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N-Oxides and *N*-ylides of π-conjugated poly(arylene)s. Preparation and properties of the polymers

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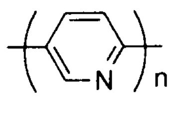
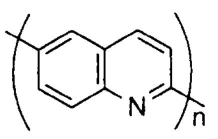
Treatment of poly(pyridine-2,5-diyl) PPy, poly(quinoline-2,6-diyl) P(2,6-Q), and poly(naphthyridine-2,6-diyl) P(2,6-N) with H_2O_2 in acetic acid gives quantitatively N-oxidized products of the polymers, PPy-ox, P(2,6-Q)-ox, and P(2,6-N)-diox, respectively. π–π^* absorption bands of the original polymers show a hypsochromic shift by 35–50 nm by the N-oxidation. Treatment of PPy and P(2,6-Q) with tetracyanoethylene oxide affords N-ylidated products with a 10–15% degree of N-ylidation. The N-oxidized and ylidated polymers undergo electrochemical reduction in a range of about -1.7 to -2.2 V *vs* Ag/Ag$^+$. The electrochemical reduction is accompanied by colour change, and colours of the reduced polymers are considerably different from those of the original polymers (e.g. PPy). The N-oxidized and -ylidated polymers have a d.c. electrical conductivity of 2.8×10^{-7}–3.4×10^{-6} S cm^{-1}. © 1997 Elsevier Science Ltd.

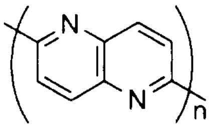
(Keywords: N-containing π-conjugated poly(arylene); *N*-oxide; *N*-ylide)

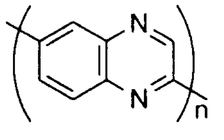
INTRODUCTION

Recently preparation of various N-containing π-conjugated poly(arylene)s such as poly(pyridine-2,5-diyl) PPy[1], poly(quinoline-2,6-diyl) P(2,6-Q)[2], poly(naphthyridine-2,6-diyl) P(2,6-N)[3], and poly(quinoxaline-2,6-diyl) P(2,6-Qx)[4] has been reported.


PPy

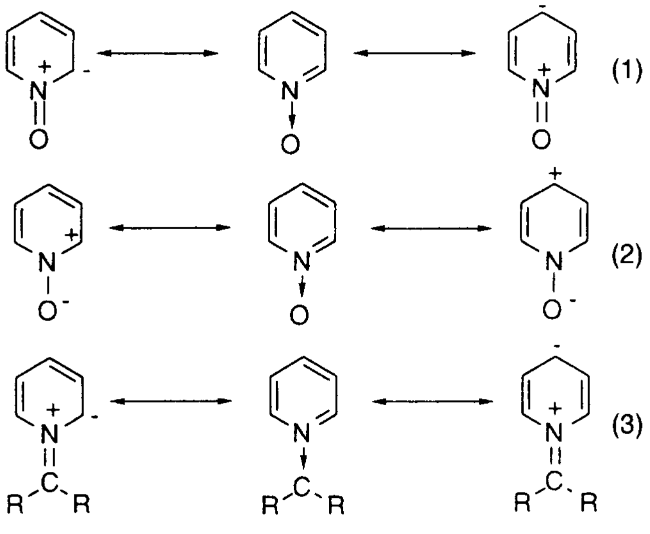

P(2,6-Q)


P(2,6-N)


P(2,6-Qx)

On the other hand, it is well known that nitrogen-containing low molecular weight compounds such as pyridine and quinoline undergo various reactions, and chemistry of such nitrogen-containing aromatic compounds has been extensively developed. However, chemical reactivity of the above shown π-conjugated poly(arylene)s has received much less attention, and only a few examples of chemical transformation of the polymers (e.g. quaternization of nitrogen with organic halides RX[5] and complex formation with transition metals[1]) have been reported.

We report chemical conversion of the above shown polymers to their N-oxides[6,7] and N-ylides[8] as well as optical, electrochemical, and electrical properties of the products. Both the N-oxide and N-ylide are considered to take similar resonance forms[6–8] such as those shown below.



Of the two types of resonances expressed by equations (1) and (2), that expressed by equation (1) is considered to contribute to a larger extent, and due to its contribution the ring of N-oxide has certain electron-donating nature in contrast to electron-accepting nature

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of the N-containing aromatics[6,7]. A part of the results of the preparation of the *N*-oxides has been reported previously[9,10].

EXPERIMENTAL

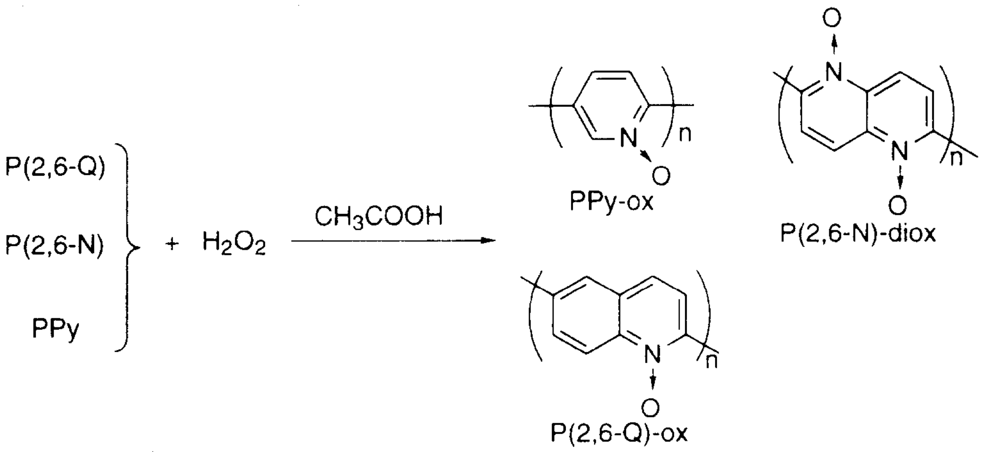
Materials

The N-containing π-conjugated poly(arylene)s (PPy, P(2,6-Q), and P(2,6-N)), poly(quinoline-4,7-diyl), P(4,7-Q), and bis(1,5-cyclooctadiene)nickel(0) Ni(cod)$_2$ were prepared according to the literature[1–4]. The starting polymers were prepared by organometallic polycondensation using Ni(cod)$_2$. Tetracyanoethylene oxide was used as purchased from Tokyo Chemical Industry Co. Ltd.

N-Oxidation

Powdery PPy (100 mg) was stirred in a mixture of acetic acid (20 cm^3) and 30% H_2O_2 (aq) (8 cm^3) for 3 days at 60°C. The precipitate was collected by filtration, washed with an aqueous solution of NaOH and diluted hydrochloric acid, and dried under vacuum to yield 52 mg (43%) of PPy-ox. Anal.: Found: C, 53.2; H, 3.8; N, 12.1. Calcd. for $(C_5H_3NO \cdot 1.05H_2O)_n$: C, 53.6; H, 4.6; N, 12.5.

Powdery P(2,6-Q) (100 mg) was added to a mixture of acetic acid (20 cm^3) and 30% aqueous solution of H_2O_2 (8 cm^3), and the mixture was stirred for 3 days at 60°C. After cooling to room temperature, the precipitate was collected by filtration, washed with an aqueous solution of NaOH and diluted hydrochloric acid, and dried under vacuum to yield brownish yellow P(2,6-Q)-ox (21%). Anal.: Found: C, 71.0, H, 3.7; N, 9.2. Calcd. for $(C_9H_5NO \cdot 0.49H_2O)_n$: C, 71.1; 4.0; N, 9.2. N-Oxidation of P(2,6-N) was carried out in the same manner to yield reddish brown P(2,6-N)-diox (33%). Anal.: Found: C, 56.3, H, 2.9; N, 16.4. Calcd. for $(C_8H_4N_2O \cdot 0.41H_2O)_n$: C, 57.4; H, 2.9; N, 16.7.



(4)

N-Ylidation

Powdery PPy (100 mg, 1.29 mmol unit) was added to an ether solution (17 cm^3) containing 190 mg (1.32 mmol) of tetracyanoethylene oxide. After addition of one drop of water, the mixture was stirred for 2 days under reflux. After cooling to room temperature, the brown precipitate was separated by filtration, washed with ether, and dried under vacuum. Anal.: Found: C, 71.3; H, 3.8; N, 19.8. Calcd. for $[(C_5H_3N)_{0.85}(C_8H_3N_3)_{0.15} \cdot 0.27H_2O]_n$: C, 71.5; H, 3.9; N, 19.9. I.r.: 2206 cm^{-1}. N-Ylidation of P(4,7-Q) was carried out analogously. Anal.: Found: C, 74.9; H, 3.7; N, 12.7. Calcd for $[(C_9H_5N)_{0.77}(C_{12}H_5N_3)_{0.23} \cdot 0.7H_2O]_n$: C, 75.3, H, 4.1; N, 13.2. N-Ylidation of P(2,6-Q) was also carried out analogously. Anal.: Found: C, 76.4; H, 3.8; N, 10.9. Calcd. for $[(C_9H_5N)_{0.9}(C_{12}H_5N_3)_{0.1} \cdot 0.65H_2O]_n$: C, 76.9; H, 4.4; N, 11.6. IR: 2208 cm^{-1}.

Measurements

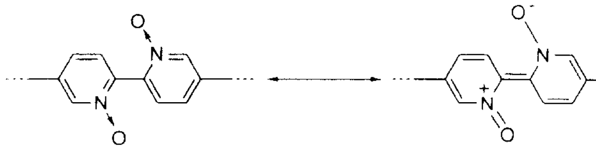
I.r. and u.v.-visible spectra were recorded on a Jasco IR-810 spectrophotometer and Shimadzu UV-3100PC spectrophotometer, respectively. Electrical conductivity was measured with an Advantest R8340 resistance meter. Powdery polymer was compressed into a pellet under a pressure of 200 kg cm^{-2}, and a bar for the measurement of electrical conductivity was obtained by cutting the pellet. Cyclic voltammograms were obtained by using a Hokuto Denko HA-501 galvanostat/potentiostat and a Hokuto Denko KB-104 function generator. ^{1}H n.m.r. spectra were obtained with JEOL JNM-FX-400.

RESULTS AND DISCUSSION

N-Oxidation

It is known that N-oxidation of N-containing heterocycles with H_2O_2 in acetic acid proceeds quantitatively[6,7]. Application of this method to the π-conjugated poly(arylene)s also gives the N-oxidized products.

Figure 1 shows i.r. spectra of PPy-ox, PPy, P(2,6-N)-diox, and P(2,6-N). As shown in *Figure 1*, the N-oxidation of PPy leads to a profound change in the i.r. absorption pattern, similarly to cases of N-oxidation of low molecular weight heterocyclic compounds[11]. The low molecular weight N-oxides give ν(N–O) band(s) in a region of 1200–1300 cm^{-1} [11], and a new peak of PPy-ox observed at about 1250 cm^{-1} seems to be assignable to the ν(N–O) band. However, observation of additional strong absorption band(s) in a region of 1340–1400 cm^{-1}, which is not observed with low molecular weight N-oxide, suggests stabilization of the resonance form containing an N=O bond (equation 1) in the polymer system by participation of the following



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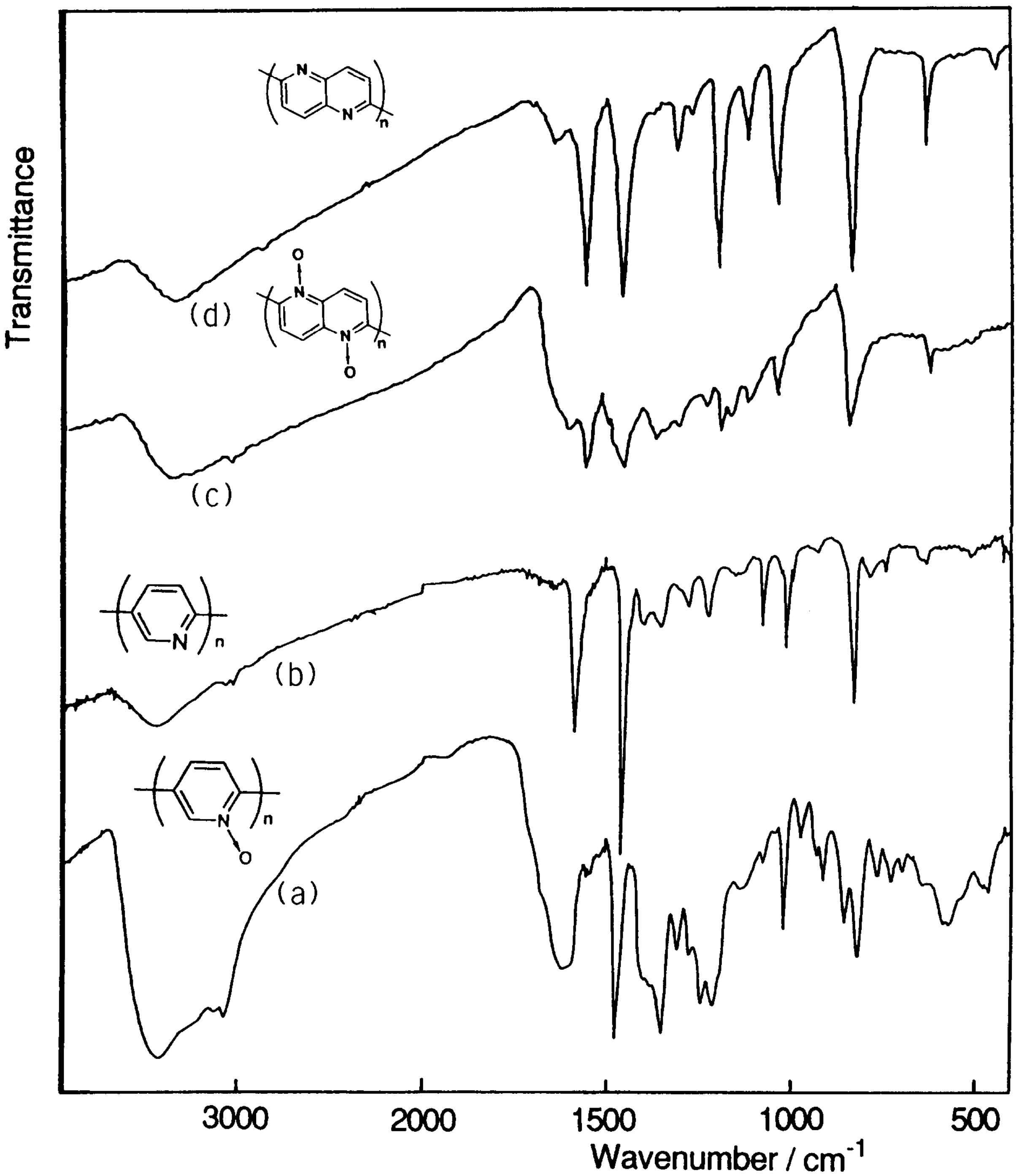


Figure 1 I.r. spectra of (a) PPy-ox, (b) PPy, (c) P(2,6-N)-diox, and (d) P(2,6-N)

resonance form in the head-to-head H–H unit of PPy-ox. PPy contains the H–H unit in a high content. The I.r. spectrum of PPy-ox also exhibits a new absorption band at 850 cm^{-1} assigned to a bending vibration of the N–O group. N-oxidation of P(2,6-N) (chart c in *Figure 1*) and P(2,6-Q)[9] causes similar changes in the absorption pattern between 1250 and 1400 cm^{-1}. The N-oxidized product absorbs water which is difficult to remove by treatment under vacuum, and the i.r. spectra show ν(O–H) and δ(O–H) bands at about 3500 and 1620 cm^{-1}, respectively. Data from elemental analysis (cf. Experimental) agree with the hydrated structure.

Figure 2 shows comparison of the ^{1}H n.m.r. spectra of original P(2,6-Q)[3] and P(2,6-Q)-ox. As depicted in *Figure 2*, the ^{1}H n.m.r. absorption pattern of P(2,6-Q) is profoundly changed by the N-oxidation, supporting the quantitative N-oxidation of nitrogen in P(2,6-Q). For example, the 4-H signal of P(2,6-Q) at δ 9.4 ppm (*Figure 2a*) disappears after the N-oxidation, and new peaks appear at about δ 9.6 and 9.3; the total peak area of the two new peaks corresponds to one proton.

The original P(2,6-Q) prepared by the organometallic polycondensation contains head-to-head HH units in a high content (about 90%)[3], and only several weak peaks in a range between δ 8.1 and 8.5 originated from head-to-tail HT are observed in the ^{1}H n.m.r. chart of P(2,6-Q) (*Figure 2a*)[3]. In addition, clear splitting of the signal of the 4-H proton due to the presence of both the HH and HT units is not observed in the ^{1}H n.m.r. spectrum of P(2,6-Q). In contrast to the ^{1}H n.m.r. signals of P(2,6-Q),

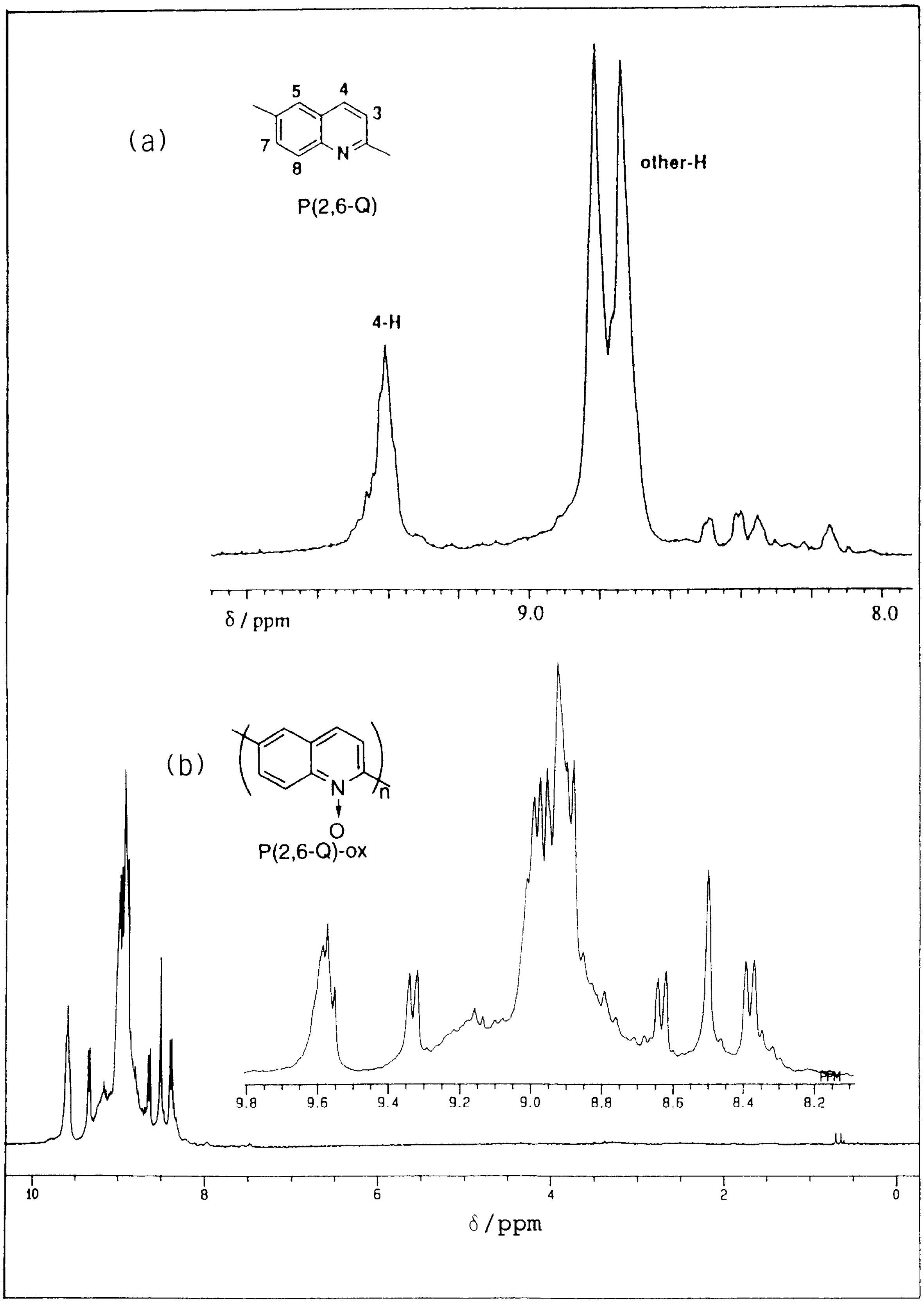


Figure 2 ^{1}H n.m.r. spectra of (a) P(2,6-Q) and (b) P(2,6-Q)-ox in trifluoroacetic acid-d_1. The spectrum in a region of δ 8–10 is expanded

those of P(2,6-Q)-ox show complex splitting, and this indicates that the ^{1}H n.m.r. signals of P(2,6-Q)-ox receive effects of its long-range microstructures (e.g. microstructures in triad and tetrad units) in addition to the splitting based on the diad microstructures (HH and HT).

Since no distinct peak is observed in a region of signals of epoxide hydrogen (δ 2.5–3), occurrence of epoxidation of the quinoline ring in equation (4) can be neglected.

The N-oxidation of P(2,6-Q) leads to a hypsochromic shift of the π–π^* absorption band of P(2,6-Q) as shown

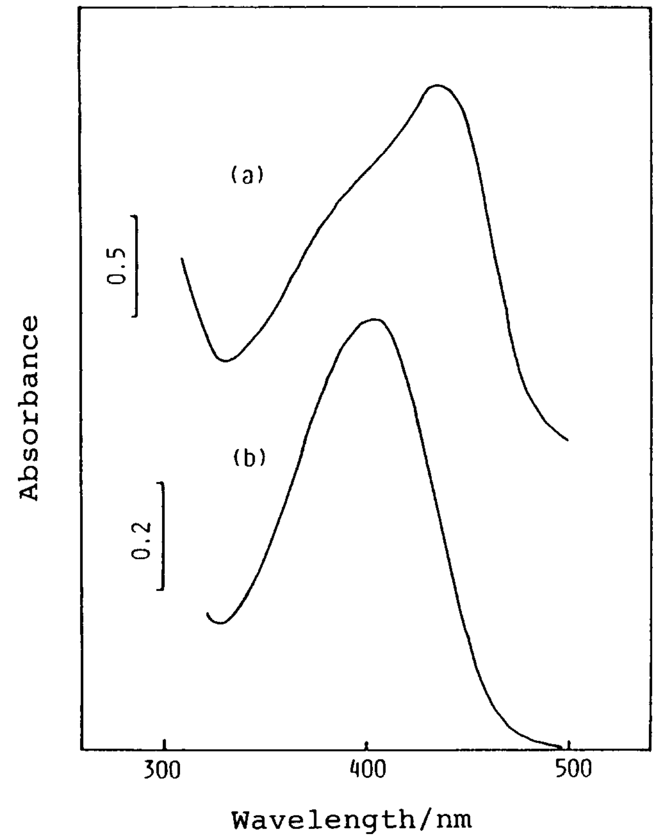


Figure 3 U.v.-visible spectra of (a) P(2,6-Q) and (b) P(2,6-Q)-ox in formic acid

in *Figure 3*. PPy-ox[9] and P(2,6-N)-diox also show similar shifts to a shorter wavelength, and the u.v.-visible data are summarized in *Table 1*. Since monomeric N-oxides give rise to a u.v.-visible absorption peak at a wavelength comparable (or somewhat longer) to that of the corresponding N-containing heterocycles[12,13], the hypsochromic shift is attributed to increase in the steric repulsion between the monomeric units caused by the N–O group. A film of P(2,6-Q)-ox exhibits moderate photoluminescence with a peak at 494 nm.

The N-oxidized polymers are soluble in organic acids such as formic acid and trifluoroacetic acid. Removing formic acid by evaporation under vacuum recovers the original polymer as proved by i.r. spectroscopy. They are partially soluble in alkaline solution such as NaOH (aq) and NH_3 (aq), and this seems to cause loss of the polymer during work-up (cf. Experimental). In a 29% aqueous ammonium solution, the π–π^* absorption band of PPy-ox at 330 nm (*Table 1*) is weakened (to about 1/4) and appears as a shoulder of an absorption band at 254 nm assigned to π–π^* absorption in the monomeric pyridine unit. It is reported that the π–π^* absorption pattern of pyridine-N-oxide depends on the kind of solvent[13] presumably due to the polar structure of the N-oxide. The polymeric-N-oxides obtained in this study are not soluble in non-acidic organic solvents.

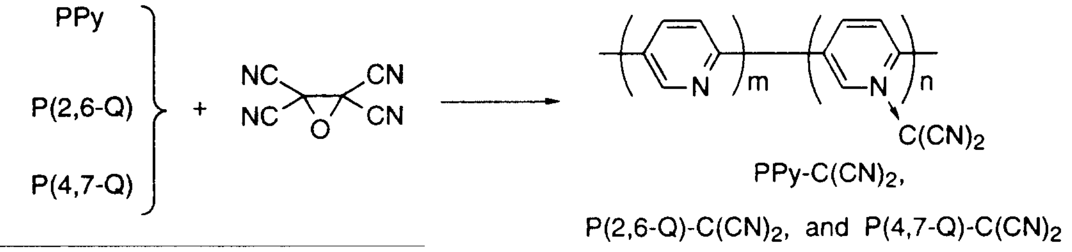
Table 1 UV-visible data of polymers

Polymer	λ_{max} (nm)[a]
PPy	380
PPy-ox	330 (ϵ = 8500 M^{-1} cm^{-1})[b]
PPy-(CN)$_2$	380
P(2,6-Q)	430 (film: 415 nm)
P(2,6-Q)-ox	397 (film: 371 nm)
P(2,6-Q)-C(CN)$_2$	430
P(2,6-N)	439
P(2,6-N)-diox	404
P(4,7-Q)	342
P(4,7-Q)-C(CN)$_2$	342

[a] In formic acid
[b] Molarity is based on the monomer unit

N-Ylidation

Carbenes CR_2 with electron-withdrawing R groups like CN form stable *N*-ylides with several heterocyclic compounds, and tetracyanoethylene oxide has been used as an efficient N-ylidating reagent[8,14,15]. The N-ylidation of the polymers with tetracyanoethylene oxide also proceeds in a heterogeneous reaction system as judged from observation of a ν(C$\equiv$N) absorption band in the i.r. spectra of the products. However, a relatively weak ν(C$\equiv$N) absorption band and data from elemental analysis indicate that the N-ylidation proceeds only partly, and degrees of the N-ylidation estimated from the elemental analytical data are 15, 10 and 23% for PPy, P(2,6-Q), and P(4,7-Q), respectively.



(6)

The relative intensity of the ν(C$\equiv$N) band of PPy-C(CN)$_2$ against that of a ring deformation band of PPy observed at about 1450 cm^{-1} agrees with the degree of the N-ylidation. The ν(C$\equiv$N) band (2206 cm^{-1}) of PPy-C(CN)$_2$ appears at a somewhat higher frequency compared with that (2182 and 2148 cm^{-1}) of isolated N-ylidated pyridine, pyridine-C(CN)$_2$[14,15]. Due to the low degree of N-ylidation, the u.v.-visible spectra of the products show their π–π^* absorption peak essentially agreeing with those of original polymers.

Figure 4 shows the ^{1}H n.m.r. spectrum of P(2,6-Q)-C(CN)$_2$. As depicted in *Figure 4*, the 4-H signal of the original P(2,6-Q) at δ 9.4 (*Figure 2a*) is observed as a major signal even after the ylidation. However, a new peak centred at δ 9.17, which is also assigned to 4-H, has a higher peak area than that expected from the degree of the ylidation (10%) if only the 4-H proton in the ylidated unit is shifted to δ 9.17. The peak area of the new peak suggests that not only the 4-H proton in the ylidated unit

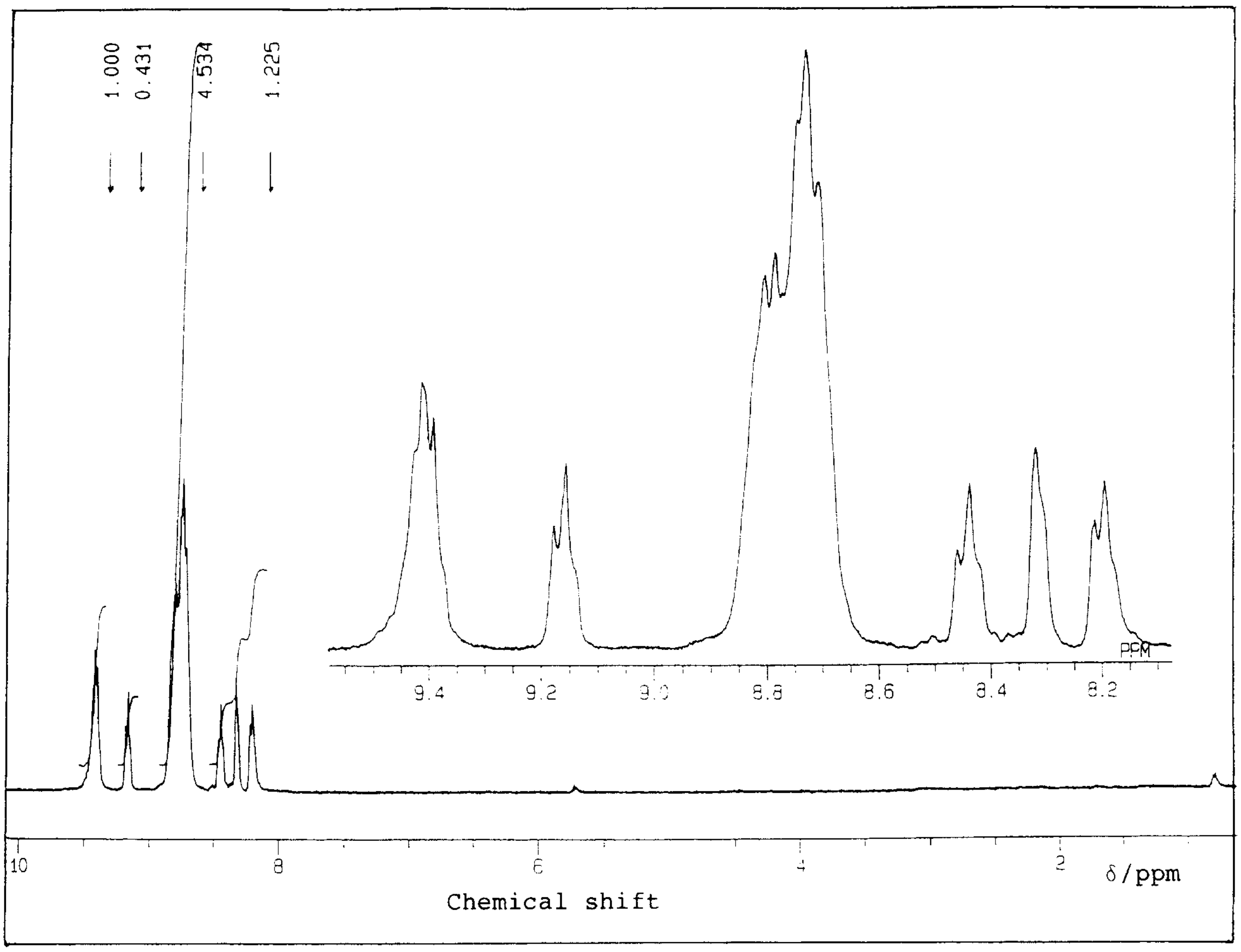


Figure 4 ^1H n.m.r. spectrum of P(2,6-Q)-C(CN)$_2$ in trifluoroacetic acid-d_1

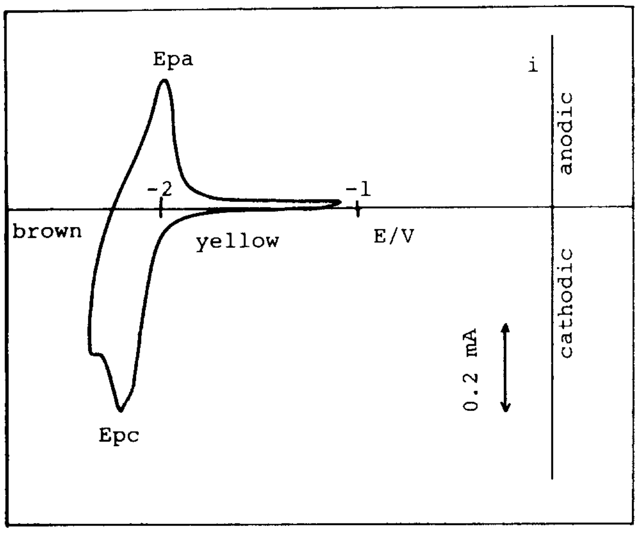


Figure 5 Cyclic voltammogram of PPy-ox film laid on a Pt plate. In a 0.1 M acetonitrile solution [NEt$_4$][BF$_4$]

but also those in the two adjacent units also give peaks near δ 9.17. The absence of a distinct peak assignable to cyclopropane hydrogen (*ca* δ 1–4) also supports the carbene reaction at the quinoline ring in equation (6) being negligible.

Electrochemical and electrical properties

PPy-ox film formed on a platinum plate is redox active and receives reversible electrochemical reduction at

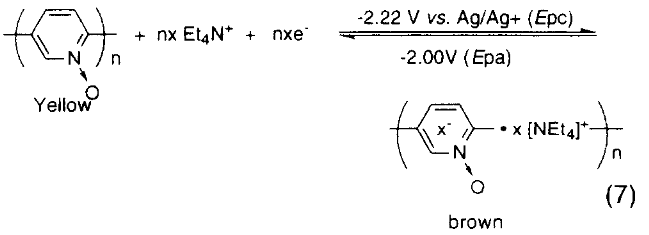
Table 2 Reduction potential of polymers[a]

No.	Polymer	E_{pc}	E_{pa}	E^0
1	PPy[b]	−2.43 (blue)	−1.90 (yellow)	−2.21
2	PPy-ox	−2.22 (brown)	−2.00 (yellow)	−2.11
3	PPy-C(CN)$_2$	−2.28 (dark brown)	−1.96 (yellow)	−2.12
4	P(2,6-Q)[c]	−2.21 (dark blue)	−1.94 (yellow)	−2.08
5	P(2,6-Q)-ox[c]	−2.31 (purple)	−2.00 (yellow)	−2.16
6	P(2,6-Q)-C(CN)$_2$	−2.22 (brown)	−1.92 (light yellow)	−2.07
7	P(2,6-N)[c]	−1.83 (dark brown)	−1.67 (brown)	−1.75
8	P(2,6-N)-ox[c]	−1.8	−1.6	−1.7

[a] E_{pc} = peak cathode (n-doping) potential. E_{pa} = peak anode (n-undoping) potential. $E^0 = (E_{pc} + E_{pa})/2$. Potential is given against Ag/Ag$^+$. Colour shown in the parentheses indicates colour of the polymer film after the electrochemical reaction; e.g. neutral PPy is yellow whereas reduced (n-doped) PPy is blue. Measured with polymer film in an acetonitrile solution of 0.1 M [NEt$_4$][BF$_4$] unless otherwise noted

[b] In a 0.1 M acetonitrile solution [NEt$_4$][BF$_4$]

[c] In a 0.1 M acetonitrile solution [NEt$_4$][ClO$_4$]



(7)

Table 3 Electrical dc conductivity of polymers[a]

Polymer	σ/S cm^{-1}
PPy	$<10^{-14}$
PPy-ox	3.4×10^{-6}
PPy-C(CN)$_2$	6.0×10^{-7}
P(2,6-Q)	4.0×10^{-10}
P(2,6-Q)-ox	2.3×10^{-6}
P(2,6-Q)-C(CN)$_2$	2.8×10^{-7}
P(2,6-N)	1.1×10^{-9}
P(2,6-N)-ox	3.2×10^{-6}

[a] Measured at room temperature with compressed powders (cf. Experimental)

about -2.1 V vs Ag/Ag$^+$ (*Figure 5*)*. Electrochemical redox data are summarized in *Table 2*.

Although electrochemical reduction of pyridine-*N*-oxide ($E^0 = -1.36$ V *vs* Hg pool)[16] proceeds more easily than that of pyridine ($E^0 = -2.20$ V vs Hg pool)[17], PPy-ox gives almost the same reducing potential E^0 as PPy (Nos 1 and 2 in *Table 2*). This may be attributed to the difference in the length of effective π-conjugation between PPy and PPy-ox. As discussed above, PPy is considered to have a longer effective π-conjugation system than PPy-ox, and it may make the electrochemical reduction easier to give the reduction potential similar to that of PPy-ox.

The electrochemical redox reaction is accompanied by a colour change [electrochromism; equation (7) and *Table 2*], and reduced PPy-ox film has a considerably different colour from that of reduced PPy film. The doping level x in equation (7) is 0.2 as determined from the electric current. PPy-ox is inert against electrochemical oxidation (up to 1.0 V vs Ag/Ag$^+$) similarly to the case of PPy[1]. P(2,6-Q)-ox and P(2,6-N)-diox also give redox behaviour similar to that of P(2,6-Q) and P(2,6-N) (*Table 2*); the colours of their reduced films are also different from those of reduced P(2,6-Q) and P(2,6-N) films. The N-oxidized polymers show no obvious oxidation (p-doping) peak up to 1.7 V vs Ag/Ag$^+$, similarly to the cases of the original polymers[1–4].

The N-ylidated polymers also show reducing potentials comparable to those of original polymers (*Table 2*). The colours of their reduced films are again considerably different from those of reduced films of the original polymers, in spite of the small degree of N-ylidation.

Table 3 summarizes electrical conductivity of the N-oxidized and N-ylidated polymers. As shown in *Table 3*, the N-oxidized and N-ylidated polymers have some electrically conducting properties with d.c. conductivity of 2.8×10^{-7}–3.4×10^{-6} S cm^{-1} even in a non-doped state; this is in contrast to electrically insulating properties of the original polymers (*Table 3*). The enhancement of the electrical conductivity by the N-oxidation and N-ylidation even in the non-doped state may be attributed to generation of carrier in the main chain through the resonances discussed above (equations (1)–(3)). Similar enhancement of d.c. electrical conductivity is observed with the transition metal complexes of the N-containing π-conjugated aromatic polymers (e.g. ruthenium and nickel complexes of poly(2,2′-bipyridine-5,5′-diyl)[1] with electrical conductivity of 10^{-7}– 10^{-5} S cm^{-1}), and in this case the enhancement of the electrical conductivity seems to be attributable to formation of carrier in the polymer main chain due to an MLCT structure of the transition metal complex. Since the electrical conductivity of the N-oxidized and N-ylidated polymers does not give observable time dependence, the electrical conductivity is essentially ascribed to electronic conduction, and ionic conduction, if any, is considered to not contribute to the electrical conductivity as much.

The electrical conductivity of the N-oxidized and N-ylidated polymers may be sufficient to remove static electricity in some cases, and the polymers may be usable in these cases.

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*The E_{pc} value shifts to a more negative side to some extent with repeated scanning, whereas E_{pa} value remains unchanged