Poly(3-butylthiophene) and poly(3-benzylthiophene) films

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Poly(3-butylthiophene) (PBUT) and poly(3-benzylthiophene) (PBZT) films were electrochemically prepared and their properties examined. The conductivities of PBUT and PBZT were 110 and 13 S cm^{-1}, respectively. Cyclic voltammograms of PBUT were similar to those of poly(3-ethylthiophene) (PET). Cyclic voltammograms of PBZT were sharp, well defined and symmetric. Spectral change during electrochemical doping indicated the bipolaron bands to be evolved at intermediate stages of doping. In the case of PBUT, the position of the peak corresponding to transition between valence and higher bipolaron bands was independent of doping levels. In the case of PBZT, the positions of both the above peak and the peak of $\pi-\pi^*$ transition did not shift until the former peak began to decline. This inconsistency with the bipolaron theory was tentatively attributed to high density of energy states at the band edges. The conductivities, oxidation potentials and band gaps of PBUT and PBZT were compared with those of polythiophene (PT), poly(3-methylthiophene) (PMT) and PET.

(Keywords: poly(3-butylthiophene); poly(3-benzylthiophene); electrochemical polymerization; cyclic voltammogram; visible-near i.r. spectra)

INTRODUCTION

Many kinds of conducting polymers have been prepared since remarkable effects of doping on conductivity of conjugated polymers were found in 1977[1]. The properties of the polymers depend primarily on their chemical structures, but the relation between structure and conductivities has not been studied intensively. This might be due to the fact that chemical modification of polymers usually has undesirable effects on their conductivities. For example[2,3], although the conductivity of polyacetylene is higher than 10^4 S cm^{-1}, substituted polyacetylenes show conductivites less than 10^{-3} S cm^{-1}. Polythiophenes (PT) were shown to be an exception to this. Poly(3-methylthiophene) (PMT) and poly(3-ethylthiophene) (PET) were more conducting than PT[4]. We have been preparing polythiophene derivatives systematically and examining their properties[5-10]. In the present paper, the preparation, cyclic voltammograms and spectral changes of poly(3-butylthiophene) (PBUT) and poly(3-benzylthiophene) (PBZT) are described. PBUT was on the extrapolation of PET, but PBZT showed interesting properties different from poly(3-alkylthiophenes).

EXPERIMENTAL

3-Butylthiophene (BUT) was prepared by the previously reported method (b.p. 85–86°C at 28 mmHg)[11]. 3-Benzylthiophene (BZT) was synthesized by the coupling of benzylmagnesium chloride with 3-bromothiophene in the presence of a nickel catalyst (b.p. 91–92°C at 3 mmHg). The structures of these monomers were confirmed by n.m.r. and i.r. spectra.

The solvents used were propylene carbonate (PC), benzonitrile (BN), acetonitrile (AN) and nitrobenzene (NB). Purification of these solvents, electrochemical polymerization and measurements of conductivity and spectral change during PF_6^- doping were carried out in the same way as previously reported[7]. In electrochemical polymerization and measurements, platinum plates were used as anode and cathode. Spectra during ClO_4^- doping of a neutral film were measured *in situ* in an acetonitrile solution containing 0.01 mol l^{-1} of $AgClO_4$ and 0.1 mol l^{-1} of Et_4NClO_4. The anode was a plate of indium–tin oxide conducting glass. The cathode was a silver wire. Visible–near i.r. spectra were recorded on a Hitachi U-3400 spectrophotometer.

RESULTS AND DISCUSSION

Electrochemical polymerization

The films were obtained by the galvanostatic polymerization of BUT and BZT. The results are summarized in *Table 1*. PC and tetraethylammonium hexafluorophosphate (Et_4NPF_6) were the preferred solvent and electrolyte, respectively. BN and tetraethylammonium tetrafluoroborate (Et_4NBF_4) were also effective as solvent and electrolyte, respectively. The conductivity of PBUT was lower than that of PET prepared under the same conditions. PBUT contained

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Table 1 Results of electrochemical polymerization[a]

Run	Monomer	Solvent	Electrolyte	Current density (mA cm^{-2})	Conductivity[b] (S cm^{-1})	Dopant[c] content
1	BUT	PC	Et_4NPF_6	10	110	0.18
2	BUT	BN	Et_4NPF_6	10	58	–
3	BUT	NB	Et_4NPF_6	10	–[d]	–
4	BUT	AN	Et_4NPF_6	10	–[d]	–
5	BUT	PC	Et_4NBF_4	10	51	–
6	BZT	PC	Et_4NPF_6	10	–[e]	–
7	BZT	PC	Et_4NPF_6	5	13	0.37

[a] [Monomer] = 0.2 mol l^{-1}, [Electrolyte] = 0.03 mol l^{-1}, charge = 2.4 C cm^{-2}, at 5°C

[b] At room temperature

[c] Dopant per monomer unit determined from elemental analysis of sulphur and phosphorus

[d] The film was heterogeneous

[e] The polymerization could not continue owing to increase in voltage

almost the same amount of dopant as PT, PMT and PET prepared under the same polymerization conditions. PBZT showed a lower conductivity than PBUT, although the dopant concentration was much higher.

Neutral films were obtained by the electrochemical reduction of as-grown films and their i.r. spectra were measured on a Fourier transform i.r. spectrophotometer. There was a band at 830 cm^{-1}, assignable to C–H deformation vibration of a 2,3,5-trisubstituted thiophene ring. There were no bands in the range between 600 and 1000 cm^{-1} except for a band at 700 cm^{-1}, assignable to a monosubstituted benzene ring of PBZT[12,13]. The i.r. spectra show that PBUT and PBZT have the same regular structure as PMT and PET, which can be denoted as poly(3-alkyl-2,5-thiophenediyl).

Cyclic voltammetry

The cyclic voltammograms of PBUT and PBZT measured in an AN/Et_4NPF_6 system are shown in *Figures 1* and *2*, respectively. The films could be cycled repeatedly between oxidized and neutral states with no appreciable decomposition of material. The oxidized films were blue in colour and the neutral ones red. The cyclic voltammograms of PBUT showed an anodic peak at 0.49–0.52 V, a shoulder at about 0.65 V and a cathodic peak at 0.52–0.50 V. The shapes of the voltammograms were similar to those of PET. The cyclic voltammograms of PBZT had an anodic peak at 0.67–0.70 V, a small shoulder at around 0.75 V and a cathodic peak at 0.63–0.61 V. The shapes were considerably different from those of the other thiophene derivatives. The oxidation and reduction waves were sharp, well defined and symmetric, suggesting charge transfer to be rapid. PBZT may be useful as the electrode material of a rechargeable battery. The oxidation potential of 3-substituted polythiophenes increased in the order PMT < PET < PBUT < PT < PBZT. This indicates the effect of the substituents on the doping process. The electron-donating effects of alkyl groups lower the oxidation potential. Since the bulky benzyl group hinders successive thiophene rings from taking on a coplanar configuration, conjugation along the polymer chains becomes less effective, causing an increase in the oxidation potential of PBZT.

Visible–near infra-red spectra

The spectra of PT films were reported by several groups[5,14–16]. Spectral changes during electrochemical doping of PF_6^- were measured *in situ* in acetonitrile solution[7]. In neutral states, a peak corresponding to the transition between the valence and conduction bands was observed. When the films were electrochemically doped, two additional peaks appeared in the gap region and these three peaks shifted to higher energy with increasing levels of doping, indicating that the two bipolaron bands were derived from the edges of the valence and conduction bands and that the band gap increased. At

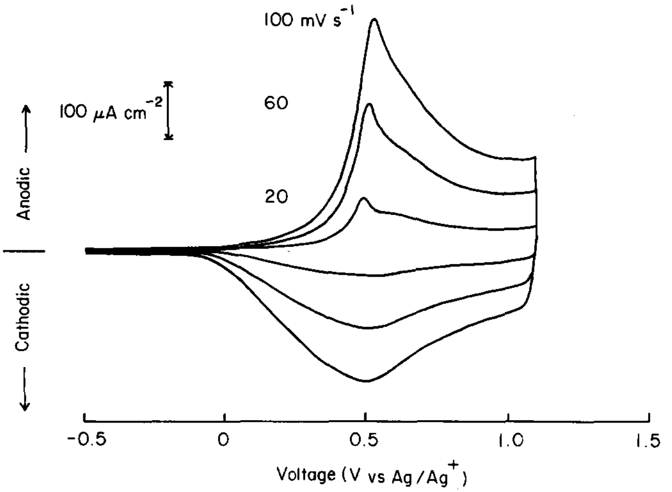

Figure 1 Cyclic voltammograms of a PBUT film

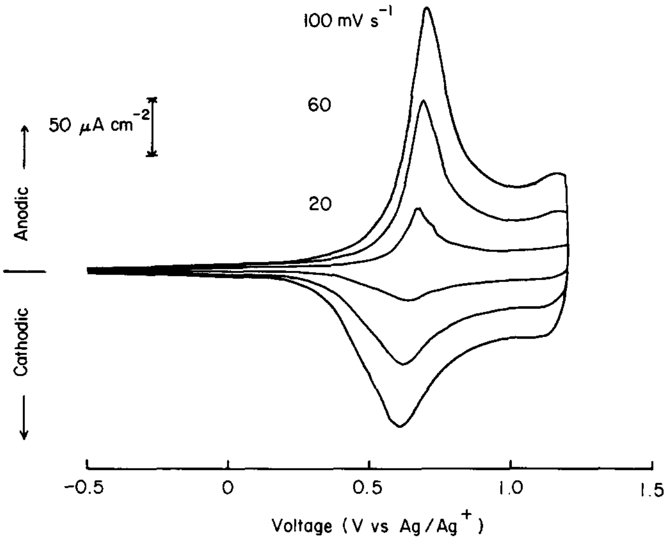

Figure 2 Cyclic voltammograms of a PBZT film

higher levels of doping, two peaks disappeared and a broad one remained, showing that the bipolaron bands merged with the valence and conduction bands. These spectral changes are consistent with results of the theoretical study by Brédas *et al.*[17]

The spectra of PBUT are presented in *Figure 3*. The peak of the transition between the valence and conduction bands shifted to higher energy and its height decreased as the doping level increased. Two additional peaks appeared in the gap region and their height increasd as doping proceeded. The position of the middle peak corresponding to the transition between the valence and higher bipolaron bands was independent of the doping level. The same trends were observed in PMT and PET[7]. In these poly(3-alkylthiophenes), the bipolaron bands are derived from the edges of the valence and conduction bands, and the energy of the higher bipolaron band decreases to the same extent as the edge of the valence band is deleted.

Visible–near i.r. spectra of PBZT are shown in *Figure 4*. The bipolaron bands were clearly evolved, but the positions of peaks corresponding to $\pi-\pi^*$ transition and transition between the valence and higher bipolaron bands were independent of the applied voltage until the peak of the latter transition began to decline at 0.7 V, then abruptly shifted to higher energy. The band gap did not increase as doping proceeded. Brédas *et al.* predicted from their theoretical study that two bipolaron bands would be derived from the edges of the valence and conduction bands and that the band gap would increase as a result. The change in spectra of PBZT is inconsistent with this prediction. One explanation for this is to assume that the bipolaron bands are not derived from the band edges but from the whole bands evenly. If this were the case, the band gap might not become larger. Another is to assume that the density of energy states is high, especially at the band edges. In this case, the band gap would not be completely independent of doping levels, but should gradually increase with increasing levels of doping.

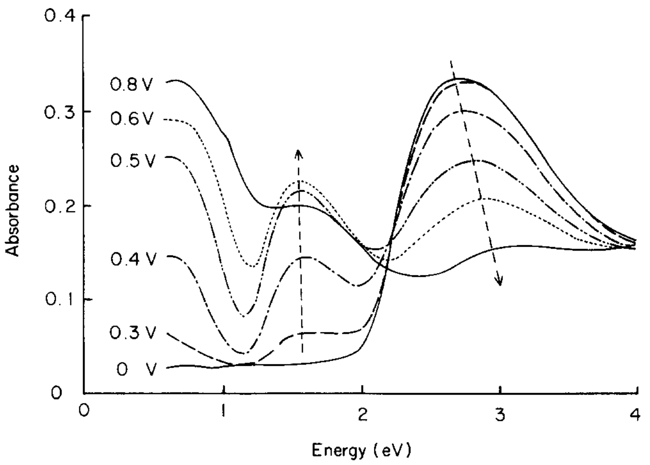

Figure 3 Spectra of a PBUT film at different doping levels. Electrolyte: Et_4NPF_6. (Applied voltage is shown on the left)

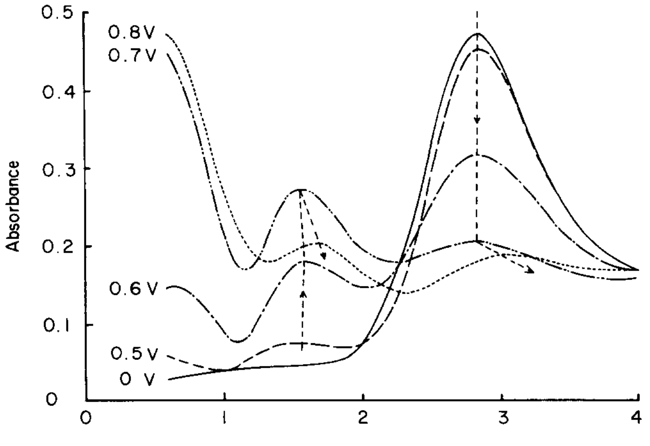

Figure 4 Spectra of a PBZT film at different doping levels. Electrolyte: Et_4NPF_6. (Applied voltage is shown on the left)

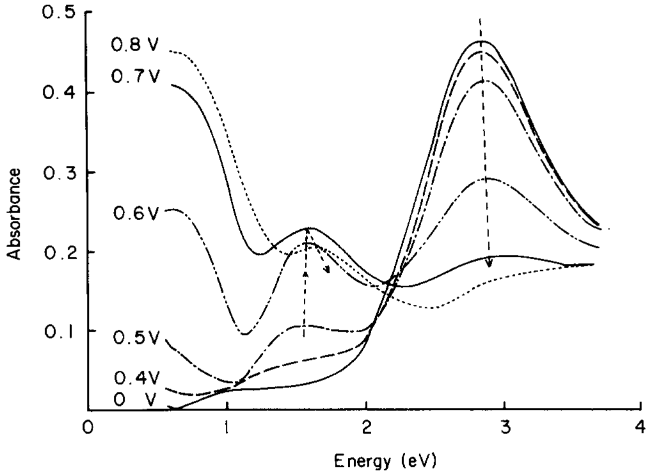

Figure 5 Spectra of a PBZT film at different doping levels. Electrolyte: Et_4NClO_4. (Applied voltage is shown on the left)

Table 2 Properties of poly(3-alkylthiophenes)

Polymer	Conductivity[a] (S cm^{-1})	Anodic peak[b] (V)	Band gap (eV)
PT	190	0.69	2.5
PMT	500	0.28	2.45
PET	240	0.47	2.7
PBUT	110	0.52	2.7
PBZT	13	0.70	2.8

[a] At room temperature
[b] At scan rate of 100 mV s^{-1}

In order to clarify this point, the spectra of a PBZT film were measured using another electrolyte. The PBZT film was prepared and undoped in the same procedure as the film used in *Figure 4*. Then the electrolyte solution was thoroughly replaced with an Et_4NClO_4 solution in acetonitrile. The results are shown in *Figure 5*. The spectra changed in a similar way as seen in *Figure 4*, but the peak position of $\pi-\pi^*$ transition was slightly shifted to higher energy (0.1 eV from 0 to 0.7 V), indicating the density of the states to be really high at the band edges.

Since the $\pi-\pi^*$ transition peak of PBZT was sharper than that of PBUT, the bandwidth of PBZT would be smaller. On the presumption that the numbers of energy states were equal, the density of states would be higher in PBZT than in PBUT. This would corroborate the above explanation.

Comparison with other thiophenes

The properties of five polymers prepared under the same polymerization conditions are summarized in *Table 2*. The electron-donating effects of substituents led to smaller band gap, higher conductivity and lower oxidation potential, but was offset by a steric effect.

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