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Comparative study on poly(3-alkylpyrroles)

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Polypyrrole(PPY), poly(3-methylpyrrole)(PMPY) and poly(3-octylpyrrole) (POCPY) were prepared under the same electrochemical polymerization conditions and their properties were comparatively studied. Electrical conductivity increased in the order POCPY < PMPY < PPY. Absorption spectra measured *in situ* showed that while peak energy of the interband transition increased in the order PPY < PMPY < POCPY, the absorption edge of PPY was located at almost equal energy as that of PMPY and POCPY. Stability, indicated by decrease in the ratio of conductivities after storage to the initial conductivity, was primarily dependent on the length of alkyl chains, secondly on dopants and associated with spectral deterioration. While the initial conductivity was strongly dependent on temperature and current density during electrochemical polymerization, the stability was virtually independent of these conditions. The stability increased in the order: POCPY < PMPY < PPY. Spectral change during storage in air was dependent on the chemical structure of polymers but almost independent of dopants. The spectral change indicated PPY to be in nearly initial states after 10 days and POCPY to be in almost completely undoped states after 200 days. In cyclic voltammograms, PPY and POCPY showed one anodic peak and PMPY two anodic peaks. Their peak potentials were associated with conjugation length.

1. Introduction

Among the electrically conducting polymers, polymers from five-membered heterocyclic compounds have attracted a great attention, because in addition to moderate electrical conductivity they show such interesting properties as electrochemical activity, stability, and electrochromism [1–3]. Polythiophenes and polypyrroles have been most intensively studied. Of the polythiophenes, poly(3-substituted thiophenes) has been extensively studied, due to such desirable characteristics as solubility, fusibility and self-doping [4–6]. Thus, it is now possible to determine molecular weight, measure solvatochromism, perform melt-spinning, and enhance conductivity without adding external dopants. On the other hand, of the polypyrroles, polypyrrole has been studied intensively (for example [7, 8]) but poly(3-substituted pyrroles) have not. This difference could be attributable to the complexity of preparing polypyrrole derivatives. Thus, while properties of poly(3-alkylthiophenes) have been considerably revealed, those of poly(3-alkylpyrroles) have not yet been clarified.

Recently, preparation and properties of some poly(3-substituted pyrroles) have been reported. This is partly due to the finding of a new synthetic route to 3-substituted pyrroles via Friedel-Crafts acylation of *N*-substituted pyrrole [9]. Although the route does not give pure 3-substituted pyrrole as postulated by the original authors, it is a very useful procedure for preparing 3-acyl- and 3-alkylpyrroles [6, 10]. Ruhe *et al.* [11] electrochemically prepared films of polypyrroles having a fused alkyl ring at the 3,4-position. The films swelled in polar aprotic solvents and showed a strong frequency dependence of conductivity. Havinga *et al.* [12] reported poly[3-(4-sulphonylbutyl)pyrrole] to be soluble in water and self-doped. Bryce *et al.* [13] reported that polymers from 3-dodecanoylpyrrole and 3-octadecanoylpyrrole were moderately conducting. Wegner *et al.* [14] prepared poly(3-alkylpyrroles) and measured the temperature dependence of electrical conductivity, while Garnier *et al.* [15] showed poly(3-octylpyrrole) to have a lipophilic character.

Recently, we have been studying preparation and characterization of poly(3-substituted pyrroles). Electrochemical polymerization of 3-methylpyrrole gave conducting films which could be cycled between oxidized and reduced states [16]. Electrochemical polymerization of 3-octylpyrrole also gave films, but their morphology was rough [17]. Its oxidative coupling yielded polymer powder [18]. These films and powders were soluble in polar solvents. In the

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present work, polypyrrole (PPY), poly(3-methylpyrrole) (PMPY) and poly(3-octylpyrrole) (POCPY) were prepared under the same electrochemical polymerization conditions and their conductivity, absorption spectra, stability and spectral change were compared.

2. Experimental procedure

2.1. Electrochemical polymerization

Electrochemical polymerization was galvanostatically carried out in propylene carbonate under an argon atmosphere. The anode was indium–tin oxide conducting glass (ITO) and the cathode, a platinum plate. The concentrations of the monomers and electrolytes were 0.1 and 0.05 $\text{mol}\,l^{-1}$, respectively. The electrolytes used were tetraethylammonium salts of hexafluorophosphate (Et_4NPF_6), tetrafluoroborate (Et_4NBF_4), and perchlorate (Et_4NClO_4). Polymerization temperatures were 5 and − 20 °C, and current densities were 0.2 and 0.5 mA cm^{-2}.

2.2. Electrical conductivity

Electrical conductivity measurements were performed according to the usual four-probe arrangement for a film prepared at 0.8 C cm^{-2}. The conductivity at time, 0, was measured for films washed with *n*-hexane and dried *in vacuo* at room temperature for 1 h. After films were stored in air in the dark, their conductivity at time, *t*, was measured. Stability was represented by relative conductivity which was the ratio of conductivities after storage in air, σ_t, to the initial conductivity measured just after drying, σ_0.

2.3. Electrochemical spectroscopy

Absorption spectra were measured *in situ* at various doping levels during electrochemical undoping under an argon atmosphere. The electrolyte solution was propylene carbonate containing 0.1 mol/l Et_4NBF_4. The counter and reference electrodes were platinum and silver wires, respectively. Thin films were deposited on ITO by polymerizing the monomers at 20–50 mC cm^{-2} at − 20 °C in the presence of Et_4NBF_4. These as-grown films on ITO were transferred into an optical cell containing the electrolyte solution and their spectra were measured. The applied voltage was first increased until the π–π^* transition peak disappeared, then decreased until the films were undoped.

2.4. Spectral change

After films prepared at 50 mC cm^{-2} at 5 or − 20 °C were dried *in vacuo* for 1 h at room temperature, their initial spectra were measured. These films were stored in air in the dark for a given number of days, then their spectra at time, *t*, were measured.

2.5. Cyclic voltammograms

Films were prepared in propylene carbonate at 30 mC cm^{-2} and − 20 °C using Et_4NPF_6 as electrolyte. Cyclic voltammograms were measured at 5 °C using the same solvent and electrolyte on a Hokuto Denko HA-501G potentiostat and HB-105 function generator.

3. Results

3.1. Electrochemical polymerization of pyrroles

Three pyrroles were polymerized under the same polymerization conditions. The conductivities of the resulting films are summarized in Table I. The highest conductivity of each polymer was 280 S cm^{-1} for PPY, 130 S cm^{-1} for PMPY, and 4.5 S cm^{-1} for POCPY. PPY showed not only the highest conductivity at 5 °C in the presence of PF_6^- or BF_4^-, but also high conductivity under all polymerization conditions examined. On the other hand, high-quality films of PMPY were obtained only using PF_6^-. PMPY films showed higher conductivity with decreasing polymerization temperature. No highly conducting POCPY films could be obtained under the polymerization conditions examined. Although at 5 °C the optimal current density 0.5 mA cm^{-2} [19], at − 20 °C conductivity of POCPY was higher at 0.2 mA cm^{-2} than at 0.5 mA cm^{-2}.

3.2. Electrochemical spectroscopy

Electrochemical spectroscopic measurements were carried out for PPY, PMPY, and POCPY films using the same electrolyte and solvent. Spectral changes during electrochemical undoping are shown in Figs 1–3. When a PPY film was transferred into an optical cell, there were two peaks at 1.1 and 2.6 eV, corresponding to the transition from the valence band to the two bipolaron bands. There was no peak corresponding to the π–π^* transition. As the applied voltage decreased, these two peaks became smaller and shifted to the lower energy side, and concurrently a new peak,

TABLE I Polymerization conditions and conductivity. Charge density = 0.8 C cm^{-2}

Temperature (°C)	Current density (mA cm^{-2})	Conductivity (S cm^{-1})								
		PPY			PMPY			POCPY		
		PF_6	BF_4	ClO_4	PF_6	BF_4	ClO_4	PF_6	BF_4	ClO_4
5	0.5	280	280	240	100	6.2	7.1	4.5	1.5	3.5
− 20	0.5	240	230	180	120	8.6	3.4	1.1	0.8	1.2
− 20	0.2	240	240	160	130	13	20	2.0	1.3	2.0

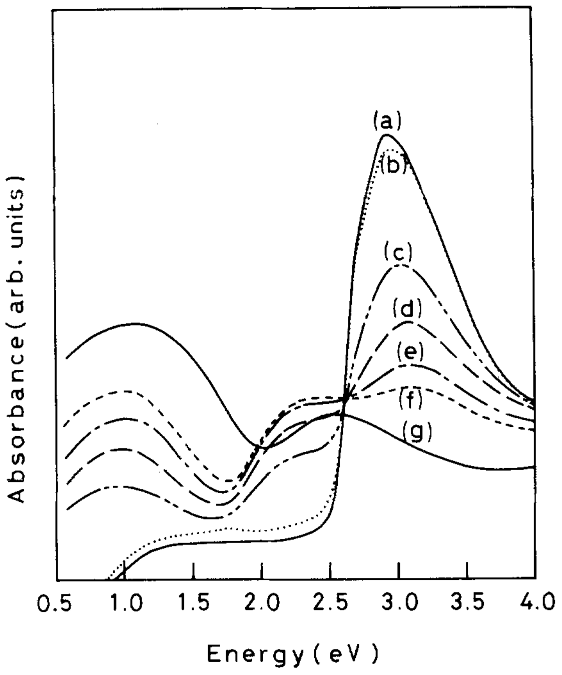

Figure 1 Absorption spectra of PPY at various doping levels. Applied potential: (a) − 1.0 V, (b) − 0.6 V, (c) − 0.5 V, (d) − 0.4 V, (e) − 0.3 V, (f) − 0.2 V, (g) as-grown film.

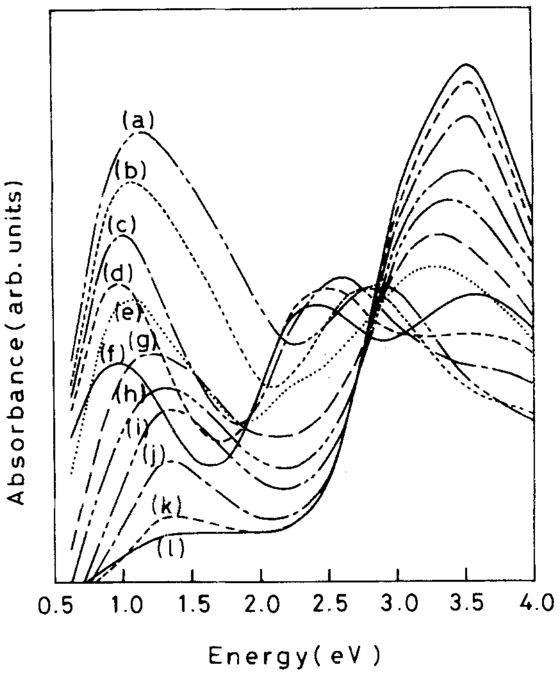

Figure 3 Absorption spectra of POCPY at various doping levels. Applied potential: (a) 0.7 V, (b) 0.5 V, (c) 0.3 V, (d) 0.2 V, (e) − 0.1 V, (f) as-grown film, (g) − 0.5 V, (h) − 0.6 V, (i) − 0.8 V, (j) − 1.2 V, (k) − 1.5 V, (l) − 1.7 V.

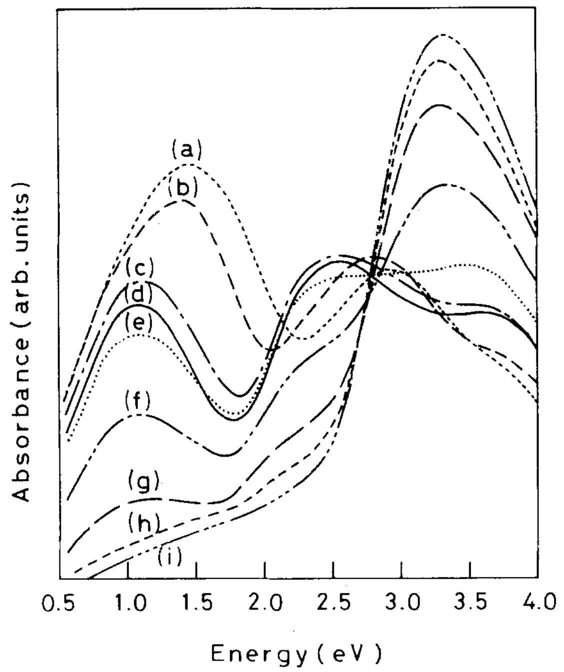

Figure 2 Absorption spectra of PMPY at various doping levels. Applied potential: (a) 0.3 V, (b) 0.1 V, (c) − 0.1 V, (d) as-grown film, (e) − 0.2 V, (f) − 0.4 V, (g) − 0.6 V, (h) − 1.0 V, (i) − 1.5 V.

due to the π–π* transition, appeared around 3 eV. At − 1.0 V, only the π–π* transition peak was observed at 2.9 eV.

When a PMPY film was transferred into an optical cell, there were three peaks at 1.1, 2.5 and 3.5 eV, indicating the film to be in a partly undoped state. When the potential increased to + 0.3 V, the π–π* transition peak disappeared and the two bipolaron peaks remained at 1.45 and 2.9 eV, showing the film to be in a fully doped state. As the potential decreased, the π–π* transition peak appeared again and the bipolaron peaks became smaller and shifted to the lower energy side, and finally the π–π* transition peak remained at 3.3 eV.

A POCPY film showed similar spectral change as PMPY. Shoulders due to a polaron were observed at 2.1–2.2 eV in spectra f and g, but not so evident as spectra measured with other electrolytes [19]. While in the spectra of PPY and PMPY the π–π* transition energy shifted to the lower energy side with decreasing doping levels, that of POCPY shifted to the higher energy side. On the other hand, the π–π* transition peak of POCPY had a small shoulder on its lower energy slope.

The data for neutral films are summarized in Table II. While the peak energies increased with increasing alkyl chain length, onset energy of PPY was a little higher than that of PMPY and POCPY. Thus, difference in energy between peak and onset energies increased in the order PPY < PMPY < POCPY. The difference is related to distribution of effective conjugation length, implying that PPY had a narrow distribution and POCPY a broad one.

3.3. Stability of polypyrroles

Fig. 4 shows stability of PPY prepared with various electrolytes at different temperatures. The conductivity ratio rapidly decreased in the initial stages, and then gradually. Because the thickness of the films did not change appreciably during storage, the decrease in conductivity was wholly attributable to increase in electrical resistance. PPY doped with PF_6^- was the stablest and retained more than 60% of its initial conductivity after 200 days. Stability of PPY was mainly dependent on dopants. Stability increased in the order $BF_4^- < ClO_4^- < PF_6^-$. For PF_6^- and BF_4^-, stability was independent of polymerization temperature, but for ClO_4^- was slightly dependent.

Fig. 5 shows stability of PMPY prepared at different current densities and temperatures. The conductivity ratio of PMPY rapidly and then gradually decreased, as in PPY, but it was always lower than that of PPY as far as the same electrolyte was used. Stability was slightly dependent on polymerization conditions. After 200 days, PF_6^--doped PMPY retained about 40% of its initial conductivity.

TABLE II The peak and onset energy for the π-π* transition

Polymer	PPY	PMPY	POCPY
Peak (eV)	2.9	3.2	3.5
Onset (eV)	2.5	2.4	2.4
Difference[a] (eV)	0.4	0.8	1.1

[a] Difference = peak energy − onset energy.

Fig. 6 shows stability of POCPY prepared at different temperatures with various electrolytes. The stability curves of POCPY were very similar to those of PPY and PMPY. But the conductivity ratio of POCPY was the lowest among the three polymers studied in the present work and decreased to a quarter of its initial value. The conductivity ratio of POCPY doped with PF_6^- or ClO_4^- was dependent on polymerization temperature.

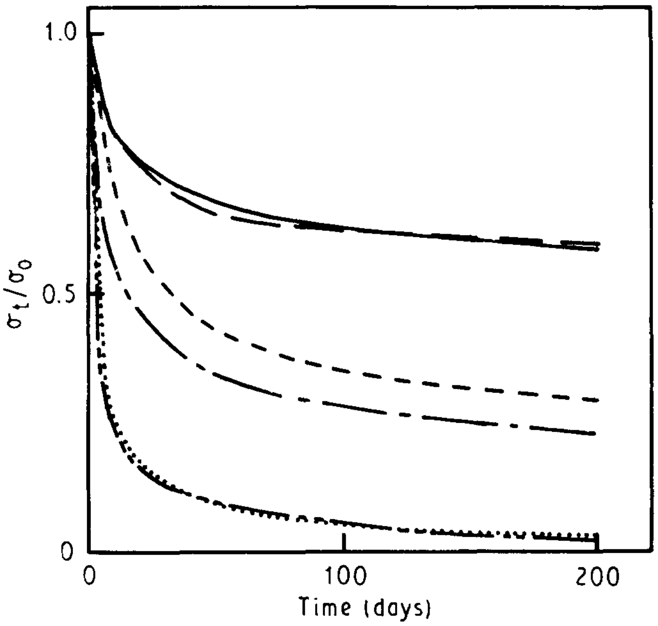

Figure 4 Stability of PPY. Polymerization conditions: current density 0.5 mA cm^{-2}, (———) 5 °C with Et_4NPF_6, (——-——) 5 °C with Et_4NClO_4, (——--——) 5 °C with Et_4NBF_4, (— — —) −20 °C with Et_4NPF_6, (---) −20 °C with Et_4NClO_4, (- - -) −20 °C with Et_4NBF_4.

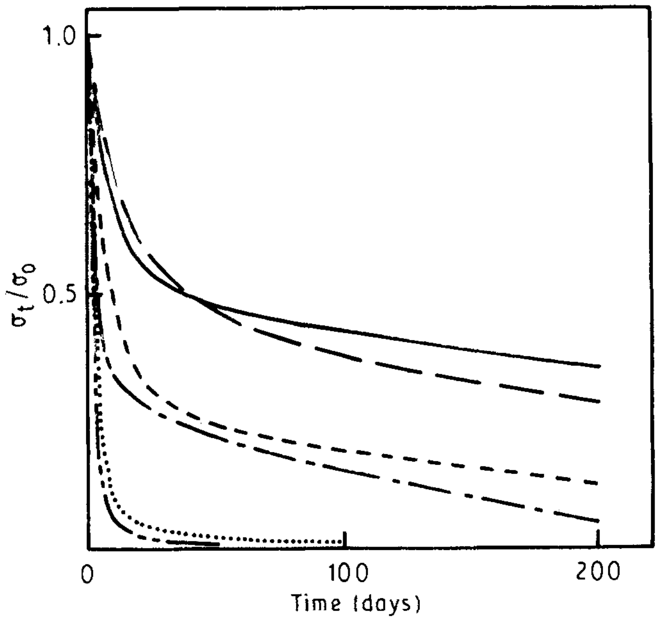

Figure 5 Stability of PMPY. Polymerization conditions: (———) 5 °C, 0.5 mA cm^{-2} with Et_4NPF_6, (——-——) 5 °C, 0.5 mA cm^{-2} with Et_4NClO_4, (——--——) 5 °C, 0.5 mA cm^{-2} with Et_4NBF_4, (— — —) −20 °C, 0.2 mA cm^{-2} with Et_4NPF_6, (---) −20 °C, 0.2 mA cm^{-2} with Et_4NClO_4, (- - -) −20 °C, 0.2 mA cm^{-2} with Et_4NBF_4.

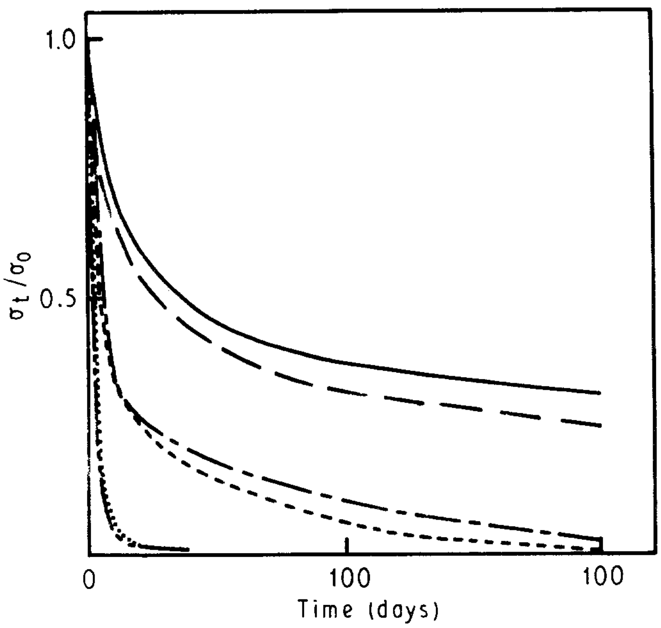

Figure 6 Stability of POCPY. Polymerization conditions: current density 0.5 mA cm^{-2}, (———) 5 °C with Et_4NPF_6, (——·——) 5 °C with Et_4NClO_4, (——··——) 5 °C with Et_4NBF_4, (— — —) − 20 °C with Et_4NPF_6, (– – –) − 20 °C with Et_4NClO_4, (- - -) − 20 °C with Et_4NBF_4.

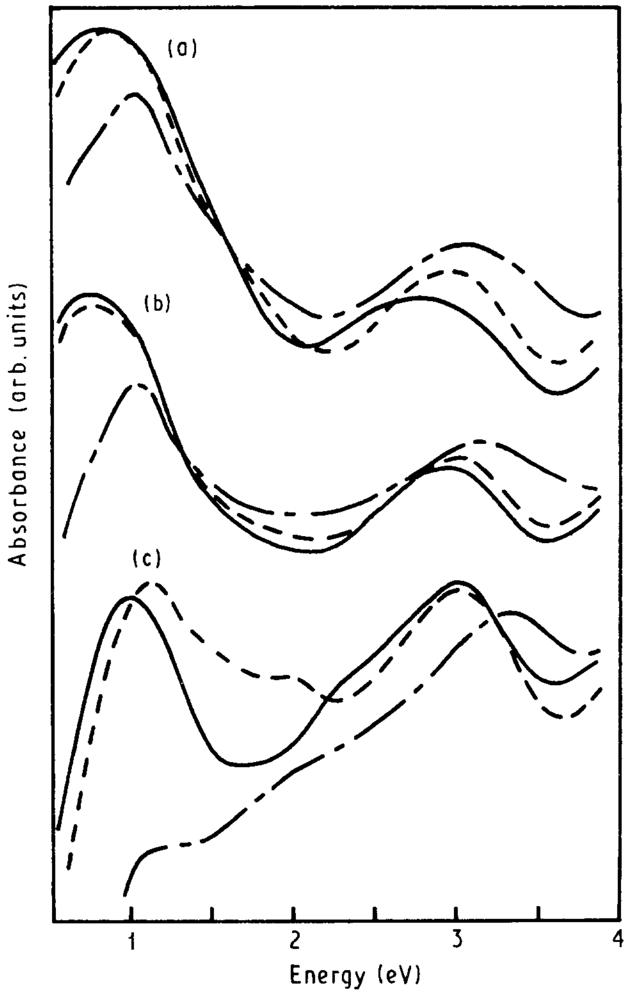

Figure 7 Spectral change of poly(3-alkylpyrroles). (a) PPY, (b) PMPY, (c) POCPY. Dopant = PF_6^-, (———) initial film, (— — —) after 10 days, (——·——) after 200 days.

3.4. Spectral change during storage

Fig. 7 shows spectral change of polypyrroles after storage in air. The initial spectra of PPY and PMPY had two peaks at 0.8 and 2.8–2.9 eV, and changed in a similar way. There were no remarkable changes after 10 days. After 200 days, the peaks at 0.8 eV became smaller and shifted to 1.1 eV and the higher-energy peak became larger and shifted to the higher-energy side. On the other hand, the initial spectra of POCPY had three peaks at 1, 2.2 and 3 eV. The last peak was as high as the first peak, indicating POCPY to be partly undoped. After 10 days, there was a clear peak at 2.0 eV, probably due to doping with oxygen. After 200 days, the lowest-energy peak almost disappeared, showing POCPY to be undoped to a large extent.

Spectral changes of PPY and PMPY containing ClO_4^- or BF_4^- were very similar to those shown in Fig. 7, but spectral change of POCPY was somewhat dependent on dopants. Fig. 8 shows the spectral change of POCPY prepared in the presence of various electrolytes. The initial spectra had three peaks. In the spectrum of a film containing BF_4^-, the lowest-energy peak was smaller than the highest-energy peak, indicating the doping level to be low at the initial stage. After 10 days, the spectra still retained the lowest-energy peaks as high as the initial spectra, indicating that undoping did not take place to a great extent. But the positions of middle peaks were different from polymer to polymer. After 200 days, these three spectra were very similar. The lowest-energy peaks almost disappeared, the positions of the middle peaks were near, and the highest-energy peaks shifted to the higher-energy side, showing these polymers to be undoped to a great extent and to be affected by oxygen.

While the conductivities rapidly decreased during the first 10 days as shown in Figs 4–6, the spectral changes were rather small during this period. On the other hand, after this period the spectra changed greatly, although the conductivities decreased gradually. Thus, the spectral changes do not exactly correspond to changes in conductivity.

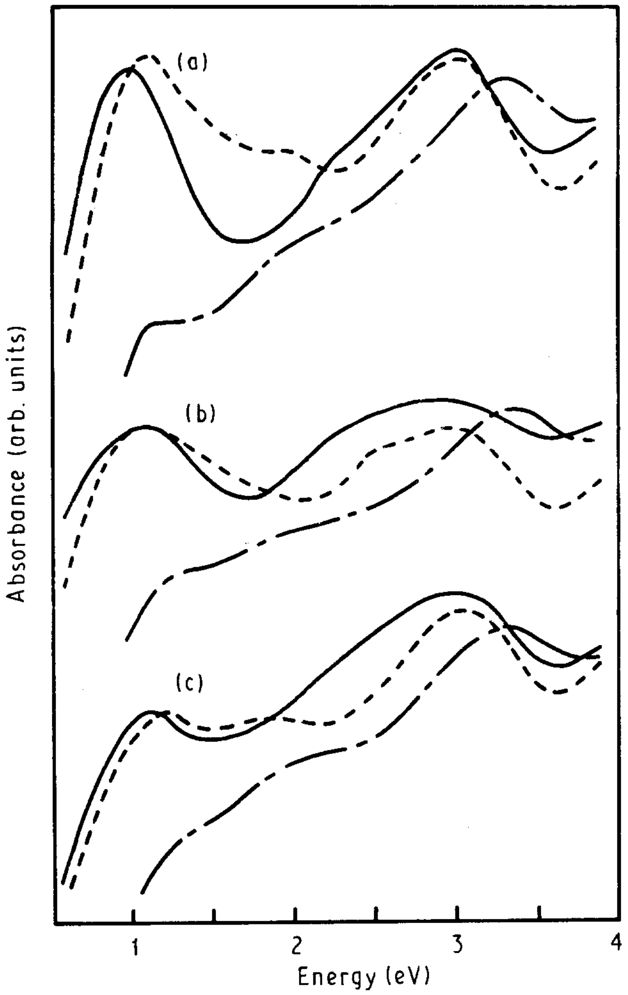

Figure 8 Spectral change of POCPY prepared with various electrolytes. (a) Et_4NPF_6, (b) Et_4NClO_4, (c) Et_4NBF_4. (———) Initial film, (– – –) after 10 days, (— — — —) after 200 days.

TABLE III Anodic and cathodic peaks at infinitesimal sweep rate. Electrolyte = Et_4NPF_6

	Anodic peak (V versus Ag)	Cathodic peak (V versus Ag)
PPY	– 0.12	– 0.29
PMPY	– 0.06, 0.22	– 0.11, 0.16
POCPY	0.16	0.12

3.5. Cyclic voltammetry

Fig. 9 shows cyclic voltammograms of PPY, PMPY, and POCPY. The anodic peaks in cyclic voltammograms of each polymer shifted to higher potentials with increasing sweep rate and the cathodic peaks to lower potentials. The peak potentials at infinitesimal sweep rate are summarized in Table III. It is evident that while PPY showed one anodic peak at the lower potential region and POCPY at the higher potential region, the cyclic voltammogram of PMPY had two anodic peaks at both lower- and higher-potential regions. The anodic peak of PPY was very sharp. While the height of the PPY peak rapidly decreased on both lower- and higher-potential sides, that of PMPY and POCPY had a plateau on the higher-potential side.

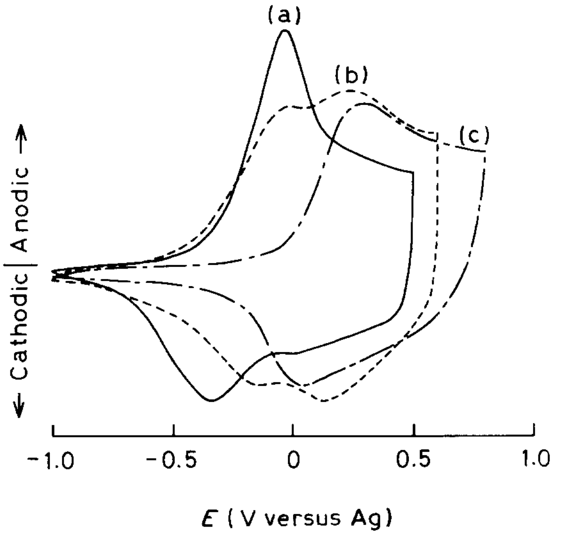

Figure 9 Cyclic voltammograms of (a) PPY, (b) PMPY, and (c) POCPY. Sweep rate: (a, b) 30 $mV s^{-1}$, (c) 20 $mV s^{-1}$. Electrolyte = Et_4NPF_6. Solvent = propylene carbonate.

4. Discussion

Figs 4–6 indicate that stability of poly(3-alkyl-pyrroles), represented in the conductivity normalized to its initial conductivity, is primarily dependent on length of alkyl chains, secondly on dopants included in the polymer, and somewhat on polymerization conditions. Stability increases in the order POCPY < PMPY < PPY. This is clearly correlated with features of the cyclic voltammograms shown in Fig. 9. PPY is the most easily oxidized, POCPY has the highest oxidation potential and PMPY shows intermediate characteristics. Figs 7 and 8 show the least-stable POCPY was almost completely undoped in 200 days. These indicate that the decrease in conductivity of poly(3-alkylpyrroles) is primarily due to the neutralization of the films.

Sun *et al.* [20] studied the stability of polypyrrole doped with *p*-toluenesulphonate. Its conductivity increased with storage time for the first few days, due to the decrease in moisture and solvent content of the films on standing. Their stability curves were quite different from those of the present study. Munstedt *et al.* [21] also studied stability of polypyrrole at 140 °C. Polypyrrole doped with benzenesulphonic acid was the least stable and polypyrrole doped with PF_6^- showed the lowest conductivity. These results are different from those of the above-mentioned studies.

The cyclic voltammogram of PPY shown in Fig. 9 has one sharp anodic peak located at the low potential, indicating PPY to have long conjugation length and a comparatively homogeneous structure. These are corroborated by the sharp absorption peak corresponding to the interband transition in Fig. 1. The cyclic voltammogram of PMPY had two anodic and cathodic peaks. Poly(3-dodecylthiophene) also showed two peaks in its cyclic voltammograms [22]. Because the same polymer gives one-peak cyclic voltammograms or two-peak cyclic voltammograms depending on the film-forming conditions, the two peaks cannot be due to two types of primary structure, but should be explained by two types of chain folding.

Similarly, PMPY has two types of chain folding, one corresponding to the conjugation length of PPY and one to that of POCPY. The cyclic voltammogram of POCPY has one anodic peak located at the high potential, corresponding to short conjugation length shown by the π–π^* transition peak in Fig. 3. The large difference between peak and onset energies in Table II suggests POCPY to have broad distribution of conjugation length.

Another problem is the difference in spectral features between Figs 1–3 and Figs 7 and 8. In the former, spectra were measured in argon for films soaked in propylene carbonate. In the latter, spectra were measured in air for films dried *in vacuo*. While the spectra of PPY and PMPY in Figs 1 and 2 had three peaks at intermediate doping levels, spectra of PPY and PMPY in Fig. 7 had two peaks. The middle peak could not be observed in these spectra. On the other hand, spectra of POCPY in Figs 3 and 7 had three peaks, but the potential of the middle peak was different from spectrum to spectrum. The peak was located at 2.5 eV in Fig. 3 but at 2 eV in Fig. 7. In some cases, slight shoulders were observed in spectra of dry PPY and PMPY films prepared at − 20 °C. These results suggest that the peak of POCPY around 2 eV is due to doping with oxygen in air. Because anions in POCPY were most easily eliminated, this peak was well observed in spectra of POCPY. Another explanation is that because the packing mode of POCPY is loose due to long alkyl chains, oxygen can diffuse easily into the inner parts of POCPY films.

References

1. A. F. DIAZ, K. K. KANAZAWA and G. P. GARDINI, *J. Chem. Soc. Chem. Commun.* (1979) 635.
2. K. K. KANAZAWA, A. F. DIAZ, R. H. GEISS, W. D. GILL, J. F. KWAK, J. A. LOGAN, J. F. RABOLT and G. B. STREET, *ibid.* (1979) 854.
3. K. KANETO, K. YOSHINO and INUISHI, *Solid State Commun.* **46** (1983) 389.
4. M. SATO, S. TANAKA and K. KAERIYAMA, *J. Chem. Soc. Chem. Commun.* (1986) 873.
5. K. YOSHINO, S. NAKAJIMA, M. FUJII and R. SUGIMOTO, *Polym. Commun.* **28** (1987) 309.
6. Y. IKENOUE, J. CHIANG, A. O. PATIL, F. WUDL and A. J. HEEGER, *J. Amer. Chem. Soc.* **110** (1988) 2983.
7. S. MACHIDA, S. MIYATA and A. TECHAGUMPUCH, *Synth. Met.* **31** (1989) 311.
8. W. WERNET and G. WEGNER, *Makromol. Chem.* **188** (1987) 1465.
9. R. X. XU, H. J. ANDERSON, N. J. GOGAN, C. E. LOADER and R. McDONALD, *Tetrahedron Lett.* **22** (1981) 4899.
10. H. MASUDA and K. KAERIYAMA, *Synth. Met.* **41** (1991) 389.
11. J. RUHE, C. KROHNKE, T. A. EZQUERRA, F. KREMER and G. WEGNER, *Ber. Bunsenges Phys. Chem.* **91** (1987) 885.
12. E. E. HAVINGA, L. W. van HORSSEN, W. HOEVE, H. WYNBERG and E. W. MEIJER, *Polym. Bull.* **18** (1987) 277.
13. M. R. BRYCE, A. CHISSEL, P. KATHIRGAMANATHAN, D. PARKER and N. R. M. SMITH, *J. Chem. Soc. Chem. Commun.* (1987) 466.
14. J. RUHE, T. EZQUERRA and G. WEGNER, *Makromol. Chem. Rapid Commun.* **10** (1989) 103.
15. D. DELABOUGLISE, J. RONCALI, M. LEMAIRE and F. GARNIER, *J. Chem. Soc. Chem. Commun.* (1989) 475.
16. K. KAERIYAMA, M. SATO and K. HAMADA, *Makromol. Chem. Rapid Commun.* **10** (1989) 171.
17. H. MASUDA, S. TANAKA and K. KAERIYAMA, *J. Polym. Sci. Polym. Chem. Edn* **28** (1990) 1831.
18. H. MASUDA, S. TANAKA and K. KAERIYAMA, *Synth. Met.* **33** (1989) 365.
19. K. KAERIYAMA and H. MASUDA, *Brit. Polym. J.* **23**(1, 2) (1990) 141.
20. B. SUN, J. J. JONES, R. P. BURFORD and M.-S KAZACOS, *J. Mater. Sci.* **24** (1989) 4024.
21. H. MUNSTEDT, H. NAARMANN and G. KOHLER, *Molec. Cryst. Liq. Cryst.* **118** (1985) 129.
22. M. SATO, S. TANAKA and K. KAERIYAMA, *Makromol. Chem.* **188** (1987) 1763.

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