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Preparation of New Redox-Active Quaternized Poly(quinolinium) and Poly(isoquinolinium) Salts Showing Viologen-like Redox Behavior

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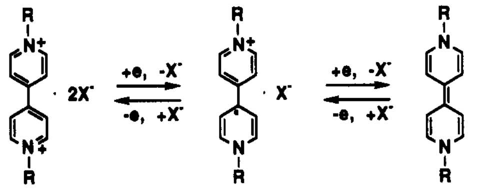
ABSTRACT: Quaternization of poly(quinoline-4,7-diyl) (P(4,7-Q)) and poly(isoquinoline-1,4-diyl) (P(1,4-iQ)) with alkylating reagents (CH_3I, $(CH_3O)_2SO_2$, and $(CH_3)_3CBr$) affords the corresponding quaternary poly(quinolinium) and poly(isoquinolinium) salts. The degree of quaternization was in the range 60–95%. The polymers are electrically conducting, with a conductivity of 10^{-6}–10^{-7} S cm^{-1}. Quaternized P(4,7-Q) is chemically and electrochemically redox active, and its cyclic voltammogram shows stable reversible redox peaks at ca. −0.5 and −0.75 V vs SCE, respectively. The color of the polymer changes from pale yellow to dark blue on reduction. On the other hand, quaternized P(1,4-iQ) does not give a stable redox cycle, presumably due to the instability of the cation radical formed by the reduction. Weitz-type two-step redox processes similar to those of 1,1′-disubstituted 4,4′-bipyridinium salts account for the redox reaction of quaternized P(4,7-Q).

Introduction

Since Michaelis first reported on the electrochemical behavior of 1,1′-disubstituted 4,4′-bipyridinium salts ("viologens"),[1] various types of viologens have been prepared and their chemical and electrochemical properties have been extensively investigated.[2] Viologens usually show the following Weitz-type two-step redox behaviors.

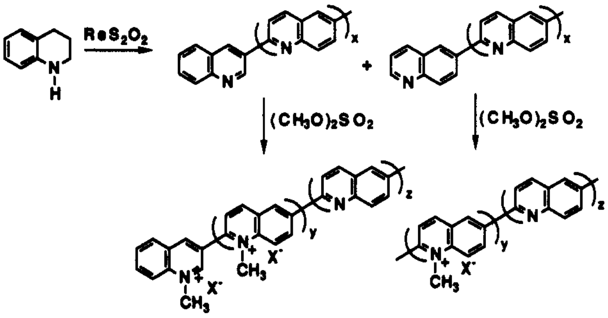


(1)

The first-step reduction forms a blue cation radical, and the second-step reduction is considered to form a neutral red quinoid. Due to the interesting redox phenomena and optical properties of viologens, various polymers containing the viologen structure in the polymer main chain[3] as well as in pendant groups[4] have been synthesized. The polymers have been applied to making modified electrodes[3e,f] as well as photochromic[3b,4b] and electrochromic devices.[3c,d]

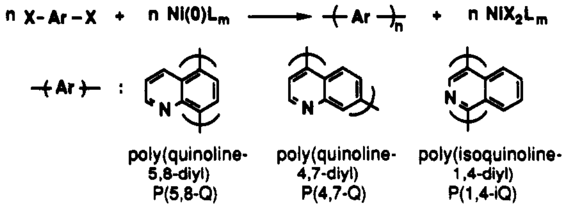
In contrast to the extensive study of the viologens having the 4,4′-bipyridinium unit, only a few reports on the Weitz-type redox behavior of other diquaternary diheterocyclic compounds with larger π-systems (e.g., 4,4′-biquinolinium salts and 1,1′-biisoquinolinium salts) have been published.[5] Especially, much less attention has been paid to polymers with diquaternary diheterocyclic units in the main chain. These polymers are expected to show redox and optical properties similar to those of viologen units.

Three groups, including our group, reported the preparation of poly(4-phenylquinoline-2,6-diyl),[6] a nonsubstituted quinoline oligomer,[7] and various poly(quinolinediyl)s;[8] however, quaternization of the polymers has received only a little attention. Chiang and co-workers recently reported quaternization of the quinoline oligomer with alkylating reagents (eq 2).[7b]



(2)

We recently reported that dehalogenation polycondensation of dihalogenated quinolines and 1,4-dibromoisoquinoline with zero-valent nickel complexes, which is based on organonickel chemistry,[9] gave various poly(quinolinediyl)s, and poly(isoquinoline-1,4-diyl) (P(1,4-iQ)), and poly(quinoline-5,8-diyl) (P(5,8-Q)) and P(1,4-iQ) were converted into electrical conductors on n-type doping.[8]



(3)

P(5,8-Q) has only a low solubility in the usual organic solvents, and its quaternization with alkyl halides is not possible. On the other hand, P(4,7-Q) and P(1,4-iQ) are soluble in chloroform, and their quaternization with alkylating reagents like alkyl halides can be easily carried out in chloroform.

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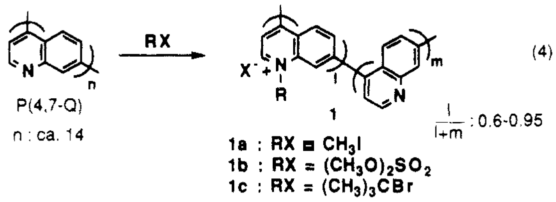

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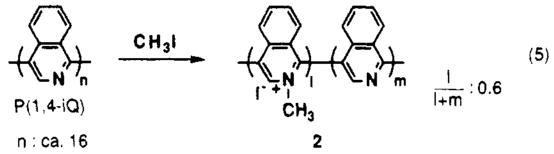


(5)

The resulting polymers have the diquaternary biquinolinium or biisoquinolinium moieties in the polymer chain, and they are expected to show the Weitz-type two-step redox processes which accompany the color change of the polymer (electrochromism). Since **1** and **2** or their reduced forms have a π-conjugation system along the polymer chain, they are expected to provide a new class of conductive polymer materials which show viologen-type redox activity. We now report results of the quaternization of the polymers and the chemical and electrochemical properties of the quaternized poly(quinolinium) and poly(isoquinolinium) salts.

Results and Discussion

Preparation of Quaternized Poly(quinolinium) and Poly(isoquinolinium) Salts. Table I summarizes results of the quaternization of P(4,7-Q) and P(1,4-iQ). As shown in Table I, reaction with iodomethane and dimethyl sulfate gives the quaternized polymers in good yields. However, quaternization of P(4,7-Q) and P(1,4-iQ) with iodoethane, iodopropane, and diethyl sulfate gave only a low degree of quaternization (<5%, **1d** in Table I), indicating that a steric hindrance of the larger alkyl groups prevents the quaternization. On the other hand, reaction with 2-bromo-2-methylpropane gives the quaternized poly(quinolinium) salt in a good yield (**1c** in Table I), presumably due to its strong reactivity toward an S_N1 type reaction.

The degree of quaternization in Table I was determined by elemental analysis. The number-average molecular weights of **1a** and **2** are 4900 and 5800, respectively, as determined by GPC using polystyrene standards, although some correction of the GPC molecular weight seemed to be necessary due to the ionic structure of **1a** and **2** as well as their considerably higher density than polystyrene. Determination of the molecular weight of **1a** and **2** by light scattering was not possible because of their absorption bands in the visible region. The GPC molecular weights of **1a** and **2** correspond to a degree of polymerization (DP) of 23 and 27, respectively, and the DP values roughly agree with those of the original P(4,7-Q) (DP = ca. 14 by light scattering in HCOOH and 62 by GPC) and P(1,4-iQ) (DP = ca. 16 by light scattering in HCOOH and 20 by GPC), respectively.[8] P(4,7-Q) and P(1,4-iQ) are essentially insulators with σ values of ca. 10^{-10} S cm^{-1}, whereas **1a** and **2** are electrically semiconducting with σ values of 10^{-6}–10^{-7} S cm^{-1}.

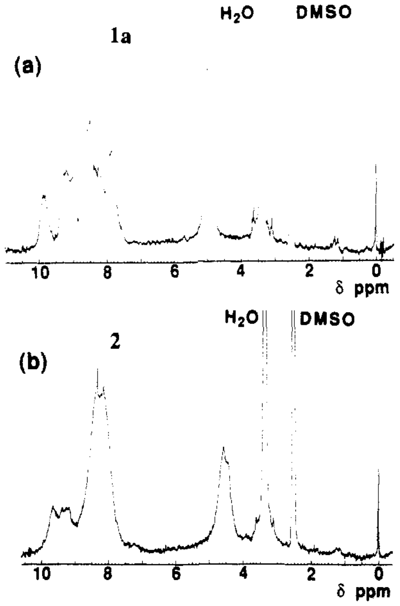


Figure 1. ^{1}H NMR spectra of (a) **1a** and (b) **2** in DMSO-d_6.

1a, **1b**, and **2** have high solubilities in polar solvents such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), and *N*-methyl-2-pyrrolidione (NMP) (up to ca. 10 mg mL^{-1}, corresponding to 4.7×10^{-2} M of monomer unit) and a moderate solubility in water (about 0.5 mg mL^{-1}, corresponding to 2.4×10^{-3} M of monomer unit). **1c** is somewhat soluble in NMP (about 1 mg mL^{-1}, corresponding to 3.9×10^{-3} M of monomer unit), partially soluble in DMSO, and insoluble in water.

Figure 1 shows the ^{1}H NMR spectra of quaternized poly(quinolinium) and poly(isoquinolinium) salts (**1a** and **2**) in DMSO-d_6. Assignment of the peaks was carried out by comparison of the positions of the peaks with those of P(4,7-Q), P(1,4-iQ),[9] and quaternized quinoline and isoquinoline.

In Figure 1a, a broad peak centered at ca. δ 5.0 is assigned to the 1-methyl protons, and broad peaks at δ 7.5–10.3 are assigned to the aromatic protons. From the peak area ratio between the methyl protons and the aromatic protons (3:8.7) in Figure 1a, the degree of quaternization of **1a** is estimated as 57%, the value being in good agreement with the degree of quaternization of **1a** determined by elemental analysis (cf. Table I). The ^{1}H NMR spectrum of **1b** in DMSO-d_6 is similar to Figure 1a, and methyl sulfate ($CH_3OSO_3^-$) protons are observed at δ 4.2. In the case of

Table I
Preparation of Quaternized Poly(quinolinium) and Poly(isoquinolinium) Salts

				elem anal./%						mol wt[c]		
no.	poly(quinolinediyl)	alkylating reagent	yield/%[a]	C	H	N	S	halogen	deg of quaternization[b]/%	M_n	M_w	σ/(S cm^{-1})
1a	P(4,7-Q)	CH_3I	80	54.9	3.6	6.0	0.0	35.5	60	4900	5200	7.1×10^{-6}
1b	P(4,7-Q)	$(CH_3O)_2SO_2$	70	55.1	4.8	5.1	11.6	0.0	85			
1c	P(4,7-Q)	$(CH_3)_3CBr$	70	58.8	4.0	7.5	0.0	29.7	95			
1d[d]	P(4,7-Q)	CH_3CH_2I	25	80.7	4.6	9.0	0.0	4.8	5			
2	P(1,4-iQ)	CH_3I	75	52.9	3.7	6.4	0.0	35.5	60	5800	6000	2.8×10^{-7}
	P(4,7-Q)[8]											6.3×10^{-10}
	P(1,4-iQ)[8]											1.2×10^{-10}

[a] The values were calculated based on the degree of quaternization. [b] The values were calculated from C/halogen and N/halogen (**1a**, **1c**, and **2**) or C/S and N/S (**1b**) ratios. [c] Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were evaluated by GPC (vs polystyrene). [d] Quaternization was carried out at room temperature for 7 days.

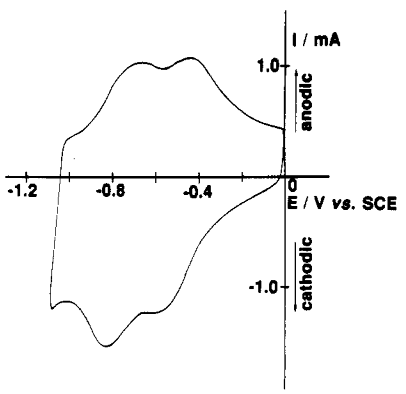
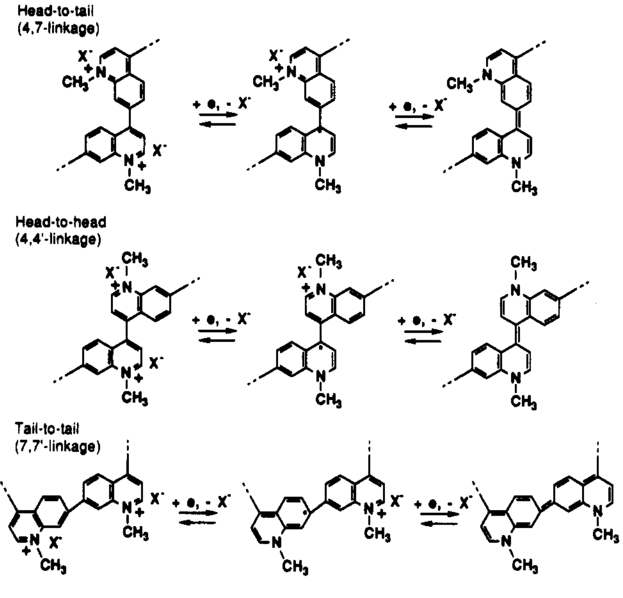


Figure 2. Cyclic voltammogram of **1a** dissolved in a 0.3 M KCl aqueous solution (sweep rate = 500 mV s^{-1}; under N$_2$; at 25 °C).

Scheme I



1c in DMSO-d_6, a broad peak centered at δ 4.9 assigned to the *tert*-butyl protons and broad peaks at δ 7.5–9.5 assigned to the aromatic protons are observed. The ^{13}C NMR spectrum of **1a** in DMSO-d_6 shows a peak at 47 ppm assignable to the 1-methyl carbon and resonances in the range 120–160 ppm due to the aromatic carbons of the quinoline ring.

In Figure 1b, a broad peak at ca. δ 4.6 is assigned to the 2-methyl protons of **2**, and broad peaks at δ 7.5–10.0 are assigned to the aromatic protons. The peak area ratio between the methyl protons and the aromatic protons in Figure 1b reveals a 52% degree of quaternization of **2**, and the value roughly agrees with the degree of quaternization of **2** determined by elemental analysis, indicating P(1,4-iQ) is also quaternized with iodomethane.

The results described above indicate that a high degree of quaternization of quinoline or isoquinoline units in the polymers can be achieved.

Redox Properties of Quaternized Poly(quinolinium) and Poly(isoquinolinium) Salts. Electrochemical Redox in Solution. Figure 2 shows a cyclic voltammogram (CV) curve of **1a** dissolved in an aqueous KCl solution. As shown in Figure 2, **1a** gives rise to an electrochemically active cycle, showing two pairs of redox waves at $E_{1/2}$ = ca. −0.50 and −0.75 V vs SCE, respectively. The electrochemical redox cycle is stable, and the CV curve is essentially unchanged even after 100 cycles. The color of **1a** in aqueous solution near the electrode surface changes from pale yellow to dark blue when the potential of the ITO working electrode is held at −0.60 V (reduction of **1a** to the cation radical).

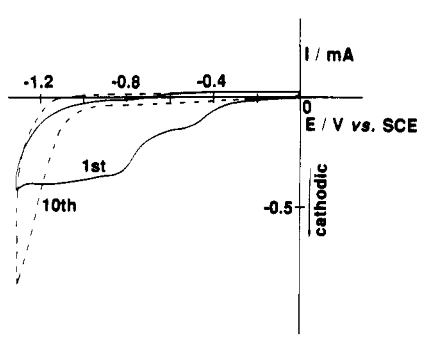


Figure 3. Cyclic voltammograms of **2** dissolved in a 0.3 M KCl aqueous solution (sweep rate = 100 mV s^{-1}; under N$_2$; at 25 °C).

The CV results in Figure 2 and the color change of **1a**, which resemble those of Weitz-type redox-active diquaternary diheterocyclic salts such as viologens[1,2,3e,4c] and diquaternary 4,4'-biquinolinium salts,[5a] respectively, indicate that **1a** undergoes the Weitz-type electrochemical redox reaction.

P(4,7-Q) is considered to be constituted of three types of biquinoline, i.e., head-to-tail (4,7-linkage), head-to-head (4,4'-linkage), and tail-to-tail (7,7'-linkage) units.[8] Therefore, the Weitz-type two-step redox reaction should be considered for each of the three possible diquaternary biquinolinium units in **1a** (Scheme I). As shown in Scheme I, every biquinolinium unit will form a cation radical by the first-step reduction and a neutral quinoid by the second-step reduction, respectively. These redox behaviors are similar to that of viologens. However, as shown in Figure 2, **1a** gives only rather broad CV peaks in comparison with those of the reported viologens[2] and the polymers containing the viologen unit.[3e,f,4c] Since these previously reported polymers do not have a π-conjugation system along the polymer chain, the individual viologen units in the polymers may undergo the Weitz-type redox reaction independently of each other. In the case of **1a**, however, the second-step reduction will form a π-conjugation system along the polymer chain, and the redox reaction of a biquinolinium unit in **1a** is considered to affect the redox reaction of other biquinolinium units through the π-conjugation system; i.e., the remaining radical electron generated by the first-step reduction may move over the whole polymer molecule through the π-conjugation system, and may cause the broadening of the CV peaks, e.g.,

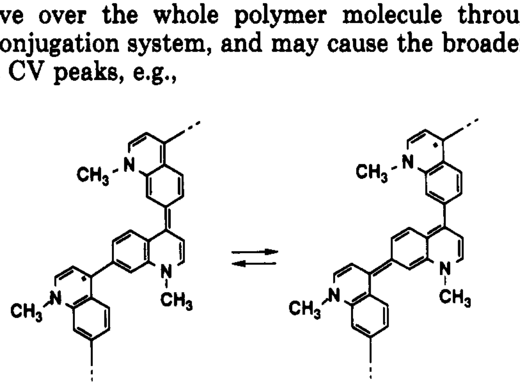


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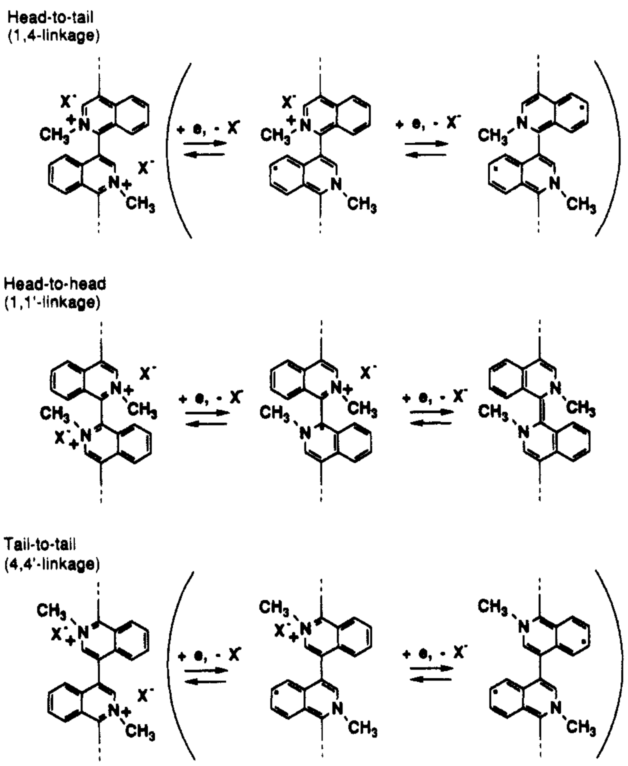
Figure 3 shows CV curves of **2** dissolved in an aqueous KCl solution. In contrast to **1a**, **2** gives irreversible CV curves. Only broad cathodic peaks are observed in the first cycle; however, the cathodic current decreases with repeated scanning. The CV results in Figure 3 suggest that diquaternary biisoquinolinium units in **2** do not undergo reversible Weitz-type electrochemical redox reactions similar to those shown in Scheme I.

Scheme II



Scheme II shows analogously plausible reduction processes for the three possible diquaternary biisoquinolinium units in **2**. The head-to-head (1,1'-linkage) unit may undergo the reversible redox reactions. However, the head-to-tail (1,4-linkage) unit and the tail-to-tail (4,4'-linkage) unit do not seem to give the reversible reactions as reported by Homer and co-workers.[10]

Homer et al. reported that diquaternary 2,2'-, 2,4'-, and 4,4'-bipyridinium salts were active for the Weitz-type redox reactions, whereas diquaternary 2,3'- and 3,3'-bipyridinium salts were not.[10] The difference is believed to be due to the difference in stability of free cation radical formed at the first-step reduction between the two categories of bipyridinium salts. The difference in delocalization energy of the radical electron is considered to be the origin of the difference in the redox behavior. The head-to-tail (1,4-linkage) and tail-to-tail (4,4'-linkage) diquaternary biisoquinolinium units in **2** may not form a stable cation radical at the first-step reduction.

Electrochemical Redox in Film. Figure 4 shows a CV curve of a film of **1c** on an ITO glass electrode in an aqueous KCl solution. The polymer film of **1c** also displays an electrochemically active cycle with a cathodic peak at −0.92 V vs SCE and an anodic peak at −0.64 V. The electrochemical redox cycle is stable during repeated scanning. The color of the film changes from pale yellow to dark purple when the working electrode is held at −0.90 V vs SCE. These results indicate the film of **1c** also forms a stable cation radical by the first-step reduction of the Weitz-type redox reaction in Scheme I. From the cathodic current observed at the reduction shown in Figure 4 and the weight of the film of **1c**, about 35% of the diquaternary biquinolinium units in the film of **1c** are estimated to participate in the reducing.

When the CV measurement was carried out at a lower switching potential (−1.2 V vs SCE), another pair of redox peaks with a cathodic peak at −1.12 V and a broad anodic peak at −0.75 V were observed, and these redox peaks are considered to correspond to the second-step reduction of Weitz-type redox reaction. However, the redox currents were gradually reduced during repeated scanning, and the film of **1c** partially peeled off from the ITO electrode. The observations that the redox reactions of **1c** take place at lower potentials than those of **1a** indicate that a larger energy is required to reduce the biquinolinium molecules with the 1-*tert*-butyl group and to form a coplanar configuration, presumably due to steric hindrance between the 1-*tert*-butyl group and the hydrogen atoms of the quinoline ring in the film of **1c**.

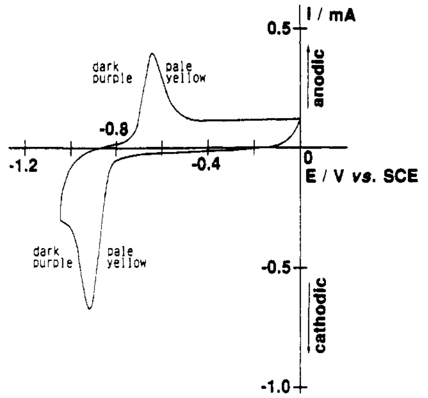


Figure 4. Cyclic voltammogram of **1c** film on an ITO electrode in a 0.3 M KCl aqueous solution (sweep rate = 100 $mV\ s^{-1}$; under N_2; at 25 °C).

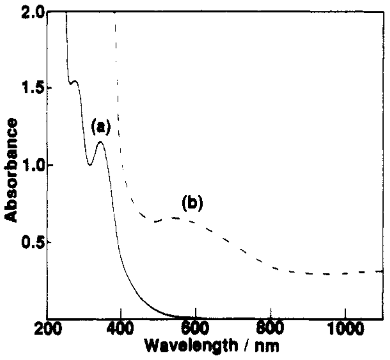


Figure 5. UV–vis spectra of (a) **1a** and (b) reduced **1a** formed by adding $Na_2S_2O_4$ (in an aqueous solution (about 5 mg/L, about 2.4×10^{-5} M of monomer unit); under N_2; at 25 °C).

Chemical Redox. Figure 5 shows the change in the UV–vis spectra of **1a** by reduction with $Na_2S_2O_4$. The aqueous solution of **1a** gives absorption peaks at 280 and 345 nm. Addition of $Na_2S_2O_4$ leads to the appearance of a new broad peak at ca. 530 nm, which disappears on exposure to air. It is reported that an aqueous solution of viologen cation radical shows an absorption peak at ca. 550–650 nm,[2-4] and the change of the UV–vis spectra in Figure 5 is reasonably explained by the formation of a similar cation radical in the reaction of **1a** with $Na_2S_2O_4$. Since the solution obtained by the addition of $Na_2S_2O_4$ looks homogeneous, the tail absorption toward the near-infrared region is attributed not to the scattering due to the formation of insoluble materials but to broad or overlapped absorptions originating from the cation radicals. It is known that cation and anion radicals (or polaron and bipolaron according to the terminology of physics) formed in π-conjugated aromatic polymer systems usually give rise to overlapped absorption bands in the visible or near-infrared region.[11]

Conclusion

Quaternization of P(4,7-Q) and P(1,4-iQ) with alkylating reagents gives the corresponding quaternary poly(quinolinium) and poly(isoquinolinium) salts with a high degree of quaternization. The resulting polymers are readily soluble in polar solvents and afford cast films. Quaternized P(4,7-Q) shows a two-step electrochemical redox behavior and electrochromism. On the other hand, quaternized P(1,4-iQ) does not exhibit an electrochemically reversible redox property. A Weitz-type two-step redox reaction similar to that of viologens accounts for the electrochemical redox behavior of quaternized P(4,7-Q). All three possible diquaternary biquinolinium units in quaternized P(4,7-Q) are considered to form a stable cation radical at the first-step reduction similar to that of viologens, respectively. These results indicate that the novel class of π-conjugated polymer having viologen-type redox activity may find a practical use in electrochromic devices and as an electron transfer catalyst in a redox system.

Experimental Section

Materials. P(4,7-Q) and P(1,4-iQ) were prepared by dehalogenation polycondensation of 4,7-dichloroquinoline and 1,4-dibromoisoquinoline with the zero-valent nickel complexes as reported previously.[8] The alkylating reagents (iodomethane, dimethyl sulfate, and 2-bromo-2-methylpropane) were used as purchased. Solvents were dried and distilled.

Quaternization. Iodomethane (2.0 mL, 32 mmol (excess)) was added dropwise to P(4,7-Q) (50 mg, 3.9×10^{-4} mol of monomer unit) in 15 mL of chloroform. The reaction mixture was stirred at room temperature for 24 h to yield a deep orange precipitate. The precipitate was separated by filtration and washed with chloroform. Yield: 67 mg (ca. 80% based on the degree of quaternization). Analytical data indicate the quaternization at 60% of the quinoline units. Anal. Found (no. **1a** in Table I): C, 54.9; H, 3.6; N, 6.0; I, 35.5. Calcd for $((C_{10}H_8IN)_{0.6}\cdot(C_9H_5N)_{0.4})_n$: C, 54.3; H, 3.2; N, 6.6: I, 35.9. IR (KBr pellet): ν_{max} 3045, 1619, 1598, 1577, 1502, 1414, 1363, 1218, 831, 682, 612 cm^{-1}.

The preparation of other quaternized poly(quinolinium) and poly(isoquinolinium) salts listed in Table I was carried out analogously.

Measurement. IR spectra and ^{1}H NMR spectra were recorded on a JASCO IR-810 spectrometer and a JEOL FX-100 spectrometer, respectively. Elemental analysis was carried out by Mrs. Tanaka of our laboratory with a Yanagimoto CHN Autocorder Type MT-2 and a Mitamura Riken Kogyo Micro Elementary Analyzer. Gel permeation chromatograms (GPC) were measured with a Toso HLC-810 apparatus at 25 °C using 0.01 M LiBr/DMF as eluent (polystyrene standards). Electrical conductivities (σ) of pellets prepared by pressing powder of the samples were measured with a Takeda Riken TR-8651 electrometer and a Hokuto Denko HA-501 galvanostat/potentiostat using two-probe and four-probe methods, respectively. The two-probe and four-probe methods gave essentially the same σ value.

Cyclic voltammetry was carried out with a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko HB-104 function generator. An ITO glass electrode (0.5 × 1.5 cm) and platinum plate (2 × 2 cm) were used as a working electrode and a counter electrode, respectively, and a saturated calomel electrode (SCE) was used as a reference electrode. In a typical experiment, **1a** (25 mg, 1.2×10^{-4} mol of monomer unit) was dissolved in an aqueous KCl (0.3 M) solution (100 mL). The solution was deaerated by bubbling nitrogen before use, and a positive pressure of nitrogen was maintained throughout the experiment. In the case of a film of **1c**, spreading 20 μL of an NMP solution of **1c** (ca. 4 mg/10 mL, ca. 1.5×10^{-3} M of monomer unit) on an ITO glass electrode and evaporation of the NMP under vacuum afforded the ITO electrode coated with a film of **1c** (ca. 1.0×10^{-5} g cm^{-2}); with this electrode the cyclic voltammogram was measured.

UV-visible spectra were measured with a JASCO Ubest-35 spectrometer. After the UV-visible spectrum of **1a** (ca. 5 mg/L, ca. 2.4×10^{-5} M of monomer unit) was measured in an aqueous solution (100 mL) under nitrogen, **1a** was reduced by $Na_2S_2O_4$ (5 mg). The visible spectrum of the reduced **1a** aqueous solution was also measured under nitrogen.

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