Ring-Opening Copolymerization of Pyridinium Salts with Piperazine To Give Ionic Polymers with Expanded π-Conjugation System Derived from Through-Space Interaction in a Piperazinium Ring

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ABSTRACT: The reactions of *N*-(2,4-dinitrophenyl)-4-arylpyridinium chlorides (aryl (Ar) = phenyl and 4-pyridyl) with piperazine caused ring-opening of the pyridinium ring to yield polymers that consisted of the 5-piperazinium-3-aryl-penta-2,4-dienylideneammonium chloride unit [−$N(CH_2CH_2)_2N^+(Cl^-)$=CH−CH=C(Ar)−CH=CH−] (Ar = phenyl, unit A, and 4-pyridyl, unit B). Copolymers having both the unit A and unit B and the model compounds were also obtained. The ^{1}H NMR spectra suggested that the π-electrons of the penta-2,4-dienylideneammonium group of the polymers, the copolymer, and the model compounds were delocalized. UV−vis measurements revealed that the π-conjugation system expanded along the polymer chain due to the orbital interaction between the electrons on the two nitrogen atoms of the piperazinium ring, and its conversion from the boat form to the chair form via the half-chair form occurred stepwise accompanied by the decrease of the π-conjugation length. Kinetic studies of the conversion of the piperazinium ring was carried out. The surface of the pellets molded from the polymers and the copolymer showed metallic luster. The polymers and the copolymer received electrochemical oxidation in a solution.

Introduction

π-Conjugated polymers have attracted considerable attention due to their interesting chemical properties and practical applications.[1] Their 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. However, the interaction between the orbitals of electrons on the nitrogen atoms present in aliphatic cyclic diamine enables the expansion of the π-conjugation system even when aliphatic cycle exists in the polymer main chain. Such a polymer will exhibit high solubility in organic solvents owing to the flexibility of the aliphatic cycle in contrast to π-conjugated polymers consisting of rigid aromatic rings.

Hoffmann first reported the through-space/through-bond interaction between the orbitals of the two lone pairs on the nitrogen atoms in 1,4-diazabicyclo[2.2.2]octane (DABCO).[2] It was proposed that the nonbonding electrons on the nitrogen atoms were able to communicate with each other in DABCO.[3] It was reported that orbital interaction occurred between electrons on amino nitrogens of cationic N,N-disubstituted piperazines.[4] Such an orbital interaction did not occur in the neutral N,N-disubstituted piperazines.[4b] On the basis of these reports, it is considered that the polymers consisting of a piperazinium ring linked by π-conjugated units may bring about the expansion of the π-conjugation system along the polymer main chain. Only a limited number of reports have been presented on through-space and/or through-bond π-conjugated polymers. Chujo and co-workers reported that through-space conjugated polymers have the [2.2]paracyclophane unit in the main chain.[5] To the best of our knowledge, until this date, no other report has been presented on the polymer with the expanded π-conjugation system along the polymer chain through nonaromatic cycle, such as piperazine; this may be ascribed to the difficulty in synthesizing the polymer having a piperazinium ring linked by π-conjugated units. The investigation of the chemical properties of the polymer having the expanded π-conjugation system derived from the through-bond and/or through-space interaction in the nonaromatic cycle will provide fundamental information for the development of new π-conjugated polymers. In this study, in order to obtain polymers having piperazinium rings linked by π-conjugated units, we attempted to carry out the ring-opening reaction of the pyridinium ring in *N*-(2,4-dinitrophenyl)-4-arylpyridinium chloride with piperazine. This reaction can provide polymers that consist of the 5-piperazinium-3-aryl-penta-2,4-dienylideneammonium chloride unit [−$N(CH_2CH_2)_2N^+(Cl^-)$=CH−CH=C(Ar)−CH=CH−] (Ar = aryl).

Polymers having isomerizable groups such as azo and vinylene in the main chain have received increasing attention because they have special properties and potential applications in actuators, molecular switches, and recording media, which rely on the changes of the polymer properties following isomerization.[6] The optical and electrochemical properties of the polymer that consists of the piperazininum ring linked by π-conjugated units will change as a result of the conversion of the piperazinium ring between the boat and chair forms according to the fact that the through-space/through-bond interaction depends on the conformation of the piperazinium ring.[4b] To the best of our knowledge, until this date, no report has been presented on the investigation of the boat−chair conversion of the piperazine ring in the polymer main chain. In this study, the conversion of the piperazinium ring in the polymer chain and its effect on the π-conjugation length are investigated by UV−vis spectroscopy.

Herein, we report the synthesis of the polymers, the copolymer, and their model compounds by using the ring-opening reactions of *N*-(2,4-dinitrophenyl)-4-arylpyridinium chlorides with piperazine and N-substituted piperazines. The optical and electrochemical properties of the polymers, the copolymer, and the model compounds in solution and solid state are also reported.

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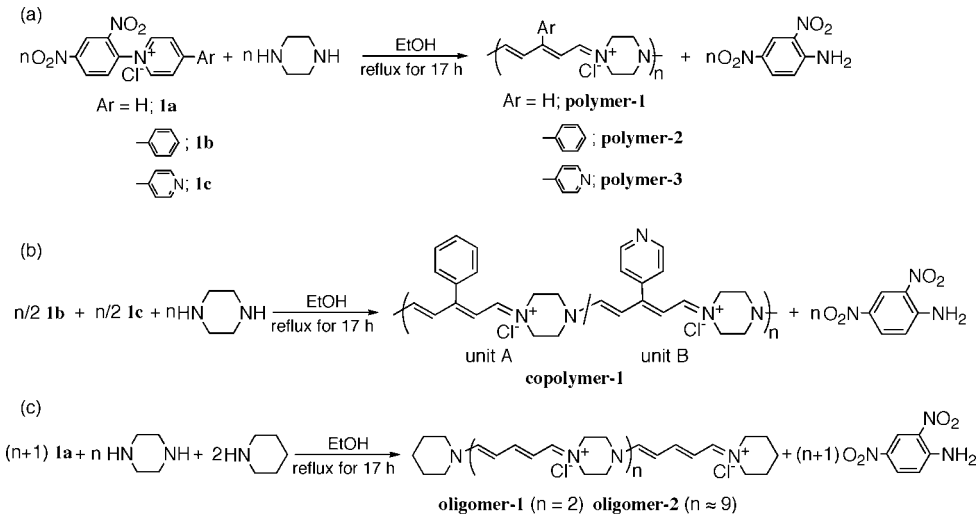
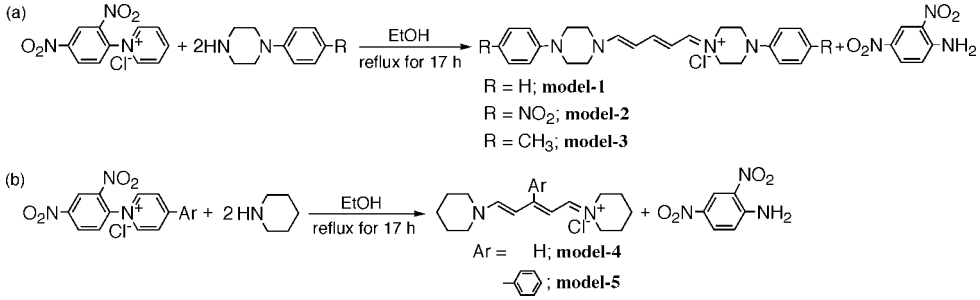
Scheme 1. Synthesis of Polymers, Copolymer, and Oligomer



Scheme 2. Synthesis of Model Compounds



Results and Discussion

Synthesis. The reactions of piperazine with *N*-(2,4-dinitrophenyl)-4-arylpyridinium chlorides **1a**−**1c** in refluxing ethanol caused ring-opening of the pyridinium ring to provide **polymer-1**, **polymer-2**, and **polymer-3** in 93%, 100%, and 79% yields, respectively (Scheme 1a). Copolymer **copolymer-1** which consisted of the 5-piperazinium-3-phenylpenta-2,4-dienylideneammonium chloride unit (unit A) and the 5-piperazinium-3-(4-pyridyl)-penta-2,4-dienylideneammonium chloride unit (unit B) was synthesized by the reaction of piperazine with a mixture of **1b** and **1c** in a 1:0.5:0.5 molar ratio in 88% yield (Scheme 1b). The reaction of **1a**, piperazine, and piperidine in a 2:1:2 molar ratio yielded an oligomer that is capped with piperidine and piperidinium groups at both ends (Scheme 1c). The oligomeric product separated into EtOH soluble part **oligomer-1** and EtOH insoluble part **oligomer-2**.

Model compounds **model-1**, **model-2**, and **model-3** were synthesized by reactions of N-substituted piperazines with **1a** in 88%, 47%, and 65% yields, respectively (Scheme 2a). The reactions of piperidine with **1a** and **1b** yielded model compounds **model-4** and **model-5** having a phenyl substituent on the aminopenta-2,4-dienylidene unit in 37% and 78% yields, respectively (Scheme 2b). The results of these reactions are summarized in Table 1.

The polymers and copolymer thus obtained were completely soluble in MeOH and partially soluble in organic solvents such as dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF). The model compounds were soluble in polar organic solvents such as MeOH, DMSO, and DMF. The structures of the polymers and model compounds were determined by FAB mass spectroscopy, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis.

NMR and IR Spectra. Figure 1 shows the ^{1}H NMR spectra of **model-1**, **model-2**, and **model-3** in DMSO-d_6. The presence of the three signals due to hydrogen atoms H^a, H^c, and H^b in a 2:1:2 integral ratio suggests that the π-electrons are delocalized along the aminopenta-2,4-dienylidene group. The coupling constants, $J_{Ha\text{-}Hb} = 12.0$ Hz and $J_{Hb\text{-}Hc} = 12.8$ Hz, of **model-1** indicate that the aminopenta-2,4-dienylidene group forms an all-trans geometrical structure, as shown in Scheme 2. Chemical shifts of the peaks of **model-1**, **model-2** having electron-withdrawing nitro groups, and **model-3** having electron-donating methyl groups due to H^a are δ 7.935, 7.949, and 7.906, respectively. ^{13}C NMR peaks due to carbon atoms adjacent to the piperazinium ring of **model-1**, **model-2**, and **model-3** were observed at δ 150.0, 153.9, and 148.0, respectively. These observations suggest that the N-substituents affect the electronic properties of the vinylene protons and carbons due to the orbital interaction between the electrons on the nitrogen atoms of the piperazinium ring.

Figure 2 shows the ^{1}H NMR spectra of **model-1** at the temperature range of 30−70 °C. The peaks at δ 3.77 and 3.72 are assignable to equatorial and axial protons of the inner methylene of the piperazinium ring, respectively. This assignment is based on the usual rule that the atom in the equatorial position is less shielded.[7] The peak due to the outer methylene protons of the piperazinium ring is duplicated with the signal of H_2O at the temperature range of 30−60 °C, and the peak is observed as a single peak at 70 °C. As depicted in Figure 2, the peak due to the axial protons of the inner methylene of the piperazinium ring is shifted to a lower magnetic field with an increase in temperature. These observations indicate that the axial−equatorial isomerization of the inner methylene protons occurred with an increase in temperature.

Table 1. Synthesis Results and Optical and Electrochemical Properties

				absorption, nm		rate constant[g]		
product	yield, %	η_{sp}/c, g^{-1} dL[a]	M_w (M_w/M_n)[b]	in EtOH	in film[f]	$k \times 10^{-5}$, s^{-1}	$k' \times 10^{-5}$, s^{-1}	E_a, V[h]
polymer-1	93	0.38	9150 (1.5)	472 (4.80),[c] 472,[d] 424[e]	485	40	5.4	0.70
polymer-2	100	0.26	9960 (1.2)	501 (4.70),[c] 474,[d] 444[e]	517	53	2.6	0.50
polymer-3	79	0.10	6240 (1.3)	506 (4.57),[c] 473,[d] 444[e]	516	52	2.8	0.81
copolymer-1	88	0.20	2360 (1.1)	504 (4.77),[c] 474,[d] 444[e]	509	54	2.9	0.80
oligomer-1	12			457 (4.61),[c] 445,[d] 419[e]				0.92
oligomer-2	73			478 (4.70),[c] 442,[d] 420[e]				0.98
model-1	88			420 (4.86)[e]				0.64
model-2	47			429 (5.23)[e]				0.90
model-3	65			420 (5.11)[e]				0.59
model-4	37			420 (4.58)[e]				0.73
model-5	78			438 (5.15)[e]				0.70

[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). [c] Measured immediately after preparation of the solutions. log ε (M^{-1} cm^{-1}) values 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] Prepared by cast MeOH solutions on a quartz glass plate and immediate evaporation of the solvent. [g] 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 35 °C, respectively. [h] Peak potential measured by cyclic voltammetry in DMSO solution of $[Et_4N]BF_4$ (0.10 M).

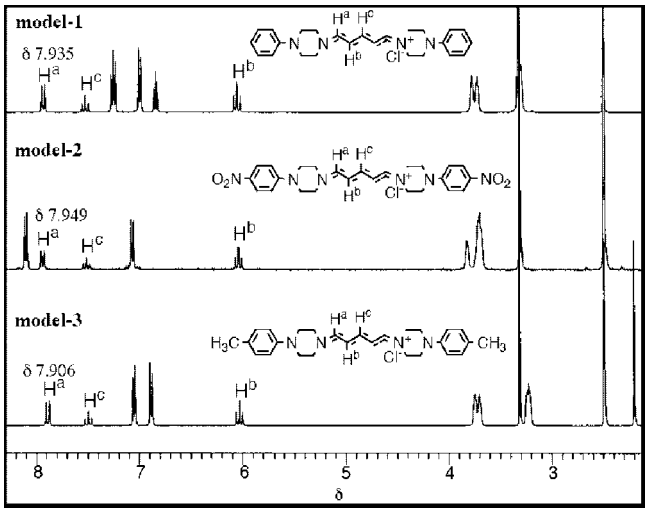


Figure 1. ^{1}H NMR spectra of **model-1**, **model-2**, and **model-3** in DMSO-d_6.

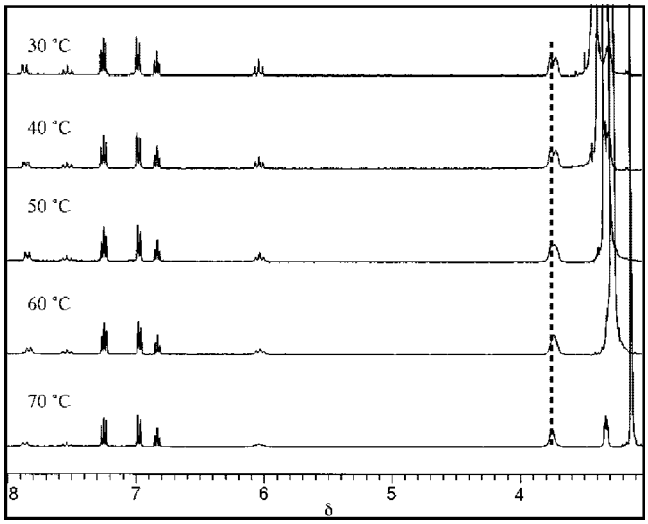


Figure 2. ^{1}H NMR spectra of **model-1** at the various temperatures.

Figure 3 depicts the ^{1}H NMR spectra of **polymer-1**, **polymer-2**, **polymer-3**, and **copolymer-1** in CD_3OD that are measured immediately after the preparation of the solutions. The peaks due to vinylene protons of **polymer-1** are observed at the positions similar to those of **model-4**. The observation of the two signals assignable to the vinylene protons of **polymer-2** and **polymer-3** at approximately δ 6.3 and 7.1 in a 1:1 integral ratio suggests that the π-electrons are delocalized along the aminopenta-3-phenyl-2,4-dienylidene group. The ^{1}H NMR chemical shifts of **copolymer-1** are essentially the same as those of the corresponding homopolymers. The ratio of the unit A and unit B in **copolymer-1** estimated from the peak integral between the peaks due to the pyridyl protons in unit B at δ 8.60 and the piperazinium protons in the range δ 3.86−3.78 is 0.46:0.54; this value is largely consistent with the monomer feed ratio. The peaks ascribed to the terminal groups of the polymers and copolymer are not observed in the ^{1}H NMR spectra.

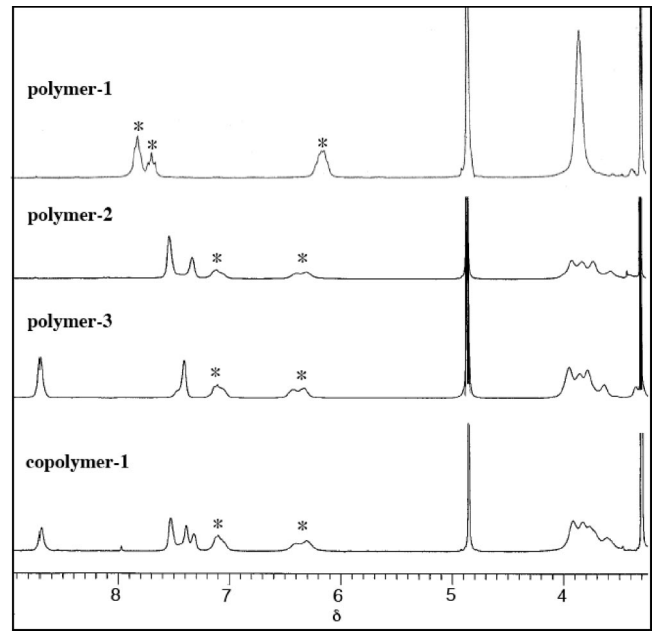


Figure 3. ^{1}H NMR spectra of **polymer-1**, **polymer-2**, **polymer-3**, and **copolymer-1** in CD_3OD. Peaks with an asterisk are due to protons of penta-2,4-dienylideneammonium chloride unit.

The chain lengths (n) of **oligomer-1** and **oligomer-2** were estimated as 2 and 9 from the peak integral between the peaks due to the central piperazinium and terminal piperizine rings.

IR spectra of the polymers and the copolymer showed absorptions assignable to ν(C=C) and ν(C=N) of the 5-piperazinium-penta-2,4-dienylideneammonium group at approximately 1625 and 1180 cm^{-1}, respectively. In contrast, no absorption due to ν(C=C) of the penta-2,4-dienylideneammonium group was observed in the IR spectra of the model

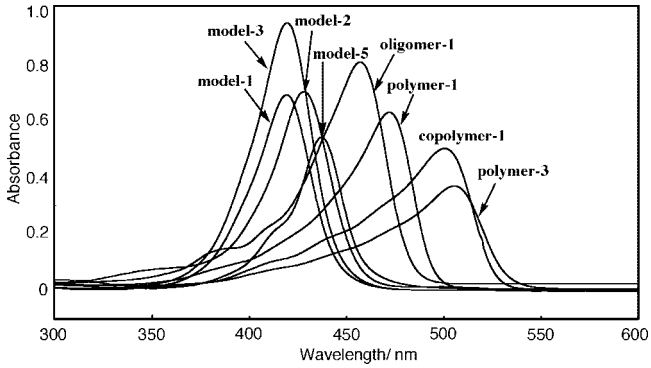


Figure 4. UV−vis spectra of freshly prepared MeOH solutions of the polymers and the model compounds.

compounds, probably due to their symmetric structures caused by delocalization of the π-electrons along the penta-2,4-dienylideneammonium group.

Molecular Weight and Viscosity. The GPC measurements suggested that the weight-average molecular weights (M_ws) of the DMF-soluble part of **polymer-1**, **polymer-2**, **polymer-3**, and **copolymer-1** were 9150, 9960, 6240, and 2360, respectively. The lower M_w value of **copolymer-1** is apparently due to the low solubility in DMF. The reduced viscosities (η_{sp}/c) in methanol solutions of **polymer-1**, **polymer-2**, **polymer-3**, and **copolymer-1** were 0.38, 0.26, 0.10, and 0.20 g^{-1} dL (c = 0.1 g dL^{-1}), respectively. The η_{sp}/c values of the polymers in methanol increased when their concentration c was reduced, suggesting that the polymers behaved as polymeric electrolytes in the dilute solutions.[8]

UV−vis Spectra. Figure 4 compares the UV−vis spectra of freshly prepared MeOH solutions of the polymers and the model compounds. The absorption data are summarized in Table 1. As shown in Figure 4, the absorptions of the methanol solutions of the polymers and the copolymer are observed at longer wavelengths than those of the model compounds due to the expansion of the π-conjugation system between the aminopenta-2,4-dienylidene groups through the piperazinium ring. Besides, the absorption maximum (λ_{max}) of **oligomer-1** locates between those of **model-4** and **polymer-1**. As judged from these data, the orbital interaction between the electrons on the two nitrogen atoms of the piperazinium ring may contribute to the expansion of the π-conjugation system. The observation of λ_{max} of **model-5** at a longer wavelength than that of **model-4** suggests that the π-conjugation system is expanded to the phenyl group. The polymer obtained by the reaction of 4,13-diaza-18-crown 6-ether (DA18C6) with **1a** showed λ_{max} at a shorter wavelength (429 nm)[9] than **polymer-1** in MeOH. These data suggested that the expansion of the π-conjugation system derived from the orbital interaction depended on the distance between the two nitrogen atoms of the cyclic diamine.

The absorption wavelengths of freshly prepared MeOH solutions of the polymers vary with the duration for which they are left standing in air, as shown in Figure 5. The changes of UV−vis spectra of **polymer-2** appear to correspond to the two-step conversion of the pieprazinium ring from the boat form to the chair form via the half-chair form, as illustrated in Scheme 3.

It is reported that the orbital interaction between the electrons on the nitrogen atoms of cationic *N*,*N*-dimethylpiperazine depends on its conformation; that is, the through-space coupling requires a boat-type conformation to bring the nitrogen atoms close together.[4b] Therefore, the through-space interaction in the piperazinium ring of the polymers is predominant rather than the through-bond interaction for the expansion of the π-conjugation system.

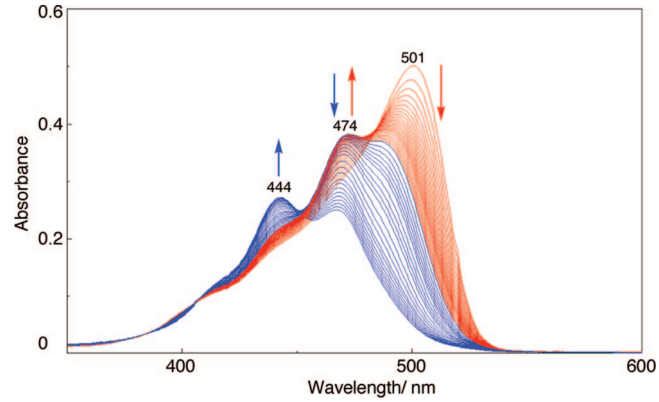
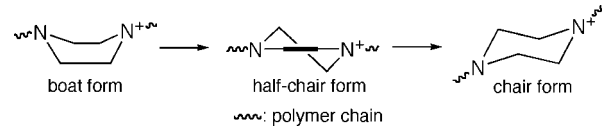


Figure 5. Changes of UV−vis spectra of MeOH solution of **polymer-2** with time upon standing in air at 30 °C. Spectra indicated by red and blue lines were measured in every 3 and 10 min, respectively.

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



At the fist step indicated by red lines in Figure 5, the absorption at 501 nm decreases with a gradual shift to a shorter wavelength and that at 474 nm increases simultaneously. The variations in the two absorptions apparently correspond to the decrease of the π-conjugation length caused by the conversion of the piperazinium ring from the boat form to the half-chair form and the formation of the polymer having the half-chair piperazinium rings, respectively. The through-space interaction in the piperazinium ring is considered to decrease in the half-chair form rather than in the boat form since the nitrogen atoms in the half-chair piperazinium ring are more distributed than those in the boat form. The decrease in the absorption at 474 nm and the increase in the absorption at 444 nm in the second step indicated by blue lines in Figure 5 are ascribed to the conversion of the pieprazinium ring from the half-chair form to the chair form. When the piperazinium rings of the polymers are in the chair form, the expansion of the π-conjugation system does not occur because the through-space interaction in the piperazinium ring is inhibited. This inference confirmed by the result indicating that the value of λ_{max} of **polymer-2** having the piperazinium ring in the chair form is close to that of the model compounds. These absorption changes of the polymers are not observed in the solid state.

The changes of the absorbances at 501 and 444 nm in the first and second steps with time t obey the first-order rate law with rate constants of 5.3 × 10^{-4} and 2.6 × 10^{-5} s^{-1} at 30 °C, respectively. Rate constants of the other polymers for the conversion of the piperazinium ring from the chair form to the chair form via the half-chair form are summarized in Table 1. Computational calculation predicts that the methyl groups of cationic *N*,*N*-dimethylpiperazine are at the axial position in the boat form and at the equatorial position in the chair form. Thus, penta-2,4-dienylidene groups bonded to the piperazinium ring of the polymers apparently locate at the axial position in the boat and half-chair forms and at the equatorial position in the chair form. The k' value at 30 °C is by about 20 times smaller than the k value probably due to the assumption that the conversion from the half-chair form to the chair form causes a greater conformation change of the polymer chain as compared to that from the boat form to the half-chair form.

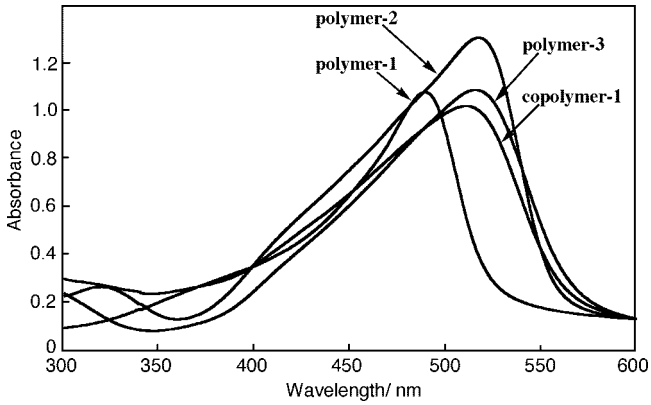


Figure 6. UV−vis spectra of cast films of the polymers and the copolymer on a quartz glass plate.

On the other hand, the UV−vis spectra of the solutions of the model compounds did not vary with time. As observed from the UV−vis results, the piperazinium rings of the freshly synthesized model compounds apparently assume an energetically favorable chair form rather than the boat form.

It has been reported that the π-conjugated alternative copolymers consisting of π-rich and π-deficient aromatic rings show the intriguing optical and electrochemical properties attributable to the charge transfer (CT) between the π-rich and π-deficient aromatic rings.[10] However, no absorption due the CT is observed in the UV−vis spectrum of **copolymer-1** in spite of the presence of the π-deficient pyridyl group in the unit B and the relative π-rich phenyl group in the unit A. A possible reason for this result is that **copolymer-1** is a random copolymer consisting of the unit A and unit B.

The polymers were hydrolyzed by the treatment with a methanol solution of NaOH. The hydrolysis caused decrease of the conjugation length, as revealed from the UV−vis measurements. It was reported that N-substituted 5-anilino-2,4-pentadienylideneammonium chloride $R_2N-CH=CH-CH=CH-CH=N^+(Cl^-)R_2$ were hydrolyzed by the treatment with NaOH(aq) to convert into aldehydes $R_2N-CH=CH-CH=CH-CH=O$.[11]

Solid State Properties. To investigate optical properties in the solid state, films of the polymers were prepared by casting their MeOH solutions on a quartz glass plate and immediate evaporation of the solvent. In the cast film of the polymers, the peak positions are shifted to longer wavelengths than those in MeOH, as depicted in Figure 6. It has been reported that π-conjugated polymers that form π-stacked structures in the solid state often cause a bathochromic shift of λ_{max}.[12,13] On the basis of these results, the polymers may form ordered structures in the solid state.

The surface of the pellets that are molded from the polymers and the copolymer shows metallic luster, and their colors depend on the structures of the polymers. As shown in parts a and b of Figure 7, the colors of the pellets that are molded from **polymer-1** and **polymer-2** are blue and green, respectively; these observations are consistent with the absorption data that the cast film of the **polymer-2** shows absorptions at longer wavelengths (λ_{max} = 517 nm) than **polymer-1** (λ_{max} = 485 nm). The metallic luster is apparently attributed to the ordered structures of the polymers and the copolymer in the solid state. A similar metallic luster has been reported for the films of π-conjugated poly(aryleneethynylene)s consisting of electron-accepting benzothiadiazole unit and electron-donating alkylthiophene or dialkoxybenzene unit, which form π-stacked structures in the solid state.[13]

As depicted in Figures 7c,d, solids obtained by evaporation of the solvent of EtOH solution of **polymer-1** that is left

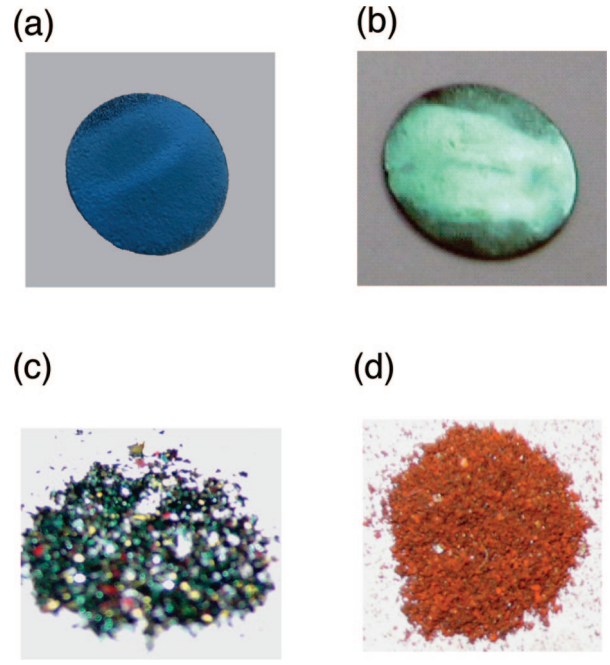


Figure 7. Photographs of pellets molded from (a) **polymer-1** and (b) **polymer-2**, (c) solids obtained by evaporation of the solvent after EtOH solution of **polymer-2** was left standing for 4 days, and (d) intact **polymer-2**.

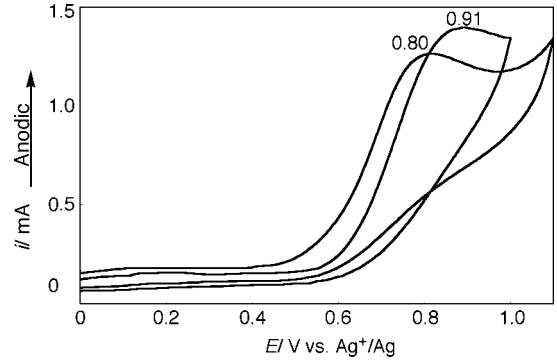
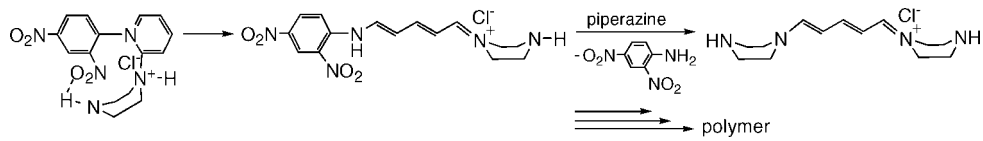


Figure 8. Cyclic voltammograms of **copolymer-1** in DMSO solution including $[Et_4N]BF_4$ (0.1 M) measured at immediately after preparation of the solution and after the solution was left standing for 14 h. The scan rate was 50 mV s^{-1}.

standing for 4 days show metallic luster; this color is quite different from the reddish-brown color of intact **polymer-1**. These observations suggest that the polymer having the piperazinium ring in the chair form is subjected to take the stacked structure than that in the boat form.

Cyclic Voltammograms. Cyclic voltammetry (CV) measurements suggested that the polymers and the copolymer underwent an electrochemical oxidation in the DMSO solution including $[Et_4N]BF_4$ (0.1 M). The peak potentials of the freshly prepared solutions are summarized in Table 1. The peak potentials of **polymer-2** and **copolymer-1** are higher than that of **polymer-1** due to the presence of electron-withdrawing pyridyl groups in **polymer-2** and **copolymer-1**. As shown in Figure 8, the oxidation peak of the DMSO solution of **copolymer-1** is shifted to a higher potential after the DMSO solution is left standing for 14 h. These results are consistent with the fact that the π-conjugation length of the copolymer decreases with time, corresponding to the conversion of the piperazinium ring from the boat form to the chair form. The peak potential and peak current of the polymers almost unchanged with change of scan rates. The solutions of the polymers after the CV

Scheme 4. Possible Reaction Mechanism



measurements showed λ_{max} at a shorter wavelength than those of the polymers having piperazinium rings in the chair form. As judged form these results, the disappearance of the corresponding reduction peak for the oxidative doping appears to be attributed to the instability of the polymers toward electrochemical reaction.

Reaction Mechanism. Scheme 4 shows a possible reaction pathway for the polymers, where nucleophilic addition of amine to the pyridinium ring of **1** occurs first, followed by the ring-opening of the dihydropyridyl ring and elimination of 2,4-dinitroaniline by the reaction of the ring-opening compound with piperazine to form the polymer repeating unit. It has been reported that the reaction of **1** with amine is initiated with nucleophilic addition of the amine to the 2-position of the pyridinium ring of **1**.[14]

The reaction of *N*-(2,4-dinitrophenyl)penta-2,4-dienylidene-1-*N*-arylinium chloride with piperizine to provide *N*-(5-piperidino-2,4-pentadienylidene)piperizinium chloride has been reported.[11] It is known that piperazine derivatives usually assume the energetically stable chair form rather than the boat form.[4b] However, the piperazinium ring of the freshly synthesized polymers primarily assumes the boat form, which contributes to the expansion of π-conjugation system, as revealed by the UV−vis measurements. The intramolecular hydrogen bond between the nitro group and the NH group in the intermediate adduct seems to play an important role in the predominant formation of the piperazinium ring with the boat form in the polymers, as illustrated in Scheme 4.

In contrast, an intermediate adduct formed by the addition reaction of the NH group of *N*-arylpiperazines to the pyridinium ring of **1** has no NH group to form the hydrogen bond. Thus, the ring-opening reaction of the intermediate adduct apparently provides the model compounds whose piperazinium rings assume the energetically favorable chair form. This inference is consistent with the UV−vis results described above.

Conclusions

The reactions of *N*-(2,4-dinitrophenyl)-4-arylpyridinium chloride (aryl = H, phenyl, and 4-pyridyl) with piperazine yielded new types of π-conjugated polymers that consisted of the 5-piperazinium-3-aryl-penta-2,4-dienylideneammonium chloride unit. UV−vis measurements revealed that the π-conjugation system expanded along the polymer chain due to the through-space interaction in the piperizinium ring. The conversion of the piperazinium ring from the boat form to the chair form via the half-chair form occurred stepwise accompanied by the decrease of the π-conjugation length. The results obtained in this study will enable the use of the interaction between electrons in nonaromatic heterocyclic compounds for the synthesis of polymers with the expanded π-conjugation system, which, in turn, would lead to the development of new π-conjugated polymers.

Experimental Section

General. Solvents were dried, distilled, and stored under nitrogen. *N*-(2,4-Dinitrophenyl)pyridinium chloride,[15] *N*-(2,4-dinitrophenyl)-4-phenylpyridinium chloride,[16] and *N*-(2,4-dinitrophenyl)-4-(4-pyridyl)pyridinium chloride[16] were prepared according to the literature. Other reagents were purchased and used without further purification. 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 and FAB-MS analyses were carried out on a Yanagimoto MT-5 CHN corder and a JEOL JMS-700, respectively. *m*-Nitrobenzyl alcohol was used as a matrix. UV−vis spectra were obtained by a JASCO V-560 spectrometer. DSC profiles were recorded on a Shimadzu DSC-50 under nitrogen. Cyclic voltammetry was performed in a DMSO solution containing 0.10 M $[Et_4N]BF_4$ with a BAS 100B. GPC analyses were carried out by a Toso HLC 8020 with polystyrene gel columns using a DMF solution of LiBr (0.006 M) as an eluent with RI and UV detectors.

Synthesis of Polymer-2. *N*-(2,4-Dinitrophenyl)-4-phenylpyridinium chloride (**1b**) (0.18 g, 0.51 mmol) and piperazine (0.044 g, 0.51 mmol) were dissolved in 3 mL of EtOH under N_2. After the solution was refluxed for 17 h, a dark brown precipitate from the reaction solution was collected by filtration. The precipitate was washed with acetone (300 mL) and dried under vacuum to give **polymer-2** (0.086 g, 76%) as a reddish-brown solid. **Polymer-2** was also obtained from the filtrate. Evaporation of the solvent of the filtrate gave a reddish-brown solid, which was washed with acetone (300 mL) and dried in vacuo to afford **polymer-2** (0.028 g, 24%). Total yield of **polymer-2** was 100%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.44 (s, 4H), 7.24 (s, 2H), 7.02 (s, 1H), 6.29 (s, 1H), 6.21 (s, 1H), 3.82−3.48 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 176.0, 159.7, 142.0, 135.7, 131.0, 129.9, 107.9, 55.3, 53.3, 47.8, 46.6. Calcd for $(C_{15}H_{17}N_2Cl\cdot 0.25H_2O)_n$: C, 67.91; H, 6.64; N, 10.56. Found: C, 67.88; H, 6.21; N, 9.91.

Polymer-1 and **polymer-3** were synthesized in a similar manner.

Polymer-1. Yield = 93%. ^{1}H NMR (400 MHz, CD_3OD): δ 7.83 (m, 2H), 7.70 (m, 1H), 6.15 (m, 2H), 3.86 (s, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 167.4, 162.5, 105.7, 55.1, 53.4, 47.7, 46.4. Calcd for $(C_9H_{13}N_2Cl\cdot 0.15H_2O)_n$: C, 57.69; H, 7.63; N, 14.95. Found: C, 57.69; H, 7.56; N, 14.76.

Polymer-3. Yield = 79%. ^{1}H NMR (400 MHz, CD_3OD): δ 8.69 (s, 2H), 7.39 (s, 2H), 7.10 (br, 2H), 6.43 (br, 1H), 6.31 (br, 1H), 3.93−3.62 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 171.7, 159.4, 150.6, 144.8, 127.3, 107.2, 55.2, 53.3, 47.9, 46.7. Calcd for $(C_{14}H_{16}N_3Cl\cdot 0.3H_2O)_n$: C, 62.94; H, 6.26; N, 15.73. Found: C, 62.95; H, 5.88; N, 14.90.

Synthesis of Copolymer-1. *N*-(2,4-Dinitrophenyl)-4-phenylpyridinium chloride (**1b**) (0.18 g, 0.50 mmol), *N*-(2,4-dinitrophenyl)-4-(4-pyridyl)pyridinium chloride (**1c**) (0.18 g, 0.50 mmol), and piperazine (0.087 g, 1.0 mmol) were dissolved in 6 mL of EtOH under N_2. After the solution was refluxed for 17 h, a green precipitate from the reaction solution was collected by filtration. The precipitate was washed with acetone (200 mL) and dried under vacuum to give **copolymer-1** (0.037 g, 15%) as a green solid. **Copolymer-1** was also obtained from the filtrate. Evaporation of the solvent of the filtrate gave a dark brown solid, which was washed with acetone (200 mL) and dried in vacuo to afford **copolymer-1** (0.18 g, 73%). Total yield of **copolymer-1** was 88%. ^{1}H NMR (400 MHz, CD_3OD): δ 8.60 (s, 1.08H), 7.44 (s, 2H), 7.31 (s, 0.7H), 7.01 (br, 1.54H), 6.28 (br, 4H), 3.86−3.78 (m, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_3OD): δ 159.7, 159.6, 155.3, 132.5, 130.1, 130.4, 129.9, 126.3, 124.5, 107.7, 107.2, 55.3, 53.3, 52.2, 48.6, 46.7, 44.6, 43.8. Calcd for $\{(C_{15}H_{17}N_2Cl)_{0.46}(C_{14}H_{16}N_3Cl)_{0.54}\}_n$: C, 66.47; H, 6.35; N, 13.62. Found: C, 66.68; H, 6.06; N, 12.82.

Synthesis of Oligomer-1 and Oligomer-2. 1a (0.56 g, 2.0 mmol), piperazine (0.086 g, 1.0 mmol), and piperidine (0.17 g, 2. 0 mmol) were dissolved in 10 mL of EtOH under N_2. After the solution was refluxed for 17 h, a brown precipitate from the reaction solution was collected by filtration. The precipitate was washed with acetone (300 mL) two times and dried under vacuum to give **oligomer-1** (0.078 g, 12%) as a brown solid. Evaporation of the solvent of the filtrate gave a reddish-brown solid, which was washed with acetone (300 mL) two times and dried in vacuo to afford **oligomer-2** (0.13 g, 73%). Data of **oligomer-1**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91 (m, 4H), 7.77 (m, 2H), 7.47 (m, 3H), 6.06 (m, 4H), 5.87 (m, 2H), 3.77 (s, 16H), 3.59−3.62 (m, 8H), 1.65 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.9, 161.1, 159.1, 103.9, 103.8, 102.1, 55.7, 47.3, 26.4, 25.3, 23.0. Anal. Calcd for $C_{33}H_{51}N_4Cl_3N_6 \cdot 0.2H_2O$: C, 64.62; H, 8.38; N, 9.13. Found: C, 64.44; H, 8.21; N, 8.83. Data of **oligomer-2**: ^{1}H NMR (400 MHz, CD_3OD): δ 7.82 (m, 2H), 7.54−7.75 (m, 1H), 7.17 (m, 2H), 3.85 (2, 8H), 3.67 (s, 1.5H), 1.76 (s, 2.2H). Anal. Calcd for $(C_9H_{13}N_2Cl \cdot 0.2H_2O)_n$: C, 57.42; H, 7.17; N, 14.88. Found: C, 56.89; H, 6.81; N, 14.47.

Synthesis of Model-1. *N*-(2,4-Dinitrophenyl)pyridinium chloride, **1a** (0.28 g, 0.99 mmol), and *N*-phenylpiperazine (0.32 g, 1.99 mmol) were dissolved in 5 mL of dry ethanol under N_2. After the solution was refluxed for 17 h, the solvent was removed under vacuum. The resulting solid was washed with acetone (300 mL) and dried in vacuo to afford **model-1** as an orange powder (0.043 g, 88%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.94 (d, J = 12.0 Hz, 2H), 7.51 (t, J = 12.8 Hz, 1H), 7.24 (t, J = 8.8 Hz, 4H), 6.99 (d, J = 8.0 Hz, 4H), 6.83 (t, J = 7.2 Hz, 2H), 6.04 (t, J = 12.0 Hz, 2H), 3.77 (s, 4H), 3.72 (s, 4H), 3.31 (s, 8H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 163.0. 160.0, 150.0, 129.1, 119.6, 116.0, 102.8, 53.3, 48.8, 47.6, 45.8. FAB-MS: [M − Cl$^-$] = 387. Anal. Calcd for $C_{25}H_{31}N_4Cl \cdot 0.2H_2O$: C, 70.39; H, 7.42; N, 13.13. Found: C, 70.27; H, 7.11; N, 12.99.

Data of Model-2. Yield = 88%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.10 (d, J = 9.6 Hz, 4H), 7.93 (d, J = 11.6 Hz, 2H), 7.51 (t, J = 12.4 Hz, 1H), 7.07 (d, J = 9.6 Hz, 4H), 6.03 (t, J = 12.4 Hz, 2H), 3.82 (s, 2H), 3.71 (m, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 163.1, 160.4, 153.9, 137.3, 125.7, 112.8, 103.1, 52.2, 46.5, 45.6, 44.6. Calcd for $C_{25}H_{29}N_6ClO_4 \cdot 0.3H_2O$: C, 57.88; H, 5.76; N, 16.20. Found: C, 57.88; H, 5.38; N, 15.47.

Data of Model-3. Yield = 63%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.91 (d, J = 12.0 Hz, 2H), 7.49 (t, J = 12.4 Hz, 1H), 7.05 (d, J = 8.4 Hz, 4H), 6.89 (d, J = 8.8 Hz, 4H), 6.03 (t, J = 12.0 Hz, H), 3.75 (br, 4H), 3.71 (br, 4H), 3.23 (t, J = 5.2 Hz, 8H), 2.20 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 163.0, 160.0, 148.0, 129.5, 128.6, 116.3, 102.8, 53.3, 49.2, 48.2, 45.8, 20.0. Calcd for $C_{27}H_{35}N_4Cl \cdot 0.2H_2O$: C, 71.33; H, 7.85; N, 12.32. Found: C, 71.29; H, 7.44; N, 11.77.

Data of Model-4. Yield = 37% (hygroscopic). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (t, J = 11.7 Hz, 3H), 5.66 (t, J = 11.7 Hz, 2H), 3.67 (s, 4H), 3.44 (s, 4H), 1.70 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 164.7, 160.1, 101.8, 55.8, 47.0, 26.3, 26.2, 23.3. Calcd for $C_{15}H_{25}N_2Cl \cdot 5.5H_2O$: C, 48.97; H, 9.86; N, 7.61; Cl, 9.64. Found: C, 48.89; H, 9.86; N, 7.04; Cl, 8.81.

Data of Model-5. Yield = 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 4H), 7.15 (m, 1H), 6.66 (d, J = 10.7 Hz, 2H), 6.10 (d, J = 11.2 Hz, 2H), 3.54 (s, 2H), 3.27 (s, 2H), 3.16 (s, 2H), 1.91 (s, 2H), 1.65 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.3, 134.5, 129.3, 128.5, 128.4, 128.3, 105.9, 56.9, 48.4, 44.9, 26.7, 25.5, 23.6, 22.4. Calcd for $C_{21}H_{29}N_2Cl \cdot 0.2H_2O$: C, 72.37; H, 8.50; N, 8.04. Found: C, 72.02; H, 8.34; N, 7.79.

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