

# Effects of Molecular Structure on the Electroactive and Optical Properties of Conjugated Rigid-Rod Poly(benzobisazoles)

John A. Osaheni<sup>†</sup> and Samson A. Jenekhe\*

Department of Chemical Engineering and Center for Photoinduced Charge Transfer,  
University of Rochester, Rochester, New York 14627-0166

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The effects of molecular structure on the electronic structure and electrochemical and linear optical properties of a series of  $\pi$ -conjugated rigid-rod poly(benzobisazoles), including three new polymers, were explored by cyclic voltammetry and measurement of the optical dispersion of the refractive index. The electrochemical reduction of the polymers was reversible, whereas oxidation was not reversible in accord with the electron-deficient nature of the benzobisazole ring. The observed variation of the reduction and oxidation potentials, electron affinity, and ionization potential of the series of polymers was related to the variation in backbone structure. The electron affinity of the polymers was 2.4–3.0 eV, which indicated that the LUMO energy level was tunable by up to 0.6 eV. The ionization potential (5.2–5.7 eV) and associated HOMO level of the polymers was tunable by up to 0.5 eV. The measured wavelength dispersion of the refractive index of the polybenzobisazoles showed that  $n(\lambda = 1064 \text{ nm})$  and  $n(\lambda = 2500 \text{ nm})$  were 1.74–2.03 and 1.55–1.95, respectively. The large refractive index variation with molecular structure was satisfactorily accounted for by the competing effects of polarizability and molar volume. These results provide a basis for understanding the electronic, optoelectronic, and optical properties of the conjugated poly(benzobisazoles) in terms of the underlying molecular and electronic structures.

## Introduction

The promise of  $\pi$ -conjugated polymers as advanced materials<sup>1–6</sup> for applications in electronics, optoelectronics, and nonlinear optics has motivated our continuing investigation of several classes of  $\pi$ -conjugated polymers.<sup>7–22</sup> These studies have included synthesis

and characterization of new conjugated polymers and copolymers,<sup>7–10</sup> thin-film processing,<sup>11,12</sup> investigation of photophysical properties (e.g., photoconductivity,<sup>13–15</sup> third-order optical nonlinearity,<sup>16–20</sup> and luminescence<sup>7b,21,22</sup>) and exploration of device applications. For example, xerographic photoreceptors made from  $\pi$ -conjugated polybenzobisazoles have good photosensitivity and high quantum efficiency for charge photogeneration.<sup>15</sup> In the areas of photonic and nonlinear optical applications, waveguiding with  $\pi$ -conjugated polymers requires materials which can be processed into high optical quality films with low linear optical losses and relatively high refractive index which ensures good field confinement.<sup>6</sup> Initial efforts in the fabrication of waveguide devices from poly(*p*-phenylenebenzobisthiazole) and poly(2,2'-(1,4-phenylene)-6,6'-bis(4-phenylquinoline)) have also been successful.<sup>23</sup> To better understand as well as to optimize the materials for these applications, the effects of molecular structure and

<sup>†</sup> Current address: General Electric Corporate Research & Development, P.O. Box 8, CEB412, Schenectady, NY 12301.

\* To whom correspondence should be addressed.

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(1) Brédas, J. L.; Chance, R. R., Eds. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Kluwer Academic Publishers: Dordrecht, Holland, 1990.

(2) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539–541.

(3) Marder, S. R.; Sohn, J. E.; Stucky, G. D., Eds. *Materials for Nonlinear Optics: Chemical Perspectives*; American Chemical Society: Washington, DC, 1991.

(4) Jenekhe, S. A., Ed. *Macromolecular Host-Guest Complexes: Optical, Optoelectronic, and Photorefractive Properties and Applications*; Materials Research Society: Pittsburgh, 1992.

(5) (a) Miller, J. S. *Adv. Mater.* **1993**, *5*, 587. (b) Miller, J. S. *Adv. Mater.* **1993**, *5*, 671.

(6) Stegeman, G. I.; Miller, A. In *Photonics in Switching*; Midwinter, J. E., Ed.; Academic Press: London, 1993; Vol. 1.

(7) (a) Osaheni, J. A.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 1282–1290. (b) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 4726–4728.

(8) (a) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1993**, *26*, 895–905. (b) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1993**, *6*, 633–640. (c) Agrawal, A. K.; Jenekhe, S. A. *Macromolecules* **1991**, *24*, 6806–6808.

(9) Chen, W. C.; Jenekhe, S. A. *Macromolecules* **1992**, *25*, 5828–5835.

(10) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1991**, *3*, 878–887.

(11) Agrawal, A. K.; Jenekhe, S. A. *Chem. Mater.* **1992**, *4*, 95–104.

(12) Jenekhe, S. A.; Johnson, P. O.; Agrawal, A. K. *Macromolecules* **1989**, *22*, 3216–3222. (b) Jenekhe, S. A.; Johnson, P. O. *Macromolecules* **1990**, *23*, 4419–4429.

(13) Abkowitz, M. A.; Stolka, M.; Antoniadis, H.; Agrawal, A. K.; Jenekhe, S. A. *Solid State Commun.* **1992**, *83*, 937–941.

(14) Antoniadis, H.; Abkowitz, M. A.; Osaheni, J. A.; Jenekhe, S. A.; Stolka, M. *Synth. Met.* **1993**, *60*, 149–157.

(15) (a) Osaheni, J. A.; Jenekhe, S. A.; Perlstein, J. *Appl. Phys. Lett.* **1994**, *64*, 3112–3114. (b) Osaheni, J. A.; Jenekhe, S. A.; Perlstein, J. *J. Phys. Chem.* **1994**, *98*, 12727–12736.

(16) Osaheni, J. A.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S.; Sun, Y.; MacDiarmid, A. G. *J. Phys. Chem.* **1992**, *96*, 2830–2836.

(17) (a) Agrawal, A. K.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *J. Phys. Chem.* **1992**, *96*, 2837–2843.

(18) Vanherzeele, H.; Meth, J. S.; Jenekhe, S. A.; Roberts, M. F. *J. Opt. Soc. Am. B* **1992**, *9*, 524–532.

(19) Jenekhe, S. A.; Osaheni, J. A.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* **1992**, *4*, 683–687.

(20) (a) Jenekhe, S. A.; Yang, C. J.; Vanherzeele, H.; Meth, J. S. *Chem. Mater.* **1991**, *3*, 985–987. (b) Yang, C. J.; Jenekhe, S. A.; Vanherzeele, H.; Meth, J. S. *Mater. Res. Soc. Proc.* **1992**, *247*, 247–252.

(21) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules* **1994**, *27*, 739–742.

(22) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765–768.

morphology on the electronic structure and solid-state properties need to be elucidated. In particular, knowledge of the effects of molecular structure on the electrochemical properties and associated electronic structure (electron affinity and ionization potential) is needed for understanding not only the well-known ground-state charge transfer complexes (i.e., doped conducting polymers)<sup>1,22</sup> but also the recently discovered *excited-state charge transfer complexes*<sup>21,22</sup> of conjugated polymers. Although the refractive index of conjugated polymers is one of the fundamental properties of interest in their applications in optoelectronic and photonic devices,<sup>3,4,6,23</sup> there have been very few reports of its measurement until the recent detailed investigation of the structure-refractive index relationships in conjugated polyimines.<sup>24</sup> This is in contrast to the large experimental data base of refractive indexes of *nonconjugated* polymers<sup>25</sup> and an accurate group contribution method for their computational prediction.<sup>26</sup>

One class of  $\pi$ -conjugated polymers that has attracted significant efforts in our laboratory<sup>7,18,19</sup> and other laboratories<sup>27–29</sup> is the heterocyclic rigid-rod poly(benzobisazole) family which includes poly(benzobisthiazoles), poly(benzobisoxazoles), and poly(benzobisimidazoles). This class of polymers exhibits high tensile strength, high modulus, and excellent thermal and environmental stability.<sup>27–29</sup> The high strength of these materials arises from the ability to achieve a high degree of molecular order during fiber or film processing. The solutions of these polymers in strong acids or in Lewis acid/nitromethane<sup>12,30</sup> can exist in either optically isotropic or anisotropic liquid-crystalline phases, depending on the concentration, molecular weight, or temperature. Recently,<sup>7a</sup> we showed that a systematic incorporation of *trans*-polyene moieties in place of the *p*-phenylene ring in poly(*p*-phenylenebenzobisthiazole) (PBZT) leads to a wide variation of the electronic absorption spectra, thus providing model polymers for probing structure–property relationships in this class of materials. We have also shown that the polybenzobisazoles are promising nonlinear optical materials as demonstrated by the large third-order nonlinear optical susceptibility of PBZT<sup>18</sup> and poly(*p*-phenylenebenzobisoxazole) (PBO).<sup>19</sup> More recently we have found that the poly(benzobisazoles) have interesting light-emitting properties<sup>7b,21,22,31</sup> and good photoconductivity.<sup>15,22</sup> Although many

Chart 1

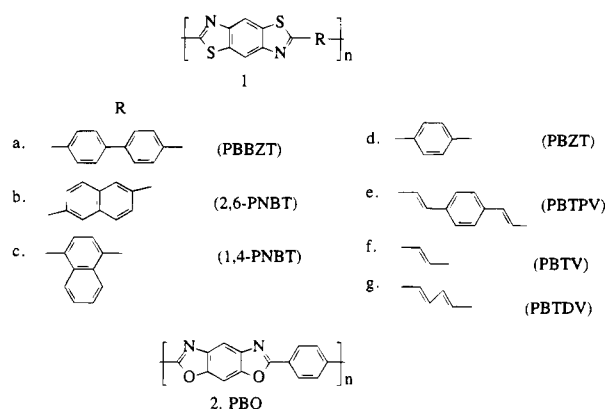
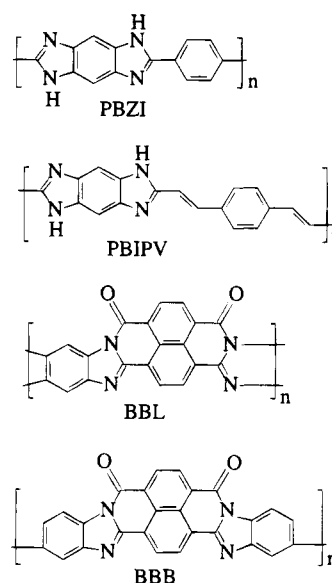


Chart 2



conjugated poly(benzobisazoles) have been synthesized and aspects of their photoactive and electronic properties investigated, a systematic study of the evolution of their electronic structure and electroactive and photoactive properties with molecular structure has not been done experimentally or theoretically. Our present study aims to explore the relationship of polymer molecular structure with electroactive and photoactive properties of the poly(benzobisazoles).

In this paper, we report investigation of the electrochemical properties of a series of eight conjugated poly(benzobisazoles) whose molecular structures are shown in Chart 1. Three of these polymers are new and were synthesized and characterized for this study: poly(4,4'-biphenylenebenzobisthiazole) (PBBZT, **1a**), poly(2,6-naphthalenebenzobisthiazole) (2,6-PNBT, **1b**), and poly(1,4-naphthalenebenzobisthiazole) (1,4-PNBT, **1c**). The synthesis and characterization of the remaining five polymers in Chart 1 have been reported.<sup>7,27</sup> The isotropic refractive index of the new polymers as well as those of PBZT (**1d**), poly(benzobisthiazole-1,4-phenylenebisvinylene) (PBTPV, **1e**), poly(benzobisthiazolevinylene) (PBTV, **1f**), poly(benzobisthiazoledivinylene) (PBTDV, **1g**), PBO (**2**), and four poly(benzobisimidazoles) (Chart 2) was also investigated. The diverse molecular structures investigated in this study provide a systematic approach for understanding the structure–

(23) Mittler-Neher, S.; Otomo, A.; Stegeman, G. I.; Lee, C. Y.-C.; Mehta, R.; Agrawal, A. K.; Jenekhe, S. A. *Appl. Phys. Lett.* **1993**, *62*, 115–117.

(24) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1994**, *6*, 196–203.

(25) Seferis, J. C. In *Polymer Handbook*; Brandrup, J., Immergut, E., Eds.; Wiley: New York, 1989; pp V1451–461.

(26) Van Krevelen, D. W. In *Computational Modeling of Polymers*; Bicerano, J., Ed.; Marcel Dekker: New York, 1992; pp 55–123.

(27) Wolfe, J. F.; Arnold, F. E. *Macromolecules* **1981**, *14*, 909–915. (b) Wolfe, J. F.; Loo, B. H.; Arnold, F. E. *Macromolecules* **1981**, *14*, 915–920.

(28) (a) Wolfe, J. F. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1988; Vol. 11, pp 601–635. (b) Stuez, D. E.; Serad, G. A. In *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1988; Vol. 11, pp 572–601.

(29) (a) Dang, T. D.; Tan, L. S.; Wei, K. H.; Chuah, H. H.; Arnold, F. E. *Polym. Mater. Sci. Eng.* **1989**, *60*, 424–425. (b) Tan, L. S.; Reinhardt, B. A.; Soloski, E. J.; Simko, S. R.; Dillard, A. G. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1992**, *33*, 1062–1063.

(30) Roberts, M. F.; Jenekhe, S. A. *Polym. Commun.* **1990**, *31*, 215–217.

(31) Osaheni, J. A.; Jenekhe, S. A. *J. Am. Chem. Soc.*, submitted.

property relationships in the electroactive and photoactive properties of the poly(benzobisazoles).

## Experimental Section

**Materials and Purification.** 2,5-Diamino-1,4-benzenedithiol dihydrochloride (DABDT) was obtained from Daychem (Dayton, OH) and was purified by recrystallization under nitrogen atmosphere using the literature method.<sup>28a</sup> 4,4'-Biphenyldicarboxylic acid (97%, Aldrich), 1,4-naphthalenedicarboxylic acid (Aldrich), and 2,6-naphthalenedicarboxylic acid (>98%, Lancaster) were also recrystallized prior to use. Polyphosphoric acid (PPA) and 85% phosphoric acid were purchased from Aldrich Chemical and were used as received to prepare 77% polyphosphoric acid used in the dehydrochlorination of DABDT and subsequently as the polymerization medium. Phosphorous pentoxide ( $P_2O_5$ ) was obtained from Baker Inc.

**Poly(4,4'-biphenylenebenzobisthiazole) (PBBZT).** 2,5-Diamino-1,4-benzenedithiol dihydrochloride (DABDT 1.3 g, 5.3 mmol) was dissolved in 13.7 g of 77% PPA (deaerated). Dehydrochlorination of DABDT was carried out at 70 °C under vacuum. After complete dehydrochlorination, the reaction vessel was cooled to 50 °C, and 1.28 g (5.3 mmol) of 4,4'-biphenyldicarboxylic acid was added under nitrogen purge together with 6.7 g of fresh  $P_2O_5$ . The reaction mixture was stirred slowly and the temperature raised to 100 °C (4 h) and then to 140 °C (8 h) and finally held at 180 °C for 24 h. The polymerization dope was cooled down to room temperature and precipitated in water. The polymer was shredded into small pieces with a blender to facilitate purification which consisted of extraction for 2 days with a large volume of water followed by drying in a vacuum oven at 80 °C for 12 h.  $[\eta] = 5.5$  dL/g (30 °C in methanesulfonic acid);  $^1H$  NMR ( $CD_3NO_2/AlCl_3$ , ppm)  $\delta = 8.3$  (m, 4H), 8.5 (m, 4H), 9.2 (s, 2H). FTIR (free-standing film,  $cm^{-1}$ ) 3068, 3022, 1605, 1554, 1515, 1481, 1426, 1402, 1313, 1249, 1208, 1182, 1130, 1115, 1057, 1003, 960, 860, 820, 700, 603.

**Poly(2,6-naphthalenebenzobisthiazole) (2,6-PNBT).** DABDT (1.0 g, 4.08 mmol) was dissolved in 9.8 g of 77% PPA (deaerated) and dehydrochlorination was carried out at 70 °C under vacuum. After complete dehydrochlorination, the reaction vessel was cooled to 50 °C, and 0.88 g (4.08 mmol) of 2,6-naphthalenedicarboxylic acid was added under nitrogen purge together with 5 g of fresh  $P_2O_5$ . The reaction mixture was stirred slowly and a temperature profile identical to that used in PBBZT synthesis was employed. The polymerization dope was cooled to room temperature and precipitated in water. Purification was carried out in a similar fashion to that of PBBZT.  $[\eta] = 7.3$  dL/g (30 °C in methanesulfonic acid);  $^1H$  NMR ( $CD_3NO_2/AlCl_3$ , ppm)  $\delta = 8.2$  (m, 2H), 8.5 (m, 4H), 9.3 (s, 2H). FTIR (free-standing film,  $cm^{-1}$ ) 3075–3033, 1625, 1603, 1506, 1429, 1404, 1382, 1337, 1309, 1277, 1250, 1210, 1192, 1170, 1055, 984, 960, 882, 860, 811, 690, 677.

**Poly(1,4-naphthalenebenzobisthiazole) (1,4-PNBT).** DABDT (1.0 g, 4.08 mmol) was dissolved in 9.8 g of 77% PPA (deaerated) and dehydrochlorination was carried out at 70 °C under vacuum. After complete dehydrochlorination, the reaction vessel was cooled to 50 °C, and 0.88 g (4.08 mmol) of 1,4-naphthalenedicarboxylic acid was added under nitrogen purge together with 5 g of fresh  $P_2O_5$ . The polymerization temperature profile and subsequent isolation and purification steps were identical to those of 2,6-PNBT.  $[\eta] = 5.0$  dL/g (30 °C in methanesulfonic acid);  $^1H$  NMR ( $CD_3NO_2/AlCl_3$ , ppm)  $\delta = 8.1$  (m, 2H), 8.6 (m, 4H), 9.4 (s, 2H). FTIR (free-standing film,  $cm^{-1}$ ) 3075–3033, 1610, 1507, 1515, 1426, 1404, 1382, 1315, 1249, 1208, 1182, 1089, 1055, 1003, 926, 854, 835, 761, 695, 684.

**Preparation of Thin Films.** Films for optical absorption spectra, FTIR spectra, and refractive index measurements were prepared by using the complexation-mediated solubilization approach.<sup>12</sup> Dilute solutions of the polymers, <0.5 wt % polymer in  $AlCl_3$  or  $GaCl_3$ /nitromethane solution were used to prepare thin films on fused silica substrates for optical absorption measurements. To obtain thicker films on fused

silica substrates or free-standing films for FTIR, solutions of varying concentrations (1–3 wt %, depending on the molecular weight of the polymer) were prepared with the Lewis acid in slight excess of the stoichiometric requirement to facilitate spin coating in ambient conditions. The polymer solutions were isotropic since the concentrations employed were well below the critical concentration at which the rigid-rod polymers exhibit liquid crystallinity (5–10 wt %).<sup>12,30</sup> The films of the polymer–Lewis acid complex were washed with deionized water and subsequently placed in a beaker of fresh deionized water to be decomplexed overnight. The films were dried at 80 °C in a vacuum oven for 6–8 h. The film thickness was measured with Alpha Step profilometer (Tencor Instruments) which has a resolution of 1 nm. The film thickness was in the range of 20–80 nm for samples used to obtain optical absorption spectra whereas 1–2.5  $\mu m$  thick films were used for the refractive index measurements.

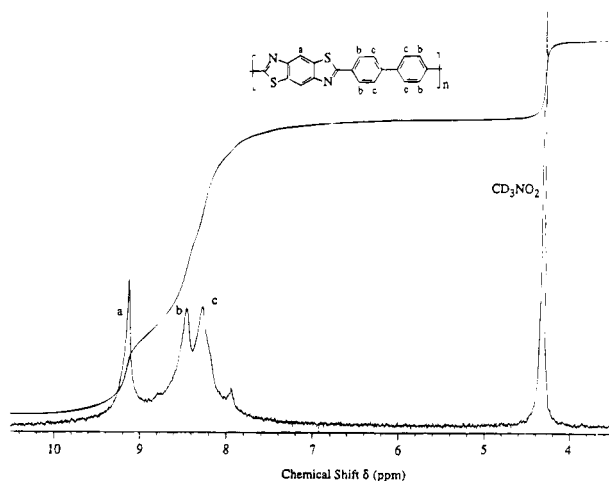
**Characterization.** Intrinsic viscosity  $[\eta]$  of the polymers was measured in methanesulfonic acid at 30 °C using a Cannon Ubbelohde capillary viscometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done using a Du Pont Model 2100 thermal analyst based on an IBM PS/2 Model 60 computer and equipped with Model 951 TGA and Model 910 DSC units. The TGA data were obtained in flowing nitrogen at a heating rate of 10 °C/min, whereas the DSC thermograms were obtained in nitrogen at a heating rate of 20 °C/min. FTIR spectra were taken at room temperature using a Nicolet Model 20SXC Fourier transform infrared (FTIR) spectrometer under nitrogen purge. The  $^1H$  NMR spectra were taken at 300 MHz using a General Electric Model QE 300 instrument. Polymer solutions for NMR spectra were prepared in a drybox, using deuterated nitromethane ( $CD_3NO_2$ ) containing aluminum(III) chloride.

Optical absorption spectra of thin films and solutions of the polymers were obtained with a Perkin-Elmer Model Lambda 9 UV–vis–near IR spectrophotometer in the wavelength range 190–3200 nm. The optical transmission spectra of thick films (1.0–2.5  $\mu m$ ) were obtained and the resulting interference fringes of the films, i.e., the consecutive wavelengths at which the maxima and minima transmission occurred were used to deduce the refractive index. The data were obtained in the range 700–2800 nm, with the probe beam perpendicular to the plane of the films. The slit of the spectrophotometer was set at 1 nm. The refractive index was calculated using the approach described by Swanepoel.<sup>32</sup> The detailed analysis and data regression for the determination of refractive index of conjugated polymers have been described previously.<sup>24</sup>

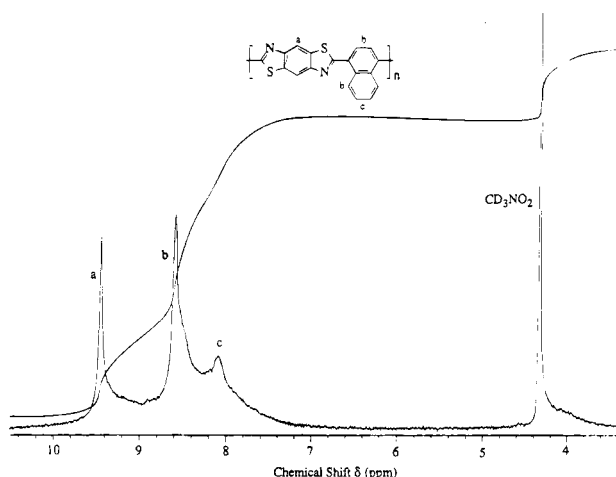
Cyclic voltammograms of thin films of the polymers were done by using EG&G Princeton Applied Research Model 270 potentiostat/galvanostat equipped with Electrochemical Analysis System software based on an IBM PS/2 Model 60 computer. The experimental setup was in the single-cell and three-electrode configuration. Platinum wires were used as both the counter and working electrodes, and  $Ag/Ag^+$  (silver wire in 0.1 M  $AgNO_3$  in the electrolyte solution) was used as a reference electrode. The  $Ag/Ag^+$  was calibrated with ferrocene as the internal standard. Thin films of the polymers on platinum electrodes were prepared by dipping the electrode into a 0.2–1.0 wt % polymer solution, and the resulting films rigorously washed with water and dried in a vacuum oven at 80 °C. A 0.1 M tetrabutylammonium tetrafluoroborate (TBABF<sub>4</sub>, Aldrich) in ultrapure acetonitrile (99+%, Johnson Matthey Electronics) was used as the electrolyte. The potential values were referenced back to the saturated calomel electrode (SCE) potential by using the ferrocene/ferrocenium couple as the internal standard. The reported cyclic voltammograms were obtained at a voltage scanning rate of 20 mV/s.

## Results and Discussion

**New Polymers: Molecular Structure and Optical Absorption Spectra.** The molecular structures of the new polymers, PBBZT, 2,6-PNBT, and 1,4-PNBT,



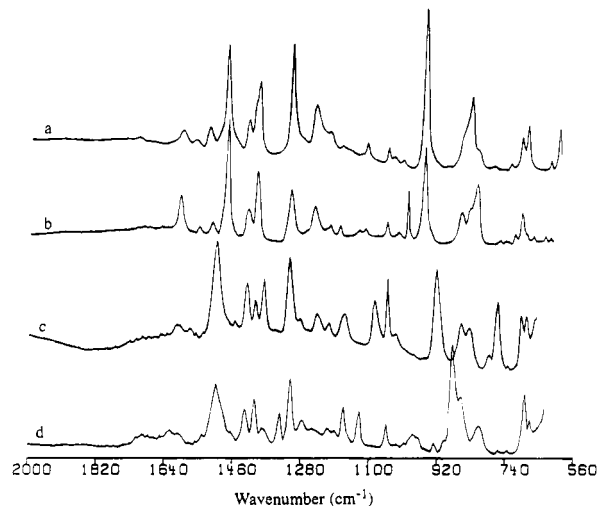
**Figure 1.**  $^1\text{H}$  NMR spectrum of PBBZT in  $\text{CD}_3\text{NO}_2/\text{AlCl}_3$  and its assignment.



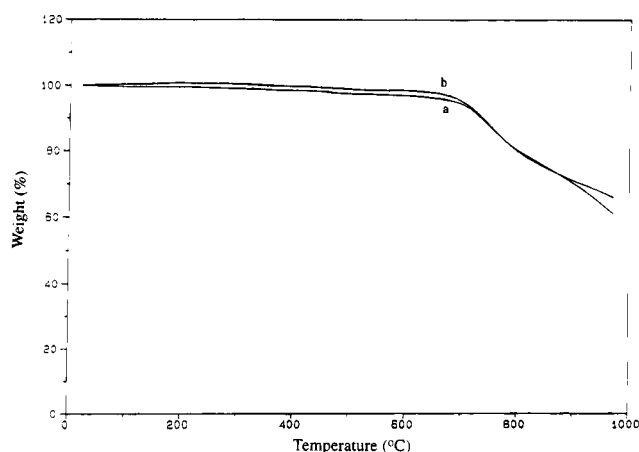
**Figure 2.**  $^1\text{H}$  NMR spectrum of 1,4-PNBT in  $\text{CD}_3\text{NO}_2/\text{AlCl}_3$  and its assignment.

were established by both  $^1\text{H}$  NMR and FTIR spectra. Figure 1 shows the  $^1\text{H}$  NMR spectrum of PBBZT obtained in nitromethane containing aluminum trichloride. The number of protons corresponding to each resonance is in agreement with the proposed structure. Figure 2 shows the  $^1\text{H}$  NMR spectrum of 1,4-PNBT and its assignment. As expected, there are three main resonances, and the number of protons corresponding to each resonance is in good agreement with the proposed structure. The  $^1\text{H}$  NMR spectrum of 2,6-PNBT was also found to be in good agreement with the proposed structure.

Figure 3 shows a comparison of the FTIR spectra of PBBZT, 2,6-PNBT, and 1,4-PNBT along with that of PBZT. The characteristic bands of the poly(benzobisthiazoles) can be observed in the three new polymers. The FTIR spectrum of PBBZT shows essentially identical bands as that of PBZT except for the new band at  $1003\text{ cm}^{-1}$  in PBBZT, and the slight differences in the relative intensities of the other bands. In PBZT, the heteroring stretch associated with the thiazole ring shows intense bands at  $1485$  and  $1314\text{ cm}^{-1}$ , while the heteroring breathing and out-of-plane ring deformation are at  $960$  and  $689\text{ cm}^{-1}$ , respectively.<sup>7,33</sup> The frequency of the heteroring stretches at  $1485\text{ cm}^{-1}$  in PBZT is



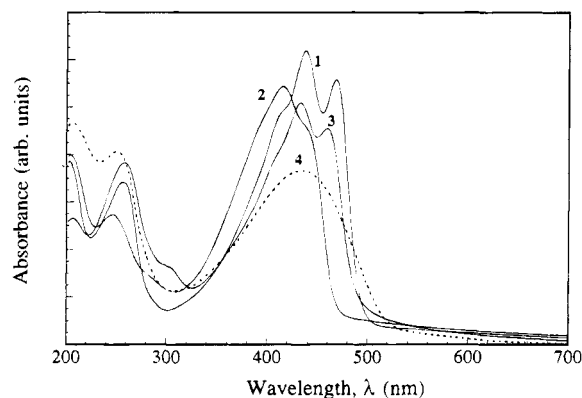
**Figure 3.** FTIR absorption spectra of (a) PBZT, (b) PBBZT, (c) 1,4-PNBT, and (d) 2,6-PNBT.



**Figure 4.** TGA thermograms of (a) PBBZT and (b) 2,6-PNBT heated in nitrogen atmosphere.

shifted in 2,6-PNBT and 1,4-PNBT to  $\sim 1507\text{ cm}^{-1}$ . The heteroring breathing bands appear at  $882$  and  $926\text{ cm}^{-1}$ , respectively, in 2,6-PNBT and 1,4-PNBT. This represents a decrease in frequency (or increase in the force constant of this motion) by  $78$  and  $34\text{ cm}^{-1}$ , respectively, relative to those of PBZT. The features of the FTIR spectra of 2,6- and 1,4-PNBT, while similar, show a number of differences especially in the out-of-plane C–H stretching region ( $860$ – $750\text{ cm}^{-1}$ ) which reflects the substitution pattern of the naphthalene ring. Overall, the FTIR spectra are consistent with the proposed structures of the new polymers.

The intrinsic viscosities of PBBZT, 2,6-PNBT, and 1,4-PNBT were  $5.5$ ,  $7.3$ , and  $5.0\text{ dL/g}$ , respectively, indicating modest molecular weights of  $\sim 15\,000$ – $17\,700$ , using the known Mark–Houwink relationship for PBZT.<sup>28a</sup> Each of these polymers was readily processed into thin films on substrates or as free-standing films for various analyses. The TGA thermograms of PBBZT and 2,6-PNBT obtained in flowing nitrogen at  $10\text{ }^\circ\text{C/min}$  are shown in Figure 4. The thermal stability of the new polymers is quite high, starting to decompose at  $\sim 700\text{ }^\circ\text{C}$  in nitrogen atmosphere, and similar to PBZT ( $720\text{ }^\circ\text{C}$ ).<sup>7</sup> The DSC thermograms of the new polymers did not show any thermal transition (such as  $T_g$  or  $T_m$ ) below the decomposition temperature similar to what is observed in PBZT. Thus, the new aromatic-linked



**Figure 5.** Optical absorption spectra of thin films of (1) PBZT, (2) PBBZT, (3) 2,6-PNBT, and (4) 1,4-PNBT.

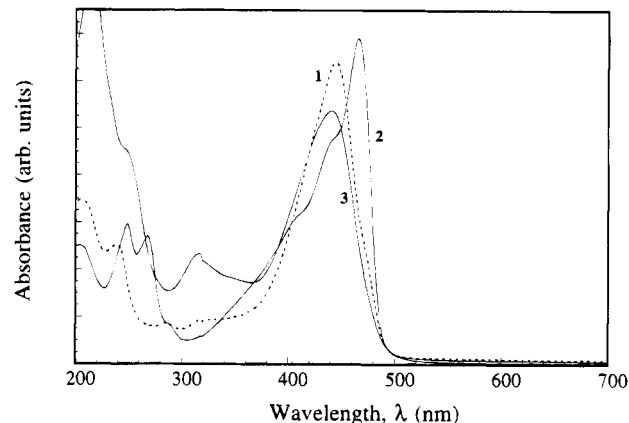
**Table 1. Summary of the Optical Absorption and Electrochemical Reduction of Thin Films of Poly(benzobisazoles)**

polymer	optical absorption		electrochemical reduction				
	$\lambda_{\max}$ (nm)	$\pi-\pi^*$ gap, $E_g^{\text{opt}}$ (eV)	$E_{\text{pc}}$ (V)	$E_{\text{pa}}$ (V)	$E^{\circ}$ (V)	$E_{\text{onset}}^{\text{red}}$ (V)	EA (V)
PBBZT	415 (2.99) <sup>b</sup>	2.61	-2.22	-1.84	-2.03	-1.80	2.6
2,6-PNBT	435 (2.85)	2.48	-2.16	-1.63	-1.89	-1.75	2.7
1,4-PNBT	435 (2.85)	2.36	-1.76	-1.56	-1.66	-1.60	2.8
PBZT	438, 468 (2.65)	2.48	-2.03	-1.69	-1.86	-1.75	2.7
PBTPV	475 (2.61)	2.25	-1.91	-1.62	-1.77	-1.68	2.7
PBTv	470 (2.64)	2.21	-1.80	-1.39	-1.60	-1.46	2.9
PBTDV	500 (2.48)	2.07	-1.75	-1.38	-1.57	-1.45	3.0
PBO	401, 427 (2.90)	2.76	-2.38	-1.97	-2.18	-1.97	2.4

<sup>a</sup>  $E_{\text{pc}}$  = cathodic peak potential;  $E_{\text{pa}}$  = anodic peak potential;  $E_{\text{onset}}^{\text{red}}$  = onset of reduction; EA = electron affinity. <sup>b</sup>  $\lambda_{\max}$  in electronvolts.

poly(benzobisthiazoles) are, as expected, also high-temperature materials.

Figure 5 shows the optical absorption spectra of thin films of PBBZT, 2,6-PNBT, and 1,4-PNBT along with that of PBZT. A summary of the optical properties, including the  $\lambda_{\max}$  and the optical absorption edge ( $E_g^{\text{opt}}$ ), of the new polymers as well as those shown in Chart 1 is given in Table 1. 2,6-PNBT and PBZT show similar absorption features ( $\lambda_{\max}$  and  $E_g^{\text{opt}}$  are identical), whereas the optical absorption spectra of PBBZT and 1,4-PNBT are different from those of PBZT. The absorption spectrum of PBBZT is blue shifted from that of PBZT's absorption edge ( $E_g^{\text{opt}}$ ) by 0.13 eV. On the other hand, the  $\pi-\pi^*$  absorption threshold of 1,4-PNBT (2.36 eV) is red shifted relative to that of PBZT. The absorption spectrum of 1,4-PNBT shows broad features unlike the well-resolved vibronic structures in the spectra of 2,6-PNBT and PBZT. This implies that the 1,4 substitution pattern of the naphthalene ring introduces significant disorder to the polymer. Figure 6 shows the solution optical absorption spectra of the new polymers in methanesulfonic acid. The trend of the optical absorption spectra in solution is quite different from that of the solid state. The absorption threshold is identical in all the polymers whereas the  $\lambda_{\max}$  is at 440, 444, and 465 nm, respectively, for 1,4-PNBT, PBBZT, and 2,6-PNBT. The results of the solution spectra imply that the planarity of the polymer repeat units is similar when they are protonated, whereas in the solid state the geometry is different for the three polymers. In addition, the difference in spectral features, e.g., line shape, between the dilute-solution (Figure 6) and the thin-film (Figure 5) optical spectra of the same polymer



**Figure 6.** Solution optical absorption spectra of (1) PBBZT, (2) 2,6-PNBT, and (3) 1,4-PNBT in methanesulfonic acid (at  $\sim 5 \times 10^{-6}$  M).

can similarly be explained by the effects of protonation in solution and strong intermolecular interactions between chains in the solid state.

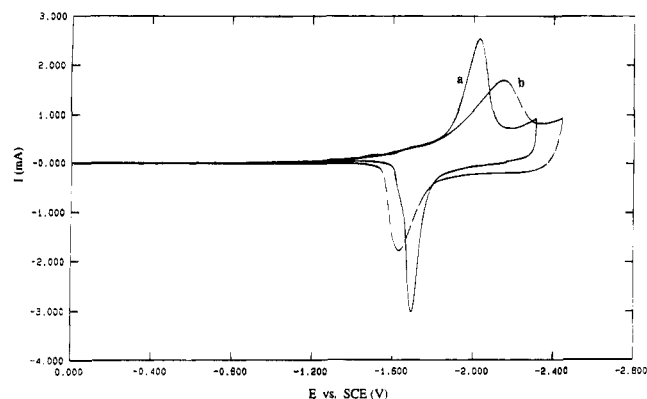
**Electrochemical Properties and Electronic Structure.** The effects of molecular structure on the electroactive properties and electronic structure of the polybenzobisazoles shown in Chart 1 were explored through measurement of the electrochemical reduction and oxidation (redox) properties. To facilitate the discussion of the results, we use the 1,4-phenylene-linked polymer (PBZT) as a reference and compare the redox properties of the other poly(benzobisazoles) to that of PBZT. It has been shown from similar studies of the redox properties of the rigid-rod polyquinolines that side-group substitution of electron-withdrawing or -donating groups had a negligible effect on the electronic structure of the polymers compared with changes in the backbone structure.<sup>34</sup> Here we explore the effects of different moieties introduced into the backbone as well as the heteroatom of the poly(benzobisazoles) (Chart 1). The heterocyclic *benzobisthiazole* and *benzobisoxazole* rings are electron-deficient groups, so that one might expect the polymers in Chart 1 to be more susceptible to reduction (electron accepting) than oxidation. It is interesting to see to what extent the different R moieties and heteroatoms (S or O) regulate or modify the redox properties and electronic structure.

**Electrochemical Reduction.** Figure 7 shows the cyclic voltammograms (CVs) of the reduction of PBZT and that of 2,6-PNBT. It is observed that both polymers exhibit reversibility with identical onset of the reduction ( $E_{\text{onset}}^{\text{red}} = -1.75$  V vs SCE). However, the cathodic peak ( $E_{\text{pc}}$ ) and anodic peak ( $E_{\text{pa}}$ ) potentials are shifted away from each other with the difference in peak potentials ( $\Delta E_p = E_{\text{pa}} - E_{\text{pc}}$ ) being larger in 2,6-PNBT (0.53 V) compared to that of PBZT (0.34 V). These  $\Delta E_p$  values are quite large and typical of many  $\pi$ -conjugated polymers in the solid state.<sup>35,36</sup> The origin of the large peak separation may be due to redox-related structural reorganization within the films which affect diffusion

(34) Agrawal, A. K.; Jenekhe, S. A. *J. Phys. Chem.*, submitted.

(35) (a) Diaz, A. F.; Bargon, J. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker: New York, 1986; Vol. 1, Chapter 3. (b) Tourillon, G. *Ibid.*, Chapter 5. (c) MacDiarmid, A. G.; Kaner, R. B. *Ibid.*, Chapter 20.

(36) Murray, R. W. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Marcel Dekker: New York, Vol. 13, pp 191-368. (b) Pearce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *114*, 89-115.

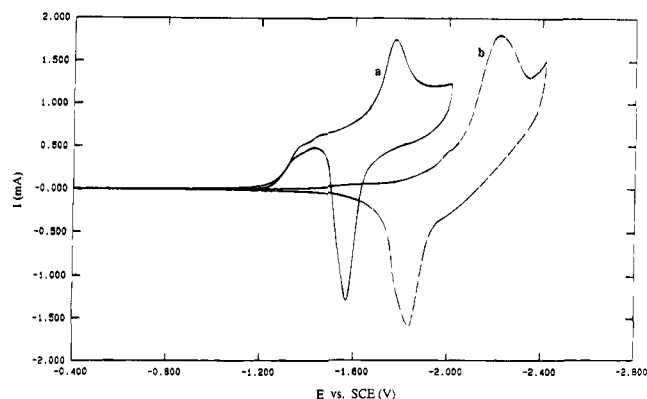


**Figure 7.** Cyclic voltammogram of the reduction of (a) PBZT and (b) 2,6-PNBT in 0.1 M TBABF<sub>4</sub>/acetonitrile at a scan rate of 20 mV/s.

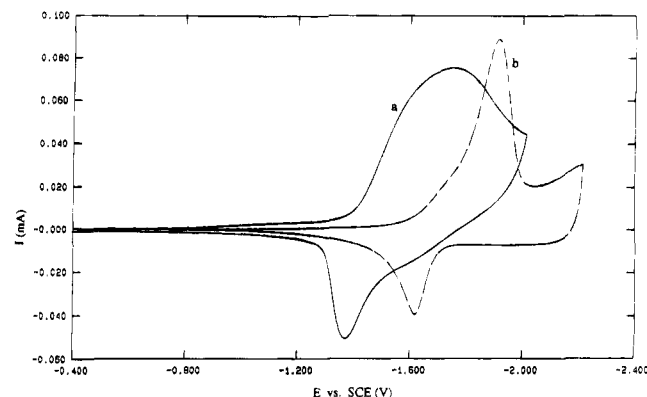
of counterions in and out of the polymers. The morphology of the polymer film is another factor that may affect  $\Delta E_p$ . Separate studies of the peak current ( $i_p$ ) and scan rate ( $v$ ) reveal direct proportionality between  $i_p$  and  $v$  when the scan rates were varied between 10 and 80 mV/s, as expected for surface-anchored species.<sup>35,36</sup> A summary of the peak potentials ( $E_{pa}$ ,  $E_{pc}$ ), formal potential [ $E^{\circ'} = (E_{pa} + E_{pc})/2$ ], and  $E_{onset}$  for electrochemical reduction of PBZT and 2,6-PNBT is given in Table 1. The reduction potentials (i.e.,  $E^{\circ'}$ ) of the polymers are virtually identical (-1.86 V and -1.89 V vs SCE).

Although the cyclic voltammogram (CV) for the reduction of PBZT has been reported previously,<sup>37</sup> the peak potentials and formal potential found in the present study are different from the previous report. In the earlier report,<sup>37</sup> PBZT films were prepared on platinum electrodes from a very strong protonic acid (trifluoromethanesulfonic acid) and soaked overnight in water to eliminate the acid. The previously reported reduction CV on such a film showed two cathodic peak potentials at -1.70 and -1.92 V (vs SCE) and two anodic peak potentials at -1.23 and -1.64 V. The peak with the more negative formal potential ( $E^{\circ'} = -1.78$  V) was speculated to be due to a defect or impurities. However, our results for PBZT show only one reduction wave with a corresponding formal potential of -1.86 V (vs SCE) which is close to that previously assigned to the presence of impurities. It is likely that the trifluoromethanesulfonic acid was not completely removed in the previous study.<sup>37</sup> We have seen that films of PBZT prepared from methanesulfonic acid and rigorously washed and neutralized with 0.1 M NaOH have identical CVs to that shown in Figure 7, i.e., have one reduction wave and identical formal reduction potential as for films prepared from nitromethane-AlCl<sub>3</sub>.

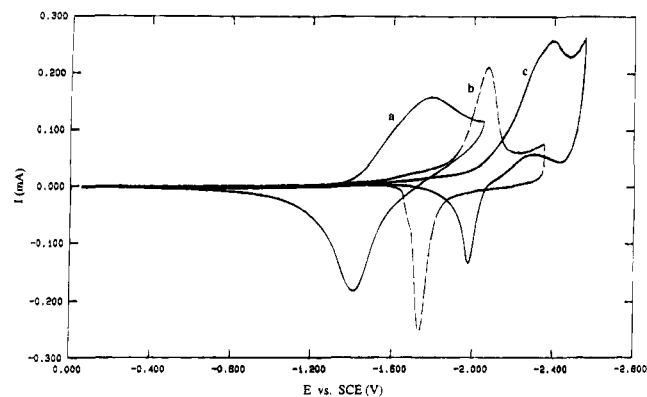
Figures 8–10 present the reduction CVs of the remaining poly(benzobisazoles) of Chart 1. As with PBZT and 2,6-PNBT, all the polymers exhibit only one reduction wave in their CVs and it is quasi-reversible. The corresponding reduction peak potentials, formal reduction potential ( $E^{\circ'}$ ), and onset potential for reduction are summarized in Table 1. From a comparison of the reduction potentials of Figures 7–10 and Table 1, one sees a wide variation with molecular structure. One



**Figure 8.** Cyclic voltammogram of the reduction of (a) 1,4-PNBT and (b) PBBZT in 0.1 M TBABF<sub>4</sub>/acetonitrile at a scan rate of 20 mV/s.



**Figure 9.** Cyclic voltammogram of the reduction of (a) PBTDV and (b) PBTPV in 0.1 M TBABF<sub>4</sub>/acetonitrile at a scan rate of 20 mV/s.



**Figure 10.** Cyclic voltammogram of the reduction of (a) PBTV, (b) PBZT, and (c) PBO in 0.1 M TBABF<sub>4</sub>/acetonitrile at a scan rate of 20 mV/s.

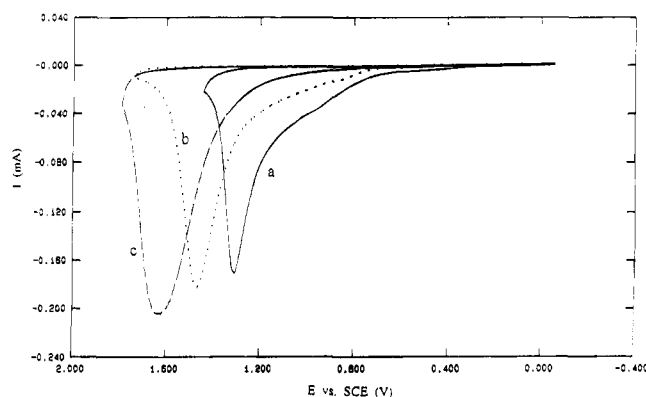
striking feature of the results is that the formal reduction potential  $E^{\circ'}$  and onset reduction potential  $E^{\circ'}_{onset}$  vary by 0.6 and 0.52 V, respectively, among the eight polybenzobisazoles. The most difficult to reduce polymer in the set is PBO, the oxygen-containing polymer, with  $E^{\circ'}$  of -2.18 V (vs SCE). This means that the reduction potential of PBZT is higher than PBOs by 0.32 V, which also implies that the reduced form of PBZT is thermodynamically more stable than that of PBO. On the other hand, the most readily reduced polymers in the set of Chart 1 are PBTDV and PBTV, which have essentially identical  $E^{\circ'}$  values of -1.57 and -1.60 V (vs SCE), respectively. This is about 0.3 V higher than the formal reduction potential of PBZT.

(37) Depra, P. A.; Gaudiello, J. G.; Marks, T. J. *Macromolecules* **1988**, *21*, 2295–2297.

A close examination of the CV results of Figures 7–10 and Table 1 reveals interesting effects of molecular structure on the reduction potentials. The large observed difference in the reduction  $E^{\circ'}$  values of PBZT and PBO may seem surprising considering that oxygen is significantly more electronegative than sulfur (Pauling electronegativities of 3.5 and 2.5, respectively) and hence the *benzobisoxazole* ring should be more electron deficient than the *benzobisthiazole* ring. However, the more positive reduction potential of PBZT compared to PBO can be rationalized in terms of the better  $\pi$ -electron delocalization in PBZT which would allow efficient delocalization of the radical anion  $PBZT^{\bullet-}$  compared to  $PBO^{\bullet-}$ . This explanation also holds for why the 4,4'-biphenylene-linked polymer, PBBZT, has an  $E^{\circ'}$  value of  $-2.03$  V (vs SCE), which is  $0.17$  V lower than PBZT. The poorer electron delocalization in PBBZT compared to PBZT is a result of steric interactions of the ortho hydrogens of the 4,4'-biphenylene moiety. Thus, fusion of the two phenyl rings as in 2,6-naphthalene and 1,4-naphthalene moieties results in  $E^{\circ'}$  values that are higher than in PBBZT. In fact, although the reduction potential of 2,6-PNBT is the same as that of PBZT, the reduction  $E^{\circ'}$  of 1,4-PNBT is more positive than that of PBZT by  $0.2$  V. This last result can again be understood in terms of the better delocalization of the radical anion.

The *trans*-vinylene- and *trans,trans*-divinylene-linked polymers, PBTv and PBTdv, have the highest  $E^{\circ'}$  values for reduction as a result of the good  $\pi$ -electron delocalization achieved in these polymers as evidenced by their electronic absorption spectra parameters ( $\lambda_{\max}$ ,  $E_g^{\text{opt}}$ ; Table 1). The reduction waves of these two polymers, especially the cathodic peaks, are generally broad as seen in Figures 9 and 10. The origin of this broad feature of the CVs of PBTv and PBTdv is either because of a wider  $\pi^*$  band compared to PBZT and other poly(benzobisazoles) or it is morphological in nature. Our previous X-ray diffraction study of PBTdv indicated that this polymer has much more closely packed chains than PBZT.<sup>7a</sup> Such a tight chain packing may affect the diffusion of the bulky counteranion ( $n\text{-C}_4\text{H}_9\text{N}^+$ ) in and out of the polymer during reduction.

The cyclic voltammetry results on electrochemical reduction of the series of poly(benzobisazoles) (Chart 1) show that each of the polymers exhibits a quasi-reversible reduction in accord with the electron-deficient nature of the *benzobisoxazole* and *benzobisthiazole* rings. The reduction potential ( $E^{\circ'}$ ) of the series of polymers varies from  $-1.57$  to  $-2.18$  V (vs SCE). Thus the relative ease of reduction is in the decreasing order: PBTdv, PBTv > 1,4-PNBT > PBTPV > PBZT, 2,6-PNBT > PBBZT > PBO. This order also represents the relative n-type dopability of the polymers into conducting polymers and the relative thermodynamic stability of the n-type doped material. We point out that it has previously been reported that PBZT can be electrochemically doped into an n-type conducting material with room-temperature conductivity as high as  $20$  S/cm.<sup>37</sup> Our results suggest that all the eight poly(benzobisazoles) can be n-type doped to conducting materials and furthermore that four of these polymers (PBTdv, PBTv, 1,4-PNBT, and PBTPV) should be even superior to n-type doped PBZT. However, in terms of developing the poly(benzobisazoles) as efficient electron-transporting materials for electrophotography, the re-



**Figure 11.** Cyclic voltammogram of the oxidation of (a) PBTPV, (b) 1,4-PNBT, and (c) PBZT in  $0.1$  M TBABF<sub>4</sub>/acetonitrile at a scan rate of  $20$  mV/s.

**Table 2. Summary of Electrochemical Oxidation and Energy Gap of the Poly(benzobisazoles)**

polymer	$E_{\text{pa}}$ (V)	$E_{\text{pc}}$ (V)	$E_{\text{onset}}^{\text{ox}}$ (V)	IP (eV)	$E_g^{\text{el}}$ (V)
PBBZT	1.72	<i>b</i>	1.30	5.7	3.10
2,6-PNBT	1.60	<i>b</i>	1.1	5.5	2.85
1,4-PNBT	1.47	<i>b</i>	0.85	5.3	2.45
PBZT	1.62	<i>b</i>	1.1	5.5	2.85
PBTPV	1.31	<i>b</i>	0.80	5.2	2.48
PBTv	1.35	<i>b</i>	0.80	5.2	2.26
PBTdv	0.85	<i>b</i>	0.75	5.2	2.20
PBO	1.70	<i>b</i>	1.30	5.7	3.27

<sup>a</sup>  $E_{\text{pc}}$  = anodic peak potential;  $E_{\text{onset}}^{\text{ox}}$  = onset of oxidation; IP = ionization potential;  $E_g^{\text{el}}$  = electrochemical gap. <sup>b</sup> The oxidation process is not reversible.

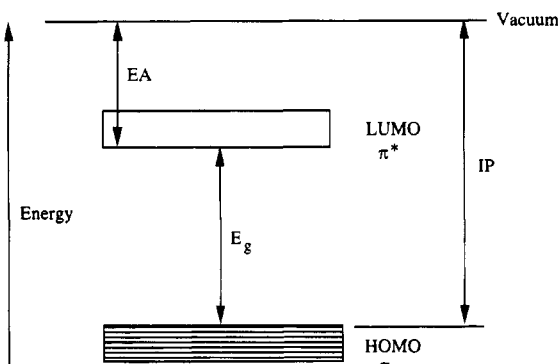
duction potential should be higher than that of molecular oxygen ( $\sim -0.8$  V vs SCE)<sup>38</sup> so that trapping of electrons by oxygen under ambient conditions is minimized. The highest reduction potential observed in these polymers ( $E^{\circ'} = -1.57$  V vs SCE) is still significantly lower than that of molecular oxygen. Thus, although the present  $\pi$ -conjugated poly(benzobisazoles) should in principle be electron-transporting materials,<sup>39</sup> this would only be in the absence of any traps for electrons such as molecular oxygen. One direction of future work on this class of polymers should be further modification of the polymers to achieve reduction potentials greater than  $-0.8$  V (vs SCE).

**Electrochemical Oxidation.** The electrochemical oxidation process in the poly(benzobisazoles) was not chemically reversible under the conditions of these experiments. Figure 11 shows representative CVs of the oxidation of PBTPV, 1,4-PNBT, and PBZT. Although the formal potential ( $E^{\circ'}$ ) of the oxidation process cannot be obtained, the effect of molecular structure on oxidation can be inferred from the onset of oxidation ( $E_{\text{onset}}^{\text{ox}}$ ) and the anodic peak potential ( $E_{\text{pa}}$ ). The onset of electrochemical oxidation of PBTPV, 1,4-PNBT, and PBZT is at  $\sim 0.8$ ,  $0.85$ , and  $1.1$  V (vs SCE), respectively; the corresponding anodic peak potential is at  $1.31$ ,  $1.47$ , and  $1.62$  V, respectively. A summary of the electrochemical oxidation parameters of all the polymers is given in Table 2. The data show that the onset of oxidation of the polybenzobisazoles varies between  $0.75$  and  $1.3$  V, whereas the anodic peak potential varies between  $0.85$  and  $1.72$  V (vs SCE).

(38) Weast, R. C., Ed. *CRC Handbook of Chemistry and Physics*, 68th ed.; CRC Press Inc.: Boca Raton, FL, 1987.

(39) Abkowitz, M. A.; Stolka, M. A. In *Polymers for Advanced Technologies*, Lewin, M., Ed.; VCH Publishers: Weinheim, Germany, 1990; pp 225–260.





**Figure 12.** Schematic illustration of the electronic structure parameters.

The cyclic voltammetry results on electrochemical oxidation of the poly(benzobisazoles) show that the onset oxidation potential ( $E_{\text{onset}}^{\text{ox}}$ ) and the peak oxidation potential ( $E_{\text{pa}}$ ) are varied by 0.55 and 0.87 V, respectively, by the variation in molecular structure. A qualitative ordering of the oxidation potential of the series of polymers is in the order: PBTDV < PBTPV, PBTB < 1,4-PNBT < PBZT, 2,6-PNBT < PBBZT, PBO. It is interesting that the same four polymers which had higher reduction potentials than PBZT also have lower oxidation potentials than PBZT. In fact, the relative ordering of the oxidation potentials of the eight polymers is similar to the reversed ordering of the reduction potentials. This means that the structural variation in Chart 1 affects the entire electronic structure of the polymers as will be discussed in more detail subsequently. The nonreversibility of the electrochemical oxidation of these polymers suggests that their one-electron-oxidized state (radical cation) is not stable, and hence p-type dopability of the polymers to conducting materials is not going to be feasible. Thus, the polymers would also be poor hole-transporting materials.

**Electronic Structure.** The measured electrochemical redox properties provide a basis for estimating and assessing the electronic structure of the  $\pi$ -conjugated poly(benzobisazoles). To facilitate the discussion of the electronic structure of the polymers, a schematic illustration of the relevant electronic energy levels and energy parameters is given in Figure 12. The electronic, optical, and optoelectronic properties of  $\pi$ -conjugated polymers have been theoretically and experimentally established to be dominated by the frontier orbitals, i.e., the highest occupied molecular orbital (HOMO or  $\pi$  level) and the lowest unoccupied molecular orbital (LUMO or  $\pi^*$  level).<sup>40</sup> The two energy parameters that establish the positions of these LUMO and HOMO levels relative to vacuum are electron affinity (EA) and ionization potential (IP) which are defined on the energy level diagram of Figure 12. The energy gap  $E_g$  is the separation between the HOMO and LUMO levels, hence  $E_g = \text{IP} - \text{EA}$ . Extensive prior studies of conjugated polymers have shown that the energy parameters EA and IP are related to the measured redox properties by<sup>40</sup>  $\text{EA} = E_{\text{onset}}^{\text{red}} + 4.4$  and  $\text{IP} = E_{\text{onset}}^{\text{ox}} + 4.4$ , where the

onset redox potentials are in volts (vs SCE) and EA and IP are in electronvolts. The EA and IP values so obtained for the series of poly(benzobisazoles) are shown in Tables 1 and 2, respectively. The electrochemically determined energy gap ( $E_g^{\text{el}} = \text{IP} - \text{EA} = E_{\text{onset}}^{\text{ox}} - E_{\text{onset}}^{\text{red}}$ ) is also given in Table 2.

The electron affinity values of the series of eight poly(benzobisthiazoles) are in the range 2.4–3.0 eV (Table 1), which reveals a 0.6 eV variation of EA with molecular structure. This means that there is a 0.6 eV difference between the LUMO levels of PBO which has the smallest electron affinity, and hence the highest lying LUMO, and the LUMO of PBTDV which has the largest electron affinity and also the lowest lying LUMO among the series of polymers. Comparing the electron affinities of PBO and PBZT, we see that the LUMO level of the sulfur-containing polymer (PBZT) is lowered by 0.3 eV relative to the oxygen-containing polymer. The LUMO levels of four of the polymers are within  $\pm 0.1$  eV of that of PBZT. The electron affinity values of the poly(benzobisazoles) (2.4–3.0 eV) are to be compared to the EA values of other well-known classes of  $\pi$ -conjugated polymers:<sup>34,40</sup> *trans*-polyacetylene (3.31 eV); polythiophene (2.96 eV); poly(*p*-phenylene) (2.58 eV); poly(*p*-phenylenevinylene) (2.71 eV); poly(2,6-(4-phenylquinoline)) (2.62 eV). Thus, some of the poly(benzobisazoles) have some of the largest known electron affinities among  $\pi$ -conjugated polymers.

The tabulated ionization potentials of the poly(benzobisazoles) are in the range of 5.2 eV for PBTDV, PBTB, and PBTPV to 5.7 for PBO and PBBZT. Thus, the variation in molecular structure seen in Chart 1 results in the observed 0.5 eV variation in the IP values and in the associated HOMO levels. Incorporation of *trans*-, *trans*-divinylene, *trans*-vinylene, or 1,4-phenylenebisvinylene in place of the *p*-phenylene moiety in the poly(benzobisthiazoles) results in an identical HOMO level which is 0.3 eV higher than that of PBZT. The effect of the heteroatoms (S, O) also shows up in the IP values, indicating that the HOMO of PBZT is shifted upward relative to the HOMO of PBO by 0.2 eV. These ionization potentials of the poly(benzobisazoles) are also to be compared to those of other well known conjugated polymers:<sup>34,40</sup> *trans*-polyacetylene (4.73 eV); polythiophene (5.2 eV); poly(*p*-phenylene) (5.42 eV); poly(*p*-phenylenevinylene) (5.11 eV); poly(2,6-(4-phenylquinoline)) (5.35 eV). Two of the poly(benzobisazoles) (PBO, PBBZT) have IP values that are much higher than the well-known conjugated polymers.<sup>34,40</sup> The other polymers in Table 2 have IP values that are comparable to the cited, previously studied,  $\pi$ -conjugated polymers<sup>34,40</sup> except *trans*-polyacetylene. Although the ionization potentials of some of the polymers (e.g., PBTDV, PBTB, and PBTPV) are sufficiently small to make oxidative (p-type) doping feasible,<sup>1,34,40</sup> our previous discussion of the irreversibility of the electrochemical oxidation process suggests that such p-type doped materials would be unstable.

The electrochemical energy gap  $E_g^{\text{el}}$  of the series of polymers varies from 2.20 to 3.27 eV (Table 2), indicating that this electronic structure parameter is tunable over about a 1 eV range. The energy gap determined from the optical absorption edge  $E_g^{\text{opt}}$  for the same polymers is in the range 2.07–2.76 eV, indicating that the tunability is only over about 0.7 eV. A comparison

(40) (a) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. *J. Am. Chem. Soc.* **1983**, *105*, 6555–6559. (b) Eckhardt, H.; Jen, K. Y.; Shacklette, L. W.; Lefrant, S. In ref 1, pp 305–320. (c) Brédas, J. L.; Chance, R. R.; Baughman, R. H.; Silbey, R. *J. Chem. Phys.* **1982**, *76*, 3673.



of  $E_g^{\text{el}}$  and  $E_g^{\text{opt}}$  shows that they are, within experimental errors, identical in three of the polymers (PBTDV, PBTVP, and 1,4-PNBT) but that they differ by as much as 0.2–0.5 eV in the other polymers. Although the finding that  $E_g^{\text{el}}$  is not identical with  $E_g^{\text{opt}}$  may be explained in part by experimental uncertainties in the two different techniques, there is also a definitional or conceptual problem. The  $E_g^{\text{opt}}$  of conjugated polymers has commonly been taken as the optical absorption edge,<sup>1,34,40</sup> a view which assumes that the polymers are semiconductors and holds that the optical transitions are a result of band-edge-to-band-edge photoexcitations which produce free carriers. However, more and more evidence is pointing to the excitonic nature of the optical transitions in conjugated polymers<sup>15b,22</sup> in which case  $E_g^{\text{opt}}$  is best defined as the peak of the lowest energy HOMO–LUMO ( $\pi$ – $\pi^*$ ) transition. The energy of the lowest energy absorption maximum in the optical spectra of the poly(benzobisazoles) is given in Table 1, and it deviates from the corresponding absorption edge by about 0.14–0.43 eV. Thus, taking  $E_g^{\text{opt}}$  to be the energy at the  $\lambda_{\text{max}}$  gives a better match with  $E_g^{\text{el}}$  of the series of polymers.

**Refractive Index.** We have measured the wavelength dispersion of the isotropic refractive index  $n(\lambda)$  of the conjugated rigid-rod poly(benzobisazoles) shown in Charts 1 and 2 to probe the effects of molecular structure on the linear optical properties of this class of materials which is of growing interest in photonics and nonlinear optics.<sup>18,19</sup> The measurement techniques and the details of the  $n(\lambda)$  data analysis have previously been reported by our laboratory.<sup>24</sup> To interpret the measured refractive indexes in terms of molecular structure, we assume that the effects of molecular orientation and crystallinity are negligible. The polymer thin films (1.0–2.5  $\mu\text{m}$ ), prepared from isotropic solutions by spin coating, were optically transparent in the visible, and excellent interference fringes could be obtained from them over a wide wavelength range and hence judged to be isotropic and largely amorphous. In contrast, semicrystalline and nonisotropic films were not optically transparent in the visible and were highly scattering, and interference fringes could not be obtained from them. Thus, we can examine the effects of molecular structure on refractive index of the series of polymers through two molecular parameters, i.e., polarizability ( $\alpha$ ) and molar volume ( $V$ ) which appear in the Lorentz–Lorenz theoretical model<sup>41</sup> of the refractive index  $n$ :

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi N_A \alpha}{3V}$$

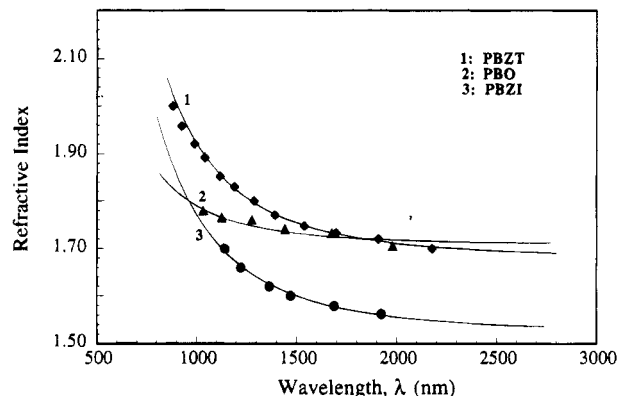
where  $N_A$  is Avogadro's number. The repeat unit molar volume  $V$  ( $\text{cm}^3/\text{mol}$ ) of each polymer was calculated by the group contribution approach and is given in Table 3.  $E_g^{\text{opt}}$  shown in Table 1 was taken as an independent and approximate measure of the polarizability.<sup>42</sup>

Figures 13–16 show the refractive index dispersion  $n(\lambda)$  of the series of poly(benzobisazoles) in Charts 1 and

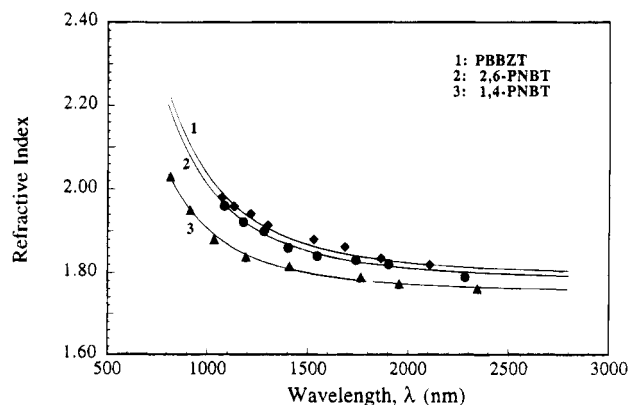
**Table 3. Molar Volume, Refractive Indexes of Thin Films at Selected Wavelengths, and Abbe Number<sup>a</sup> of Poly(benzobisazoles)**

polymer	molar vol ( $\text{cm}^3/\text{mol}$ )	$n_{1064}$	$n_{1319}$	$n_{2500}$	$\nu_d'$
PBZT	195	1.89	1.79	1.70	4.16
PBO	165	1.77	1.74	1.71	12.33
PBZI	185	1.74	1.64	1.55	3.37
PBBZT	270	1.99	1.90	1.81	5.00
1,4-PNBT	243	1.88	1.82	1.75	6.31
2,6-PNBT	243	1.97	1.88	1.80	5.18
PBTDV	184	1.93	1.90	1.87	15.00
PBTVP	249	2.03	1.99	1.95	12.38
PBIPV	239	1.78	1.76	1.73	15.20
BBL		1.99	1.93	1.88	8.45
BBB		1.91	1.87	1.84	12.43

<sup>a</sup> Abbe number  $\nu_d' = (n_{1319} - 1)/(n_{1064} - n_{2500})$ .



**Figure 13.** Wavelength dispersion of the refractive indexes of (1) PBZT, (2) PBO, and (3) PBZI and their Sellmeier equation fit.

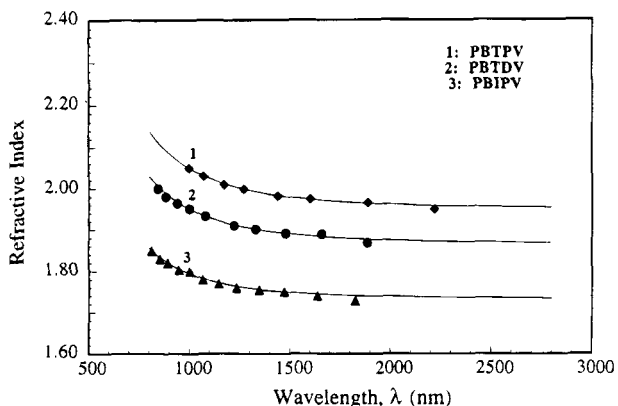


**Figure 14.** Wavelength dispersion of the refractive indexes of (1) PBBZT, (2) 2,6-PNBT, and (3) 1,4-PNBT and their Sellmeier equation fit.

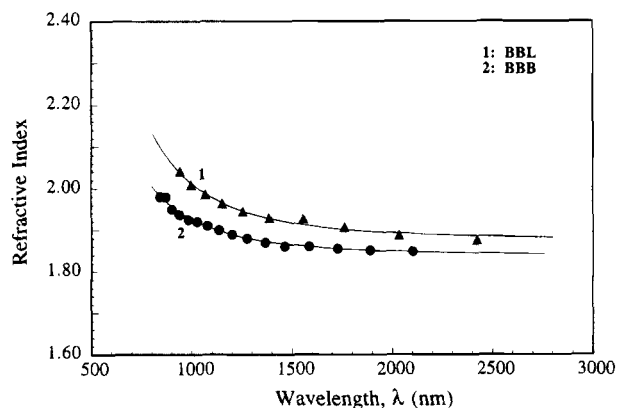
2. Each figure shows the comparative data for groups of the polymers. The solid lines through the data points in Figures 13–16 represent the fit of the  $n(\lambda)$  data by the well-known Sellmeier dispersion equation. We have previously shown that the Sellmeier dispersion equation provides an excellent description of the  $n(\lambda)$  data of many other conjugated polymers,<sup>24</sup> and the results of Figures 13–16 similarly demonstrate an excellent fit. The refractive index  $n(\lambda)$  data at selected wavelengths ( $\lambda = 1064, 1319$ , and  $2500$  nm) are shown in Table 3 along with the molar volume and Abbe number  $\nu_d'$ . The Abbe number reported here is that based on the three wavelengths indicated in Table 3, and it is a convenient numerical measure of the wavelength dispersion of the refractive index in the optically transparent and non-

(41) Lorentz, H. A. *Ann. Phys.* **1880**, 9, 641. (b) Lorenz, L. V. *Ann. Phys.* **1880**, 11, 70.

(42) Flytzanis, C. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 2, pp 121–135.



**Figure 15.** Wavelength dispersion of the refractive indexes of (1) PBTPV, (2) PBTDV, and (3) PBIPV and their Sellmeier equation fit.



**Figure 16.** Wavelength dispersion of the refractive indexes of (1) BBL and (2) BBB and their Sellmeier equation fit.

absorbing spectral region. One general observation on the refractive index data of Figures 13–16 and Table 3 is the highly dispersive nature of the refractive index of many of these polymers. In particular, the refractive indexes of PBZI, PBZT, PBBZT, 1,4-PNBT, and 2,6-PNBT with Abbe numbers of 3.4–6.3 are the most dispersive. Although the Abbe numbers of some of the poly(benzobisazoles) (e.g., PBO, PBTDV, PBTPV, PBIPV, and BBB) are relatively higher (12–15), these are still fairly low compared to inorganic glasses, nonconjugated polymers, or conjugated polyimines ( $\nu_d' \sim 10$ –38).<sup>24</sup> Another general observation is the relatively large values of the refractive index of this series of polymers. For example, at 1064 nm the refractive index is between 1.74 and 2.03 among the different polymers, whereas  $n(\lambda = 2500 \text{ nm})$  varies from 1.55 to 1.95. Thus, off-resonance at 2500 nm, the refractive index varies by 0.40 among the series of polymers.

A comparison of the wavelength dispersion of the refractive index of the three 1,4-phenylene-linked polymers PBZT, PBO, and PBZI which contain S, O, and NH heteroatoms, respectively, is shown in Figure 13. The dispersion of the  $n(\lambda)$  data is similar in PBZT and PBZI which have Abbe numbers of 4.16 and 3.37, respectively. In contrast, the oxygen-containing polymer, PBO, with an Abbe number of 12.33 is much less dispersive. On the other hand, the off-resonance refractive index is identical in PBZT and PBO (1.70–1.71), whereas it is only 1.55 in PBZI. These results mainly reflect the combined effects of the heteroatoms on polarizability and molar volume. The similarity of the

off-resonant refractive indexes of PBZT and PBO arises from a balance between the greater polarizability (smaller  $E_g^{\text{opt}}$ ) and larger molar volume of PBZT compared to PBO. However, a similar comparison between PBZI and PBZT shows that they both have similar polarizabilities (as measured by  $E_g^{\text{opt}}$ ) and PBZI has a smaller molar volume (Table 3). On account of these two molecular factors alone one would expect PBZI to have a larger off-resonance refractive index, which is contrary to the observation. An additional factor that may account for the 0.16 smaller refractive index of PBZI compared to PBZT is the electron density contribution to polarizability not accounted for by  $E_g^{\text{opt}}$ . Another factor still is the known moisture absorption of PBZI (up to 9 wt %),<sup>43</sup> which could significantly increase the molar volume above the value shown in Table 3 for the pure polymer; in contrast, PBZT, PBO, and their derivatives do not absorb any moisture.

The refractive index dispersion data for the three new polybenzobisazoles (PBBZT, 2,6-PNBT, and 1,4-PNBT) are shown in Figure 14. The optical dispersion as measured by the Abbe number (5.00–6.31) is very similar in all three polymers. Although the off-resonant refractive indexes of all three materials at 2500 nm is fairly close 1.75–1.81, the small difference (<3%) and subtle differences between them could not be accounted for by consideration of the molar volume and  $E_g^{\text{opt}}$  alone. This means that the polarizability must include the effects of electron density variation in addition to electron delocalization ( $E_g^{\text{opt}}$ ).

The wavelength dispersion of the refractive index of PBTPV, PBTDV, and PBIPV are shown in Figure 15. The optical dispersion in these three polymers, represented by Abbe numbers of 12.38–15.20, is the least among the series of polymers investigated (Charts 1 and 2). A comparison between the S-containing PBTPV and NH-containing PBIPV, which are otherwise structurally similar, shows a large difference of 0.22 in their off-resonant refractive indexes at 2500 nm (1.95 versus 1.73). Although PBTPV has a slightly higher molar volume and  $E_g^{\text{opt}}$  than PBIPV, its higher electron density more than compensates and thus results in a net increase of refractive index. The 0.08 (or 4%) smaller  $n(\lambda = 2500 \text{ nm})$  of PBTDV compared to PBTPV can be similarly explained by the greater electron density of PBTPV, which translates into a large polarizability. A further insight into the difference between the  $n(\lambda)$  data of this two latter polymers comes from the recently established molar refraction of functional groups found in  $\pi$ -conjugated polymers.<sup>44</sup> The *trans,trans*-divinylene moiety in PBTDV has a molar refraction, and hence polarizability, that is 32% less than the molar refraction and polarizability of 1,4-phenylenebisvinylene moiety in PBTPV.<sup>44</sup>

The effect of the ladder and semiladder structures on the refractive index of poly(benzobisimidazobenzophenanthrolines) (BBL, BBB) was also investigated. Figure 16 shows the  $n(\lambda)$  data for BBL and BBB films. The ladder polymer BBL has a slightly more dispersive refractive index than the semiladder BBB ( $\nu_d'$  of 8.45 and 12.43, respectively). BBL also has a slightly larger refractive index at 2500 nm (1.88) compared to BBB (1.84). The observed difference in the refractive index

(43) Osaheni, J. A.; Jenekhe, S. A. *Macromolecules*, in press.

(44) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.*, submitted.

data of BBL and BBB are readily accounted for by the larger polarizability (e.g., smaller  $E_g^{\text{opt}}$ , 1.78 versus 1.82 eV) and smaller molar volume of BBL.

### Conclusions

We have studied the effects of molecular structure on the redox properties, the electronic structure parameters, and the refractive index of conjugated poly(benzobisazoles). It was found that the one-electron electrochemical reduction of the series of polymers in Chart 1 was reversible, which implies that the materials can be reductively (n-type) doped to conducting polymers and also function as electron-transporting materials in the absence of oxygen. The reduction potential ( $E^{\circ'}$ ) varied from  $-1.57$  to  $-2.18$  V (vs SCE). In contrast, the one-electron electrochemical oxidation of the polymers was not reversible, which indicates that oxidative (p-type) doping to conducting polymers was not feasible. The electron affinity and ionization potential, estimated from the redox properties, were 2.4–3.0 and 5.2–5.7 eV, respectively, and are useful for establishing the relative LUMO and HOMO levels in the materials and for rationalizing their electronic and photophysical properties.

The wavelength-dependent refractive index of the poly(benzobisazoles) was found to vary with the backbone structure and heteroatom, by as much as 0.4 at 2500 nm. The off-resonant refractive index at 2500 nm was quite large (1.55–1.95). The NH-containing poly(benzobisimidazoles) have significantly lower refractive indexes compared to their corresponding sulfur- and oxygen-containing poly(benzobisazoles). The potential application of these polymers in integrated optics and nonlinear optical devices was recently explored with a demonstration of channel waveguides fabricated from PBZT<sup>23,45</sup> and 1,4-PNBT.<sup>45</sup>

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(45) Ihlein, G.; Menges, B.; Mittler-Neher, S.; Osaheni, J. A.; Jenekhe, S.A. *Nonlinear Opt.*, in press.