Optical and X-ray photoelectron spectro-scopic studies of electrically conducting benzimidazobenzophenanthroline type ladder polymers

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X-ray photoelectron spectroscopic studies of two as-grown benzimidazobenzophenanthroline-type polymers (abbreviated BBL and BBB) are reported. The results demonstrate that intermolecular charge-transfer interactions between conjugated polymers and polyphosphoric acid solvent are involved with the trend of electrical conductivity. In addition, optical absorption spectroscopy has been used to characterize the as-grown polymers. The chemical and electronic structures of BBL and BBB polymers are discussed in light of the present results.

INTRODUCTION

There has been a great deal of interest in organic conjugated polymers over the past decade. The electrical conductivity of conjugated polymers can be raised from insulating to semiconducting to metallic regime upon treatment with either electron-accepting or electron-donating species. In addition to high conductivity, the processability, environmental stability, mechanical flexibility, etc., of a conducting polymer have to be considered for practical utility. But many of the conducting polymers lack such a combination of desirable properties. This major objective could be accomplished by materials development via establishing a relationship between molecular structure and electrical conductivity. With this quest in mind, a number of conducting polymers, e.g. polyacetylene, polypyrrole, polythiophene, polyaniline, poly(p-phenylenes), poly(metallo-phthalocyanines), etc., have been investigated. Superiority and usefulness of heteroaromatic ladder polymers have also been realized in this connection.

Benzimidazobenzophenanthroline polymers have been known in the literature for more than two decades[1,2]. Poly((7-oxo-7,10H-benz[de]-imidazo[4',5':5,6]benz-imidazo[2,1-a]isoquinoline-3,4:10,11-tetrayl)-10-carbonyl), abbreviated BBL, and poly(6,9-dihydro-6,9-dioxobisbenzimidazo[2,1-b:1',2'-j]benzo[1mn][3,8]-phenanthroline-2,13-diyl), abbreviated BBB, are illustrated by the chemical structures shown in *Figure 1*. Both BBL and BBB are highly conjugated macromolecules having nearly two-dimensional, oriented and layered structures[3–5]. They exhibit high tensile strength and excellent thermal stability up to 500°C in an oxidative atmosphere[6]. BBL has a rigid ladder structure because

of the restricted rotational freedom of the polymer backbone whereas, contrary to this, the BBB backbone inherits ease of rotational freedom about the carbon–carbon single bond[2]. This structural feature to some extent contributes to distinguishing between the physical properties of these two polymers. Like polyacetylene, BBL and BBB polymers are a class of conjugated polymers that can be doped to the conducting regime with either an electron acceptor or an electron donor. These conjugated polymers are insulating in the undoped state but their electrical conductivity increases by 12 orders of magnitude on chemical doping[7,8]. Also, studies of electrochemical doping reactions of BBL show that it
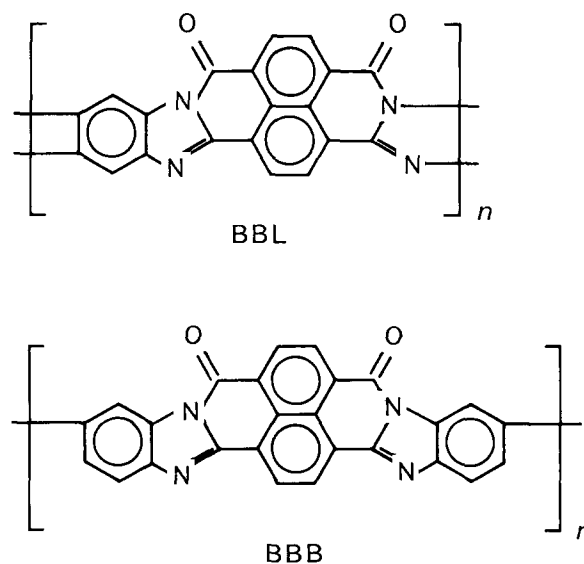

BBL

BBB

Figure 1 Structures of heteroaromatic BBL and BBB polymers

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can be electrochemically switched between conducting (oxidized) and insulating (neutral) states[9,10]. BBL polymer appeared to be more interesting because of its higher conductivity and thermal stability than that of BBB polymer. Absorption and photoluminescence spectroscopy studies indicate a band gap in the range of 1.8–2.0 eV for BBL polymer. Electron spin resonance (e.s.r.) studies suggest bond alternation defects referred to as polarons[11]. These polarons in BBL and BBB are localized over ~22 carbon sites as evidenced by the electron nuclear double resonance (ENDOR) technique[12]. The conductivity of BBL polymer is very anisotropic (~2 orders of magnitude) and originates from the localization lengths of the localized states[11]. This observation also suggests that BBL has a planar polymer backbone close to a two-dimensional structure.

It has been observed that the 'as-grown' BBL and BBB polymers exhibit semiconducting properties. In particular, high electrical conductivity ($\sim 10^{-4}$ S cm^{-1}) of as-grown BBL polymer raised questions of whether the conductivity is of intrinsic or extrinsic type. Keeping this in view, BBL and BBB as-grown polymers were investigated by employing X-ray photoelectron spectroscopy (X.p.s.). X.p.s. techniques have been found useful for studying electron acceptor–donor interactions in conducting polymers. The chemical and electronic structures of conducting polyacetylene[13], polyphenylacetylene[14], polypyrrole[15], polythiophene[16], polyaniline[17] and poly-(p-phenylene vinylene)[18] have been studied by this technique. This paper reports the nature of polymer–solvent interactions involved with the trend of electrical conductivity of as-grown BBL and BBB polymers. The experimental results are discussed in accordance with optical absorption spectroscopy of BBL and BBB polymers.

EXPERIMENTAL

Benzimidazobenzophenanthroline polymers (BBL and BBB) were synthesized by the condensation polymerization previously reported in the literature[2,4]. Polycondensations of 1,4,5,8-naphthalenetetracarboxylic acid with 1,2,4,5-tetraaminobenzene tetrahydrochloride and

3,3'-diaminobenzidine produce BBL and BBB polymers respectively. In both cases, the condensation reaction was carried out in nitrogen-degassed polyphosphoric acid. Free-standing BBL and BBB thin films were grown from methanesulphonic acid solution. The solvent was allowed to evaporate in a casting chamber in a dry air atmosphere. These films have a shiny metallic golden lustre.

Optical absorption spectra of as-grown BBL and BBB polymers were obtained both in solution form by dissolving polymers in methanesulphonic acid and in solid-state form by casting optical-quality thin films on a glass slide. Ultraviolet-visible (u.v.-vis.) spectra were recorded from a Shimadzu spectrophotometer (model UV-260, Shimadzu Corporation, Japan). The X.p.s. spectra of thin films were obtained by an X-ray photoelectron spectrometer (model 5100 ESCA System, Physical Electronics) using a MgKα X-ray source (1245.9 eV photons). Electrical conductivity measurements on free-standing films were performed either by the conventional four-probe or two-probe techniques.

RESULTS AND DISCUSSION

Electrical conductivities of free-standing thin films of the as-grown samples were found to be 3.79×10^{-4} S cm^{-1} for BBL and 3.50×10^{-8} S cm^{-1} for BBB polymer. These polymers were extracted in a Soxhlet apparatus, first with water for a week and then with acetone for another 10 days. After extraction, the neutral BBL and BBB polymers exhibited conductivities of $\sim 10^{-12}$ and $\sim 10^{-14}$ S cm^{-1} respectively. Such a dramatic change in conductivity warrants the possibility of as-grown polymers being contaminated by the solvent and presumably formation of charge-transfer complexes between polymers and solvent.

X.p.s. survey spectra of the as-grown BBL and BBB polymers measured for binding energies from 0 to 1100 eV are shown in *Figures 2* and *3* respectively. Both heteroaromatic BBL and BBB polymers are structurally similar except that BBL has a ladder backbone. The X.p.s. survey spectra show C 1s, O 1s, P 2s, P 2p, Si 2p and F 1s signals. The low-intensity signals associated with Si and F originate due to the impurities from either
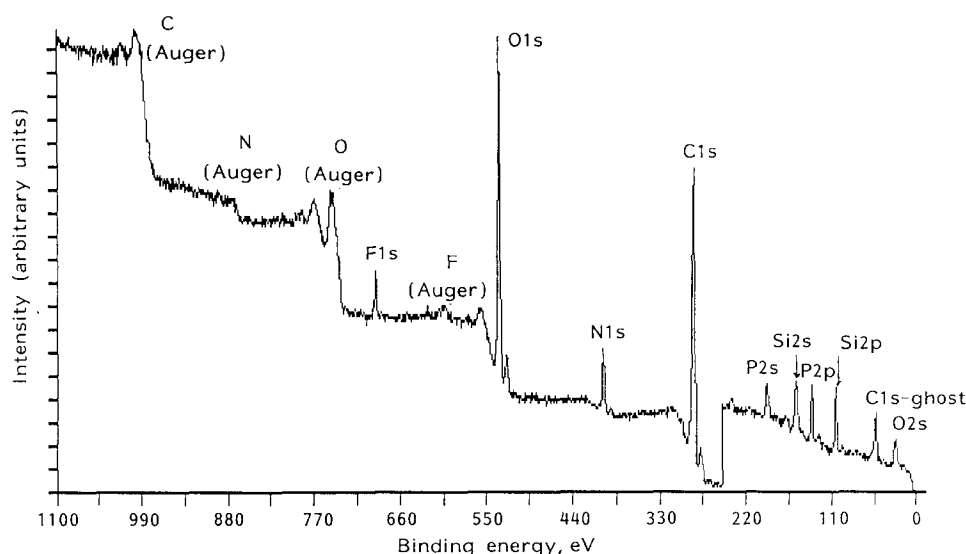

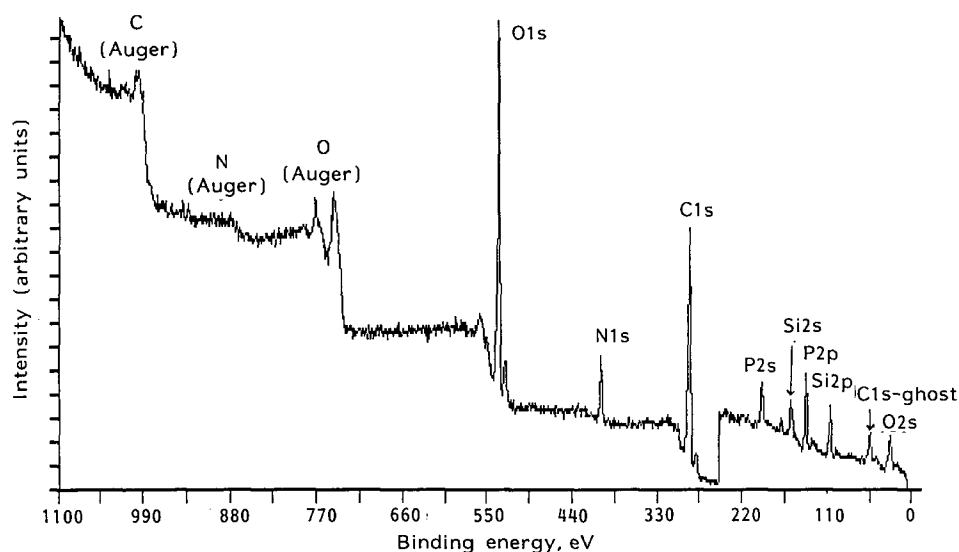**Figure 2** X.p.s. survey spectrum of the as-grown BBL polymer

Figure 3 X.p.s. survey spectrum of the as-grown BBB polymer

Table 1 X.p.s. binding energies and full width at half-maximum (f.w.h.m.) in eV for as-grown BBL and BBB polymers

	BBL			BBB		
	Area (%)	Position (eV)	F.w.h.m. (eV)	Area (%)	Position (eV)	F.w.h.m. (eV)
C 1s	69.64	286.44	1.79	64.30	287.81	1.71
	19.60	287.96	1.65	17.88	289.27	1.45
	10.76	289.71	1.86	17.82	290.98	2.00
N 1s	72.42	402.18	1.93	78.95	403.17	1.76
	27.58	400.25	1.40	21.05	401.90	1.79
O 1s	68.05	534.54	2.19	57.10	535.90	2.00
	27.45	533.02	1.90	38.69	534.52	1.99
	4.50	536.50	2.09	4.21	537.56	1.74
P 2p	65.11	135.38	1.82	99.00	137.14	2.39
	34.89	136.65	2.21	1.00	140.20	

the glass substrate on which the free-standing films were grown or the impurities scavenged from polyphosphoric acid solvent. The chemical analysis of the BBL film surface yielded 61.96% C, 7.60% N, 23.03% O, 3.11% Si, 2.05% P and 2.25% F. For BBB film, the atomic composition is 59.37% C, 7.96% N, 28.22% O, 2.24% P and 2.22% Si. The empirical formulae derived from the X.p.s. analyses are $C_5H_xN_{0.54}O_{1.44}P_{0.066}$ for BBL and $C_5H_xN_{0.56}O_{1.76}P_{0.07}$ for BBB polymer. In BBB film, the oxygen content is slightly higher than that of BBL film. The X.p.s. results show that polyphosphoric acid is incorporated in both polymers, although chemical components are quantitatively constant but deviate from the ideal P/O stoichiometric ratio of 1:4 with a significant oxygen abundance. The atomic ratio of phosphorus to nitrogen (P/N) is about 1:8 for both polymers but the N/O and C/N atomic ratios indicate a nitrogen deficiency. Therefore it is difficult to determine exactly the numbers of polyphosphoric acid anions per BBL and BBB repeat unit. It is worth mentioning that the C/N and P/N ratios are almost constant in both polymers but estimation of an accurate chemical composition (in agreement with theoretical calculations) for either polymer seems infeasible since X.p.s. elemental analyses lead

to ambiguous conclusions. Possibilities of incomplete cyclization, branching, impurities, defects and/or imperfect structure cannot be ruled out and may lead to unexpected quantitative analyses. In general, deviation from the ideal stoichiometric ratios similar to the present case has been reported for oxidized polypyrrole[15] and polythiophenes[16] through X.p.s. studies. The experimentally obtained X.p.s. binding energies and full width at half-maximum (f.w.h.m.) of chemical components of C 1s, N 1s, O 1s and P 2p for BBL and BBB samples are summarized in *Table 1*. The characteristic binding energy spectra of both polymers are approximately similar, and therefore high-resolution C 1s, N 1s, O 1s and P 2p core-level spectra of BBL polymer are represented throughout the text.

The C 1s core-level spectrum of BBL is shown in *Figure 4*. The standard lineshape analysis indicates Gaussian/ Lorentzian components decomposed into three lines, confirming the presence of three inequivalent carbon atoms. Similar C 1s spectral features were observed for BBB polymer. The C 1s spectrum consists of a main broad peak at 286.44 eV (69.64% area) and two smaller peaks at 287.96 eV (19.60% area) and at 289.71 eV (10.76% area). The main component peak at 286.44 eV
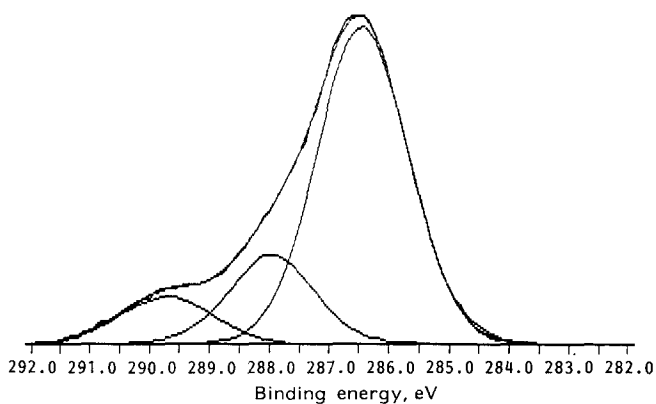
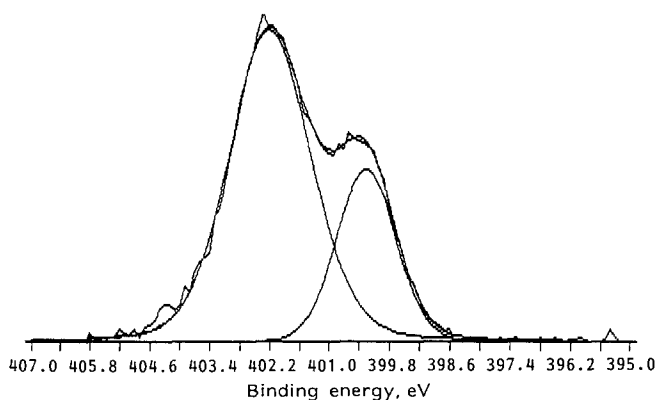**Figure 4** High-resolution C 1s X.p.s. core-level spectrum of BBL polymer
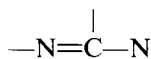

Figure 5 High-resolution N 1s X.p.s. core-level spectrum of BBL polymer. The top curve represents the best fit obtained from the experimental data. The lower curve indicates the contribution from two inequivalent nitrogen atoms in BBL polymer

(BBL) and at 287.81 eV (BBB) stems from emission from the aromatic ring carbon atoms. The small peak at 287.96 eV (BBL) and at 289.27 eV (BBB) is associated with emission from the carbon attached to an oxygen

$$-\overset{|}{C}=O$$

Another small peak of higher binding energy centred at 289.71 eV (BBL) and at 290.98 eV (BBB) is assigned to

$$-N=\overset{|}{C}-N$$

linkage. No features of any shake-up satellite were observed.

Figure 5 shows that the N 1s region photoelectron spectrum of BBL consists of two components at 402.18 eV (72.42% area) and at 400.25 eV (27.58% area). The deconvolution of N 1s X.p.s. core-level spectrum into two major components suggests the presence of two chemical environments for the nitrogen atom. The peak is asymmetric on the low-binding-energy side. The high-binding-energy main component peak at 402.18 eV (BBL) and at 403.17 eV (BBB) is assigned to the neutral nitrogen atom of

$$-C-\overset{|}{N}-C-$$
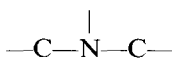
linkage. The low-binding-energy peak has a chemical shift of 1.93 eV in BBL and of 1.27 eV in BBB, which is

associated with the imino nitrogen

$$-C=N-C-$$

linkage. The chemical shift towards low binding energy suggests a transfer of electron density from imino nitrogen atom, indicating the cationic nature of the polymer (BBL$^+$ or BBB$^+$) like other polymers[13–18]. Craik *et al.*[19] reported that, on imino nitrogen, charge-transfer complex formation is facilitated by the π-polarization effect.

The features of the P 2p X.p.s. core-level spectrum are much more important to analyse than the N 1s region spectrum. *Figure 6* represents a typical P 2p X.p.s. spectrum of BBL polymer. The main component peak at 135.38 eV (65.11% area) in BBL and at 137.14 eV (BBB) can be assigned to the neutral phosphorus species of polyphosphoric acid. A chemical shift of −1.27 eV (BBL) and of −3.06 eV (BBB) indicates the presence of a negatively charged phosphorus atom. This observation suggests that polyphosphoric acid anions (PPA$^-$) are present in the as-grown BBL and BBB films. The analysis of N 1s and P 2p core-level spectral data demonstrate that charge-transfer complex formation takes place between polyphosphoric acid solvent and conjugated π-electron polymer backbone.

The features of the O 1s region spectrum are applicable to the C 1s, N 1s and P 2p region spectra. *Figure 7* shows the O 1s core-level spectrum of BBL polymer. Deconvolution gives three component peaks having X.p.s. binding energies of 534.54 eV (68.05% area), 533.02 eV (27.45% area) and 536.50 eV (4.50% area). The X.p.s. results of BBB are listed in *Table 1* and the high-
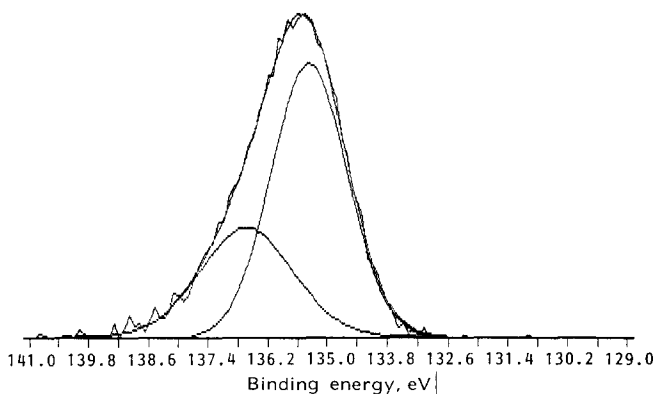

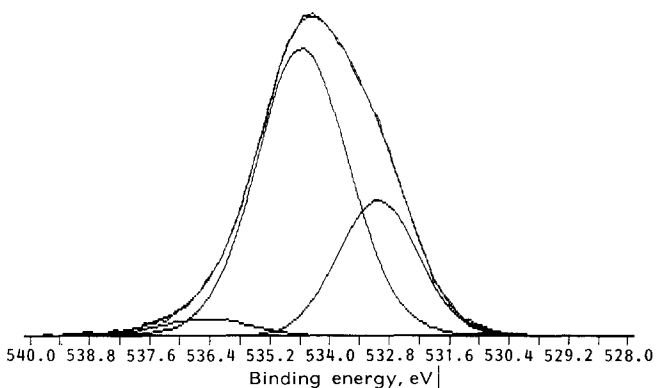**Figure 6** High-resolution P 2p X.p.s. core-level spectrum of BBL polymer

Figure 7 High-resolution O 1s X.p.s. core-level spectrum of BBL polymer

resolution O 1s spectrum has similar features to that of BBL polymer. The most prominent O 1s peak at 534.54 eV (BBL) and at 535.90 eV (BBB) is attributable to the non-bridging oxygen of polyphosphoric acid. The very low-intensity peak at 536.50 eV (BBL) and at 537.56 eV (BBB) indicates the bridging nature of oxygen. Presumably, a charge-transfer process between polyphosphoric acid (electron acceptor) and conjugated polymer backbone (electron donor) takes place through bridging oxygen. Since a positive electronic charge resides on imino nitrogen, they are the primary sites of complexations[7]. Polyphosphoric acid is a weak electron acceptor and the P 2p core-level spectrum shows the presence of phosphorus having localized negative charge. A representative bridging structure showing the process of charge transfer from polymer (BBL[+]) to polyphosphoric acid (PPA[-]) may be illustrated by the following linkage:

$$
\begin{array}{c}
H \\
| \\
O \\
| \ominus \\
H\!-\!O\!-\!P\!-\!O\cdots \\
| \\
O \\
| \oplus \\
N \\
/\!/\ \backslash
\end{array}
$$
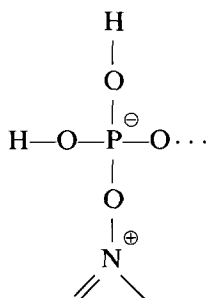
The electrical conductivity as high as $3.79 \times 10^{-4}\ \mathrm{S\,cm^{-1}}$ for as-grown BBL polymer can be explained by charge-transfer complex formation.

Figure 8 shows the optical absorption spectra of the as-grown BBL and BBB polymers recorded in methanesulphonic acid solution. Both polymers exhibit strong
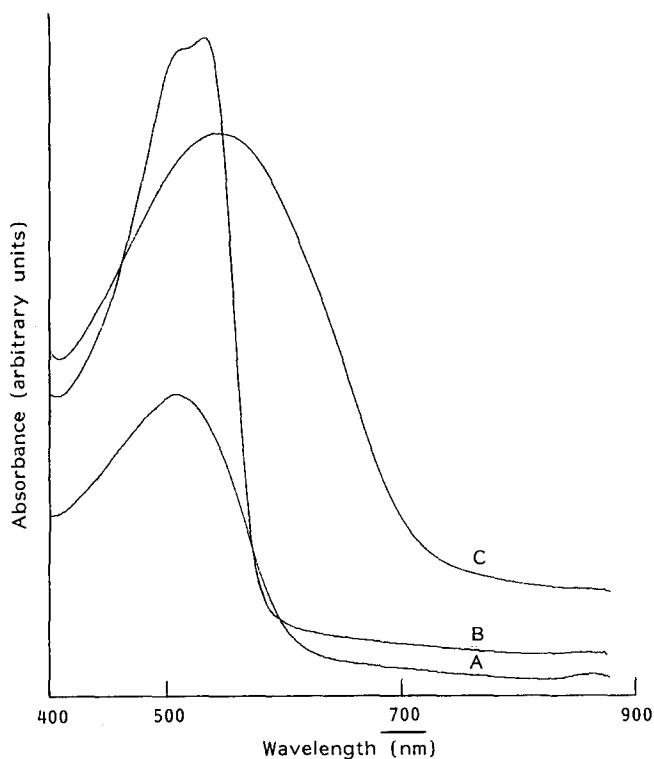

Figure 8 Electronic absorption spectra of BBB polymer in methanesulphonic acid solution (A), BBL polymer in methanesulphonic acid solution (B) and BBL polymer solution-cast film (C)

absorption from 400 to 600 nm and somewhat weaker absorption in the range of 600–900 nm. A broad absorption peak appears at 534 nm in BBL and at 509 nm in BBB polymer, showing a sharp rise in the region of 600–620 nm. The characteristic absorption maximum indicates long conjugated polymer chains in these materials, generally observed in conducting polymers[20]. The broad absorption peak is associated with the π–π^* interband transition. The band gap occurs at about 2 eV. These results of optical studies are in good agreement with that reported earlier[8,10,11,21]. The absorption peak of BBL at 534 nm recorded in methanesulphonic acid solution shifts to 550 nm and significantly broadens in solution-cast films. The characteristic difference in optical spectra of BBL noticed between the solution and solid state results from the polymer–polymer interaction. The spectral shift of BBL is similar to that reported in many poly(diacetylenes)[22–24] and poly(3-alkylthiophenes)[25–26]. The transformation of a disordered structure of solution state into a more well defined electronic structure of solid-state film leads to an optical shift, as has been previously reported[27]. The enhanced intermolecular interactions in the solid state contribute to extensive π-electron delocalization.

The doping of neutral BBL and BBB polymer with sulphuric acid gives much higher conductivity, similar to that reported by Kim[8]. Compared with sulphuric acid, polyphosphoric acid is a weak electron acceptor that could oxidize these conjugated polymers to the semiconducting regime. The high electrical conductivity of the as-grown polymers results from the interaction of delocalized π-electrons of the conjugated backbone with the incorporated polarizable solvent, which forms environmentally stable charge-transfer complexes. The electrical conductivity of as-grown BBL and BBB films does not exhibit any significant change over a period of 6 months so they show good environmental stability like polypyrrole[28–30]. The electrical conductivity of the as-grown BBL polymer is about four orders of magnitude larger than that of BBB polymer, which is due to the structural difference in polymer chain linkage. The molecular structures of BBL and BBB polymers are illustrated in *Figure 1*. Although both polymers consist of quite similar repeat units in the conjugated backbone, the BBL units are joined together through two covalent bonds whereas the BBB units are linked through a single bond. The bonding features of repeat units project a coplanar rigid ladder structure for BBL polymer while, on the other hand, such a coplanar structure is deviated for BBB polymer due to the rotational freedom of carbon–carbon single bond[2]. The coplanar structure in BBL polymer facilitates overlapping of π-electron orbitals and hence participates in enhancing π-electron delocalization. The deviation of coplanarity in BBB backbone decreases the degree of π-orbital overlap, which presumably leads to a substantial decrease in electrical conductivity, as has been noticed for BBB polymer. It should be noted that the electrical conductivities of BBL and BBB polymers are also influenced by factors such as extent of conjugation length, the degree of polymer crosslinking, concentration and nature of doping species incorporated in the backbone. Surprisingly, a profound effect of polyphosphoric acid on the electrical conductivity of BBL and BBB polymers has been observed in the present study. The free-standing BBL and BBB films developed from the soluble slurry exhibit electrical

conductivity in the semiconducting regime. The higher conductivity coupled with excellent thermal and environmental stability suggest that these heteroaromatic ladder polymers may be of interest for practical applications.

CONCLUSIONS

In conclusion, the as-grown benzimidazobenzophenanthroline polymers BBL and BBB are semiconducting materials. Electrical conductivity as high as 3.79×10^{-4} S cm^{-1} observed for BBL polymer results from the polymer–solvent interactions. The X.p.s. data show that intermolecular charge-transfer interactions between highly conjugated π-electron polymer backbone and polyphosphoric acid solvent are involved with the trend of electrical conductivity. Electronic absorption spectra evidence a band gap of approximately 2.0 eV for these heteroaromatic polymers.

ACKNOWLEDGEMENTS

REFERENCES

1   Van Deusen, R. L. *J. Polym. Sci.* (*B*) 1966, **4**, 211
2   Van Deusen, R. L., Goins, O. K. and Sicree, A. J. *J. Polym. Sci.* (*A*) 1968, **6**, 1777
3   Berry, G. C. and Fox, T. G. *J. Macromol. Sci., Chem.* 1969, **3**, 1125
4   Arnold, F. E. and Van Deusen, R. L. *Macromolecules* 1969, **2**, 497
5   Berry, G. C. *Discuss. Faraday Soc.* 1970, **49**, 121
6   Arnold, F. E. and Van Deusen, R. L. *J. Appl. Polym. Sci.* 1971, **15**, 2035
7   Kim, O. K. *J. Polym. Sci., Polym. Lett. Edn.* 1982, **20**, 663
8   Kim, O. K. *Mol. Cryst. Liq. Cryst.* 1984, **105**, 161
9   Polyak, L., Rolison, D. R., Kessler, R. J. and Nowak, R. J. 163rd Meeting of the Electrochemical Society, San Francisco, 8–13 May 1983, Extended Abstract, p. 547
10   Wilbourn, K. and Murray, R. W. *Macromolecules* 1988, **21**, 89
11   Coter, F., Belaish, Y., Davidov, D., Dalton, L. R., Ehrenfreund, E., McLean, M. R. and Nalwa, H. S. *Synth. Met.* 1989, **29**, 471
12   Dalton, L. R., Thomson, J. and Nalwa, H. S. *Polymer* 1987, **28**, 543
13   Salaneck, W. R., Thomas, H. R., Bigelow, R. W., Duke, C. B., Plummer, E. W., Heeger, A. J. and MacDiarmid, A. G. *J. Chem. Phys.* 1980, **72**, 3674
14   Kang, E. T., Neoh, K. G., Tan, K. L. and Tan, B. T. G. *J. Polym. Sci., Polym. Phys. Edn.* 1989, **27**, 2061
15   Pfluger, P. and Street, G. B. *J. Chem. Phys.* 1984, **80**, 544
16   Hotta, S. Ph.D. Thesis, University of California, Santa Barbara, 1988
17   Salaneck, W. R., Lundstrom, I., Hjertberg, T., Duke, C. B., Conwell, E., Paton, A., MacDiarmid, A. G., Somasiri, N. L. D., Huang, W. S. and Richter, A. F. *Synth. Met.* 1987, **18**, 291
18   Obrzut, M. J. and Karasz, F. E. *Macromolecules* 1989, **22**, 458
19   Craik, D. J., Brownlee, R. T. and Sadek, M. *J. Org. Chem.* 1982, **47**, 657
20   Patil, A. O., Heeger, A. J. and Wudl, F. *Chem. Rev.* 1988, **88**, 183
21   Berry, G. C. *J. Polym. Sci., Polym. Symp.* 1978, **65**, 143
22   Patel, G. N. *J. Polym. Sci., Polym. Lett. Edn.* 1978, **16**, 607
23   Wenz, G., Muller, M. A., Schmidt, M. and Wegner, G. *Macromolecules* 1984, **17**, 837
24   Rughooputh, S. D. D. V., Phillips, D., Ando, D. J. and Bloor, D. *Polym. Commun.* 1984, **25**, 242
25   Hotta, S., Rughooputh, S. D. D. V., Heeger, A. J. and Wudl, F. *Macromolecules* 1987, **20**, 212
26   Yoshino, K., Nakajima, S., Onada, M. and Sugimoto, R. *Synth. Met.* 1989, **28**, 349
27   Lim, K. C. and Heeger, A. J. *J. Chem. Phys.* 1985, **82**, 522
28   Nalwa, H. S. *Phys. Rev.* (*B*) 1989, **39**, 5964
29   Diaz, A. F. and Hall, B. *IBM J. Res. Dev.* 1983, **27**, 342
30   'Handbook of Conducting Polymers' (Ed T. A. Skotheim), Dekker, New York, 1986, Vols. 1 and 2