymers at the initial stage.[1]

During the first step, as indicated by blue lines in Figure 2a, the peaks at 446 and 482 nm decrease with a gradual shift to a shorter wavelength and those at 422 and 446 nm increase simultaneously.

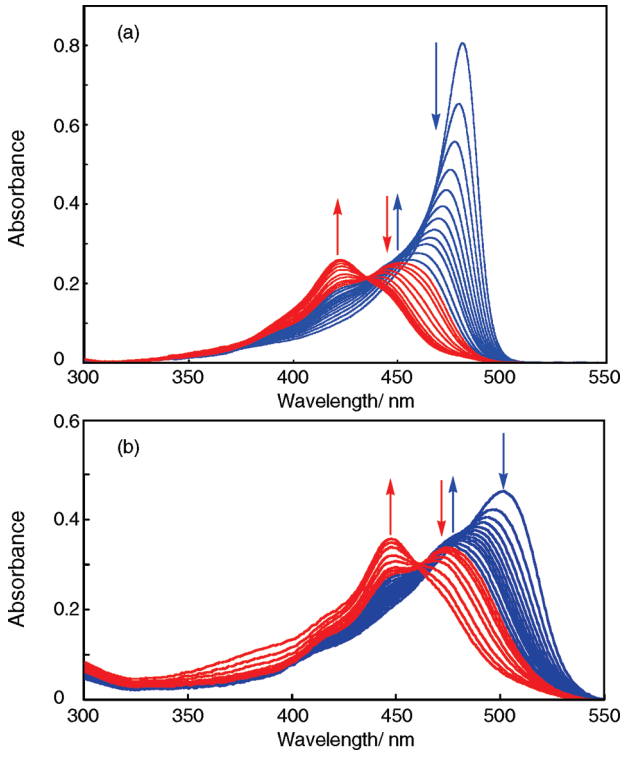
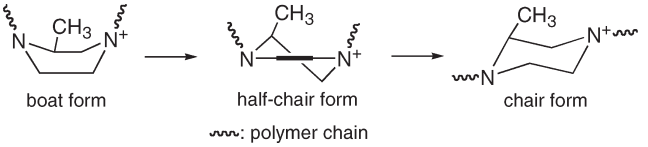


Figure 2. Changes of UV−vis spectra of methanol solution of polymer(*R*-Me;H) and polymer(*S*-Me;Py) with time upon standing in air at 30 °C ($c = 1.0 \times 10^{-5}$ M). Spectra indicated by blue and red lines were measured in every 30 min and 5 h, respectively.

Scheme 3. Conversion of Piperazinium Ring from Boat Form to Chair Form via Half-Chair Form



The variations in the two absorptions correspond to the decrease of the π-conjugation length, caused by the boat to half-chair conversion of the 2-methylpiperazinium ring and by the formation of the

dx.doi.org/10.1021/ma102870h |*Macromolecules* 2011, 44, 1273–1279

polymer containing half-chair piperazinium rings, respectively. When the 2-methylpiperazinium rings of the polymers adopt the chair conformation, the distance between the two nitrogen atoms on the 2-methylpiperazinium ring is too large to allow the through-space interaction; there is no extended π-conjugation in these polymers. The changes of the absorbances at 482 and 422 nm in the UV−vis spectra of polymer(*R*-Me;H) that occur with time *t* obey a first-order rate law with rate constants of $k = 1.0 \times 10^{-4}$ s^{-1} and $k' = 2.9 \times 10^{-5}$ s^{-1} at 30 °C, respectively, whereas the changes of the absorbances at 505 and 445 nm in the UV−vis spectra of polymer(*R*-Me;Py) obey a first-order rate law with rate constants of $k = 1.2 \times 10^{-4}$ s^{-1} and $k' = 3.1 \times 10^{-5}$ s^{-1} at 30 °C, respectively. Rate constants for the conversion of the 2-methylpiperazinium rings in polymer(*S*-Me;H) and polymer(*S*-Me;Py) from the boat to the half-chair form and from the half-chair to the chair form at 30 °C were the same as those in polymer(*R*-Me;H) and polymer(*R*-Me;Py), respectively, whereas those in polymer(Me;H) and polymer(Me;Py) were 7.2×10^{-5} s^{-1} and 5.2×10^{-5} s^{-1} and 3.0×10^{-5} s^{-1} and 2.3×10^{-5} s^{-1}, respectively. Computational calculations predict that the methyl groups of cationic *N*,*N*-dimethylpiperazine are in axial positions in the boat form and in equatorial positions in the chair form.[5] Thus, penta-2,4-dienylidene groups bonded to the 2-methylpiperazinium ring of the polymers apparently reside in the axial positions while adopting boat and half-chair conformations and in equatorial positions while in the chair form. The k' value at 30 °C is smaller than the k value in each case, probably because the conversion from the half-chair to the chair form causes a greater conformational change in the polymer than does the conversion from the boat to the half-chair form. The fact that the k and k' values of polymer(Me;H) and polymer(Me;Py) are higher than those of polymer(*R*-Me;H), polymer(*S*-Me;H), polymer(*R*-Me;Py), and polymer(*S*-Me;Py) is apparently attributed to the random coil structures of polymer(Me;H) and polymer(Me;Py). The k and k' values of polymer(Me;H) in the presence of *R*-(−)-1,1′-binaphthyl-2,2′-diyl sodium phosphate were 3.0×10^{-5} s^{-1} and 2.1×10^{-5} s^{-1}, respectively. These values are almost the same to those of polymer(Me;H) in the absence of the phosphate salt.

CD Spectra. Figure 3a shows how the CD spectra of the freshly prepared methanol solutions of polymer(*R*-Me;H) and polymer(*S*-Me;H) change when the solutions are allowed to stand at 25 °C in air. The CD spectra of polymer(*R*-Me;H) and polymer(*S*-Me;H) show relatively strong positive and negative Cotton effects, respectively, with zero crossings centered at the polymer chains' $\pi-\pi^*$ transition (at around 470 nm in the UV−vis absorption spectra; see Figure 2). Similarly, polymer(*R*-Me;Py) and polymer(*S*-Me;Py) showed relatively strong positive and negative Cotton effects, respectively (Figure 3b). These Cotton curves suggest that the main chains of polymer(*R*-Me;H) and polymer(*S*-Me;H) and of polymer(*R*-Me;Py) and polymer(*S*-Me;Py) have oppositely oriented, highly ordered structures, such as right- and left-handed helical conformation. In other words, the helical conformation is changed by varying the substituents on the piperazinium rings. In addition, the pyridyl groups in polymer(*R*-Me;Py) and polymer(*S*-Me;Py) do not affect the formation of the helical structures. The fact that polymer(Me;H) and polymer(Me;Py) showed no CD signal suggests that the polymers do not form an ordered structure.

As shown in Figure 4, the CD spectra of achiral or racemic polymer(Me;H) in the presence of *R*-(−)- or *S*-(+)-1,1′-binaphthyl-2,2′-diyl sodium phosphates showed positive and negative Cotton effects, respectively. These Cotton curves suggest that helical

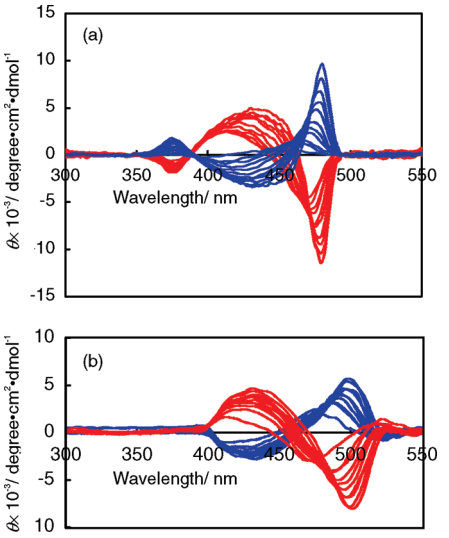


Figure 3. Changes of CD spectra of methanol solutions of (a) polymer(*R*-Me;H) (blue curves) and polymer(*S*-Me;H) (red curves) and (b) polymer(*R*-Me;Py) (blue curves) and polymer(*S*-Me;Py) (red curves) measured in every 30 min in air at 25 °C ($c = 1.0 \times 10^{-5}$ M).

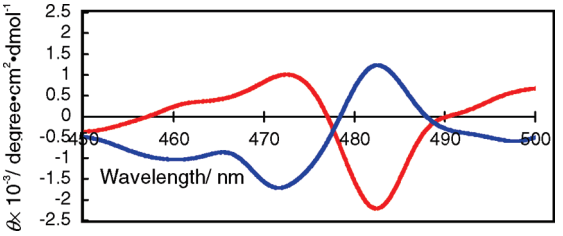


Figure 4. CD spectra of methanol solutions of polymer(Me;H) ($c = 1.0 \times 10^{-5}$ M) in the presence of *R*-(−)-1,1′-binaphthyl-2,2′-diyl sodium phosphate ($c = 5.0 \times 10^{-4}$ M, blue curve) and of *S*-(+)-1,1′-binaphthyl-2,2′-diyl sodium phosphate ($c = 5.0 \times 10^{-4}$ M, red curve) at 25 °C.

conformations are induced in the main chain of polymer(Me;H) with chiral anions incorporated through the anion exchange reaction in solution. In other words, helical conformations change with changing chiralities of the additives. This hypothesis is supported by the fact that the methanol solution of polymer(Me;H) in the presence of (±)-1,1′-binaphthyl-2,2′-diyl sodium phosphate showed no CD signal.

However, the ellipticity for Cotton curve of polymer(Me;H) in the presence of *R*-(−)-1,1′-binaphthyl-2,2′-diyl sodium phosphate was lower than that of polymer(*R*-Me;H). This lower ellipticity is consistent with the assumption that helical conformations are formed in a part of the polymer chain of polymer(Me;H) in the presence of chiral salts because the anion exchange reaction remains incomplete as mentioned above. In contrast, the methanol solution of polymer(Me;Py) in the presence of *R*-(−)-camphorsulfonic acid sodium salt whose molar size is smaller than that of *R*-(−)-1,1′-binaphthyl-2,2′-diyl sodium phosphate showed no CD signal. These results suggest that molecular size of the chiral anions is important for the formation of helical conformations of the polymer chain.

The intensity of the Cotton curves for polymer(*R*-Me;H) and polymer(*S*-Me;H) gradually decreased with time, as shown in Figure 3. This is apparently due to time-dependent dynamic conformational changes in the polymers; the helical conformation of

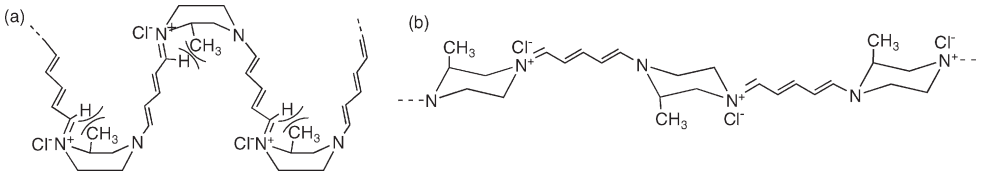


Figure 5. Polymer conformations.

the polymers disappeared as the 2-methylpiperazinium ring converted from the boat to the chair form via the half-chair form. As mentioned above, the penta-2,4-dienylidene groups bound to the 2-methylpiperazinium rings apparently reside in the axial positions in the boat and half-chair forms and in the equatorial positions in the chair form. On the basis of this assumption, the polymers appear to form a zigzag structure when the 2-methylpiperazinium ring exhibits the boat form. It has been reported that the zigzag structure of the polymers is preferred over the helical conformation.[6] The STS molecular model suggested that polymer(*R*-Me;H) and polymer(*S*-Me;H) with the 2-methylpiperazinium ring in the boat form adopt the helical conformation, avoiding steric hindrance between the methyl group and the proton at the 1-position of the aminopenta-2,4-dienylidene group, as shown in Figure S1 and Figure 5a. In contrast, when the 2-methylpiperazinium ring exhibits the chair form, the polymer does not form the helical conformation, apparently because of the linear structure along the polymer chain (Figure 5b). The intensity decrease of the Cotton curves was also occurred in the case of polymer(*R*-Me;Py) and polymer(*S*-Me;Py) when the methanol solutions of the polymers were allowed to stand in air.

Viscosity. The reduced viscosities (η_{sp}/c) in the freshly prepared methanol solutions of polymer(*R*-Me;H), polymer(*S*-Me;H), and polymer(Me;H) were 0.68, 0.58, and 0.67 g^{-1} dL (c = 0.10 g dL^{-1}), respectively. The reduced viscosities (η_{sp}/c) in the freshly prepared methanol solutions of the polymers obtained in this study were in the range of 0.14−0.68 g^{-1} dL (c = 0.10 g dL^{-1}), as summarized in Table 1. The η_{sp}/c values of the polymers in methanol increased when their concentration c was reduced, suggesting that the polymers behave as polymeric electrolytes in dilute solutions.[7] The η_{sp}/c value of polymer(*R*-Me;H) in methanol decreased with time when the methanol solution was left standing in air; it varied from 0.68 to 0.47 g^{-1} dL after 3 h from the preparation of the methanol solution. The result corresponds to the disappearance of the helical conformation of the polymer upon conversion of the 2-methylpiperazinium ring from the boat to the chair form. It has been reported that helical polymers showed greater reduced viscosities, because of their stiff structures, as compared to random coil polymers. The η_{sp}/c values of polymer(Me;H) in methanol varied from 0.67 to 0.54 g^{-1} dL after 3 h from the preparation of the methanol solution. The smaller decrease in the η_{sp}/c values of polymer(Me;H) than those of polymer(*R*-Me;H) and polymer(*S*-Me;H) appears to be attributed to a relatively small conformational change in the nonhelical polymer(Me;H) chain with the conversion of the 2-methylpiperazinium ring from the boat to the chair form.

Cyclic Voltammograms. Cyclic voltammetry (CV) measurements suggest that the polymers obtained in this study underwent an electrochemical oxidation of the piperazinium ring in DMSO solution containing 0.10 M $[Et_4N]BF_4$. The oxidation potentials of the freshly prepared solution of the polymers are summarized in Table 1. As shown in Figure 6a, the oxidation peak at 0.64 V of the DMSO solution of polymer(*S*-Me;H) decreased and a new peak at 0.74 V appeared and increased with repeated scanning for 8 h.

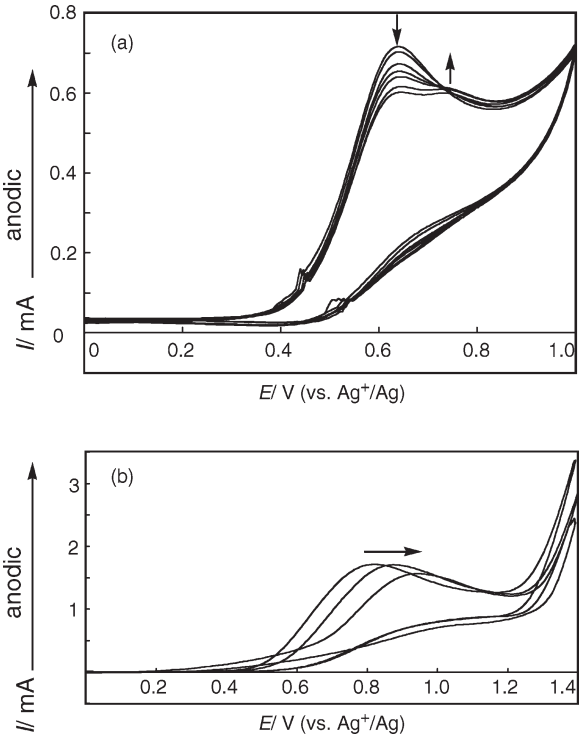


Figure 6. Changes of cyclic voltammograms of polymer(*S*-Me;H) (a) and polymer(*S*-Me;Py) (b) in DMSO solution containing 0.10 M $[Et_4N]BF_4$ with time. The scan rate was 50 mV s^{-1}.

The result is consistent with the fact that the extent of π-conjugation in the polymer decreases with time, again corresponding to the conversion of the 2-methylpiperazinium ring from the boat to the chair form. The electrochemical oxidation behavior of polymer(*R*-Me;H) is similar to that of polymer(*S*-Me;H). The oxidation potential of the freshly prepared solution of polymer(*R*-Me;Py) was 0.85 V (vs Ag^+/Ag). The fact that the oxidation potential of the piperazinium ring in polymer(*R*-Me;Py) is higher than that in polymer(*R*-Me;H) is ascribed to the presence of electron-withdrawing pyridyl groups in polymer(*R*-Me;Py). As shown in Figure 6b, the oxidation peak of the DMSO solution of polymer(*R*-Me;Py) shifted from 0.85 V (vs Ag^+/Ag) to 0.99 V (vs Ag^+/Ag) when the solution was left standing for 6 h.

■ CONCLUSION

In conclusion, ionic helical π-conjugated polymers were obtained by the reactions of *N*-(2,4-dinitrophenyl)-4-aryl-pyridinium chlorides with *R*-(−)- or *S*-(+)-2-methylpiperazines. CD measurements revealed that the polymers formed opposite helical conformations; therefore, it is clear that the helical conformation can be controlled by varying the substituent on the piperazinium ring. The helical conformations were induced in the main chain of achiral or racemic polymers through the

anion exchange reactions with chiral phosphate salts. The helical conformations disappeared as the 2-methylpiperazinium rings in the polymers converted from the boat to the chair form via a half-chair intermediate, and this conformational change was accompanied by a decrease in the amount of π-conjugation length. This affected the viscosity and the electrochemical properties of the polymer solutions. To the best of our knowledge, this is the first example of spontaneous, dynamic changes in a polymer's helical conformation that has been effected without using external stimuli. The results obtained in this study indicate that chiral piperazines and phosphate slats can be used as materials for the synthesis of ionic π-conjugated polymers with controlled helical conformations.

EXPERIMENTAL SECTION

General. *N*-(2,4-Dinitrophenyl)pyridinium chloride and *N*-(2,4-dinitrophenyl)-4-(4-pyridyl)pyridinium chloride were prepared according to the literature.[8,9] Other reagents were purchased and used without further purification. Solvents were dried, distilled, and stored under N_2. Reactions were carried out with standard Schlenk techniques under nitrogen.

IR and NMR spectra were recorded on a JASCO FT/IR-660 PLUS spectrophotometer and a JEOL AL-400 spectrometer, respectively. Elemental analysis was carried out on a Yanagimoto MT-5 CHN corder. UV−vis and CD spectra were obtained by a JASCO V-560 spectrometer and a JASCO J-720WS, respectively. GPC measurement was conducted with a Waters 150-C with polystyrene gel columns using a DMF solution of LiBr (6 mM) as an eluent with a RI detector. Cyclic voltammetry was performed in a DMSO solution containing 0.10 M $[Et_4N]BF_4$ with a Hokuto Denko HSV-110.

Synthesis of Polymer(*R*-Me;H). *N*-(2,4-Dinitrophenyl)pyridinium chloride (**1**) (0.57 g, 2.1 mmol) was dissolved in 10 mL of EtOH, and (*R*)-2-(−)-methylpiperazine (0.21 g, 2.1 mmol) was added to the solution under N_2. After the solution was refluxed for 11 h, the solvent was removed in vacuo. The resulting solid was washed with acetone (300 mL), reprecipitated from acetone (300 mL), and dried in vacuo to afford polymer(*R*-Me;H) (0.39 g, 83%). ^{1}H NMR (400 MHz, CD_3OD): δ 7.85 (2H), 7.72 (1H), 6.19 (2H), 3.47−4.57 (6H), 1.42 and 1.34 (3H). ^{13}C NMR (100 MHz, CD_3OD): 167.3, 162.8, 162.5, 161.1, 105.7, 59.6, 57.4, 54.9, 54.0, 52.8, 52.1, 50.7, 44.4, 43.3, 16.3, 15.0. Calcd for $(C_{10}H_{15}N_2Cl)_n$: C, 60.45; H, 7.61; N, 14.10. Found: C, 60.81; H, 7.55; N,13.84.

Other polymers were synthesized in a similar manner.

Polymer(*S*-Me;H). Yield = 72%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.85 (2H), 7.72 (1H), 6.19 (2H), 3.47−4.48 (7H), 1.41 and 1.34 (3H). ^{13}C NMR (100 MHz, CD_3OD): δ 167.3, 163.0, 162.5, 161.1, 105.7, 59.6, 59.3, 52.1, 49.6, 16.3, 15.0. Calcd for $(C_{10}H_{15}N_2Cl)_n$: C, 60.45; H, 7.61; N, 14.10. Found: C, 60.79; H, 7.48; N, 13.62.

Polymer(Me;H). Yield = 82%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.85 (2H), 7.73 (1H), 6.20 (2H), 3.57−4.57 (7H), 1.42 and 1.33 (3H). ^{13}C NMR (100 MHz, CD_3OD): δ 167.3, 163.7, 162.8, 162.5, 161.3, 105.7, 59.6, 59.3, 57.3, 54.0, 52.8, 50.7, 49.6, 44.5, 43.2, 16.3, 15.0. Calcd for $(C_{10}H_{15}N_2Cl)_n$: C, 60.45; H, 7.61; N, 14.10. Found: C, 61.00; H, 7.33; N, 13.98.

Polymer(*R*-Me;Py). Yield = 83%. ^{1}H NMR (400 MHz, CD_3OD): δ 8.69 (2H), 7.41 (2H), 7.07 (2H), 6.44 (2H), 3.56−4.34 (7H), 1.13−1.40 (3H). ^{13}C NMR (100 MHz, CD_3OD): δ 172.1, 159.3, 150.7, 144.8, 126.2, 107.4, 52.0, 51.5, 49.4, 44.4, 16.3, 16.0. Calcd for $(C_{15}H_{18}N_3Cl\cdot 0.5H_2O)_n$: C, 63.26; H, 6.72; N, 14.76. Found: C, 63.15; H, 7.00; N, 14.49.

Polymer(*S*-Me;Py). Yield = 92%. ^{1}H NMR (400 MHz, CD_3OD): δ 8.70 (2H), 7.41 (2H), 7.09 (2H), 6.45 (2H), 3.56−4.37 (7H), 1.13−1.41 (3H). ^{13}C NMR (100 MHz, CD_3OD): δ 172.0, 159.3, 150.7, 144.8, 126.2, 107.4, 52.0, 51.6, 49.4, 44.4, 16.3, 16.0. Calcd for $(C_{15}H_{18}N_3Cl\cdot 0.3H_2O)_n$: C, 64.07; H, 6.67; N, 14.94. Found: C, 63.59; H, 7.05; N, 14.63.

Polymer(Me;Py). Yield = 85%. ^{1}H NMR (400 MHz, CD_3OD): δ 8.62 (2H), 7.33 (2H), 7.00 (2H), 6.37 (2H), 3.50−4.40 (7H), 1.04−1.31 (3H). ^{13}C NMR (100 MHz, CD_3OD): δ 172.0, 159.3, 150.7, 144.7, 126.2, 107.4, 52.3, 51.5, 49.4, 44.2, 16.2, 15.2. Calcd for $(C_{15}H_{18}N_3Cl\cdot 0.5H_2O)_n$: C, 63.26; H, 6.72; N, 14.76. Found: C, 63.01; H, 7.09; N, 14.43.

Synthesis of *R*-(−)-1,1′-Binaphthyl-2,2′-diyl Sodium Phosphate. After a methanol solution (5 mL) of *R*-(−)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate (0.96 g, 2.7 mmol) was added to an aqueous solution (27 mL) of NaOH (0.11 g, 2.7 mmol), the reaction solution was stirred at 20 °C for 72 h. The solvents were removed under vacuum, and the resulting solid was dried under vacuum to obtain *R*-(−)-1,1′-binaphthyl-2,2′-diyl sodium phosphate as a white powder (0.94 g, 94%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.01 (t, J = 8.4 Hz, 4H), 7.43 (d, J = 7.6 Hz, 2H), 7.38 (d, J = 8.8 Hz, 2H), 7.29 (t, J = 6.8 Hz, 2H), 7.21 (d, J = 8.8 Hz, 2H). Calcd for $C_{20}H_{12}NaO_4P\cdot 0.2H_2O$: C, 64.25; H, 3.34. Found: C, 64.29; H, 3.78.

S-(+)-1,1′-Binaphthyl-2,2′-diyl sodium phosphate was synthesized in a similar manner.

Synthesis of Polymer(Me;H;*R*-BINAP). After a methanol solution (2 mL) of polymer(Me;H) (0.050 g, 0.022 mmol) and *R*-(−)-1,1′-binaphthyl-2,2′-diyl sodium phosphate (0.081 g, 0.022 mmol) was stirred at 20 °C for 24 h, the solvent was removed under vacuum. The resulting solid was reprecipitated from acetone, collected by filtration, and dried under vacuum to obtain polymer(Me;H;*R*-BINAP) as a brown powder (0.089 g, 90%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85−8.04 (6.5H), 7.58 (1H), 7.43 (d, J = 6.8 Hz, 1.5H), 7.39 (d, J = 8.2 Hz, 1.5H), 7.29 (t, J = 8.0 Hz, 1.5H), 7.21 (d, J = 8.4 Hz, 1.5H), 6.07 (2H), 3.17−4.15 (7H), 1.27 and 1.18 (3H).

Data of Polymer(Me;H;*S*-BINAP). Polymer(Me;H;*S*-BINAP) was synthesized in a similar manner. Yield = 91%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.85−8.04 (7.0H), 7.58 (1H), 7.44 (d, J = 6.8 Hz, 1.68H), 7.40 (d, J = 8.8 Hz, 1.68H), 7.29 (t, J = 8.0 Hz, 1.69H), 7.21 (d, J = 8.8 Hz, 1.68H), 6.04 (2H), 3.17−4.13 (7H), 1.27 and 1.18 (3H).

ASSOCIATED CONTENT

Supporting Information. Photograph of STS molecular model. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: iyamaguchi@riko.shimane-u.ac.jp.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research (C) from Ministry of Education, Science, Culture, and Sports Japan (No. 21550173).

REFERENCES

(1) Yamaguchi, I.; Shingai, S.; Sato, M. *Macromolecules* **2008**, *41*, 6292–6298.

(2) (a) Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. *Chem. Rev.* **2009**, *109*, 6102–6211. (b) Cornelissen, J. J. L. M.; Rowan, A. E.; Nolte, R. J. M.; Sommerdijk, N. A. J. M. *Chem. Rev.* **2001**, *101*, 4039–4070. (c) Fujiki, M. *Macromol. Rapid Commun.* **2001**, *22*, 539–563. (d) Nakano, T.; Okamoto, Y. *Chem. Rev.* **2001**, *101*, 4013–4038. (e) Green, M. M.; Peterson, N. C.; Sato, T.; Teramoto, A.; Cook, R.; Lifson, S. *Science* **1995**, *268*, 1860–1866. (f) Okamoto, Y.; Nakano, T. *Chem. Rev.* **1994**, *94*, 349–372.

(3) (a) Yashima, E.; Maeda, K. *Macromolecules* **2008**, *41*, 3–12. (b) Maeda, K.; Yashima, E. *Top. Curr. Chem.* **2006**, *265*, 47–88. (c) Yashima, E.; Maeda, K.; Nishimura, T. *Chem.—Eur. J.* **2004**, *10*, 43–51.

(4) (a) Fujii, T.; Shiotsuki, M.; Inai, Y.; Sanda, F.; Masuda, T. *Macromolecules* **2007**, *40*, 7079–7088. (b) Zhao, H.; Sanda, F.; Masuda, T. *Polymer* **2006**, *47*, 2596–2602. (c) Sanda, F.; Teraura, T.; Masuda, T. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 4641–4647. (d) Mayer, S.; Maxein, G.; Zentel, R. *Macromolecules* **1998**, *31*, 8522–8525. (e) Müller, M.; Zentel, R. *Macromolecules* **1994**, *27*, 4404–4406. (f) Maxein, G.; Zentel, R. *Macromolecules* **1995**, *28*, 8438–8440. (g) Müller, M.; Zentel, R. *Macromolecules* **1996**, *29*, 1609–1617.

(5) (a) Brouwer, A. M.; Zwier, J. M.; Svendsen, C.; Mortensen, O. S.; Langkilde, F. W.; Wilbrandt, R. *J. Am. Chem. Soc.* **1998**, *120*, 3748–3757. (b) Brouwer, A. M.; Wiering, P. G.; Zwier, J. M.; Langkilde, F. W.; Wilbrandt, R. *Acta Chem. Scand.* **1997**, *51*, 217–219.

(6) (a) Kokado, K.; Tokoro, Y.; Chujo, Y. *Macromolecules* **2009**, *42*, 9238–9242. (b) Khan, A.; Hecht, S. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 1619–1627. (c) Zhang, H.-C.; Pu, L. *Macromolecules* **2004**, *37*, 2695–2702.

(7) Fuoss, R. M.; Strauss, U. P. *J. Polym. Sci.* **1948**, *3*, 246–263.

(8) Zincke, T. H.; Heuser, G.; Möller, W. I. *Ueber Justus Liebigs Ann. Chem.* **1904**, *333*, 296.

(9) Yamaguchi, I.; Higashi, H.; Shigesue, S.; Shingai, S.; Sato, M. *Tetrahedron Lett.* **2007**, *48*, 7778–7781.