changed out, as evidenced by the color, IR, XPD, etc. This observation is consistent with the proposed pillared layered structure and excludes the possibility that the product is the Keggin ion salt of the di- or trivalent cations from hydrolysis of the LDHs.

In summary, we have studied a complete range of reactions in aqueous media between the layered double hydroxides and the polyoxometalate anions of Keggin-type structure. The results demonstrate that Keggin ions with a variety of negative charge can be pillared into almost all kinds of layered double hydroxides, provided that the latter are completely wet and the layers swollen with extended soaking. Full exchange of $[PW_{12}O_{40}]^{3-}$ into $Ni_2Al(OH)_6NO_3$ and $Mg_2Al(OH)_6NO_3$ and the observation of broad X-ray diffraction peaks around 12 Å in the XPD are evidence that strong interactions take place between the Keggin ions and the LDH layers.

Acknowledgment. This research was supported in part by grants from the National Science Foundation (DMR-8801283) and the AMOCO Chemical Co. for which grateful acknowledgement is made.

Synthesis and Processing of Heterocyclic Polymers as Electronic, Optoelectronic, and Nonlinear Optical Materials. 1. New Conjugated Rigid-Rod Benzobisthiazole Polymers

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New conjugated rigid-rod polymers, poly(benzobisthiazole) (PBBT), poly(benzobisthiazole-2,6-diylvinylene) (PBTV), and poly(benzobisthiazole-2,6-diyldivinylene) (PBTDV), have been synthesized, and their structures and optical properties have been characterized, and they have been processed into thin films from their soluble coordination complexes. The molecular structure of the polymers was established by solution ^1H NMR spectra and infrared spectra of thin films or solid samples. The optical bandgap of the new polymers was in the range 2.07–2.34 eV, which is 0.14–0.41 eV smaller than the well-known nonlinear optical polymer poly(*p*-phenylenebenzobisthiazole) (PBZT). The solution processability and improved intrinsic electronic properties of the new polymers suggest that they have potential for electronic, optoelectronic, and nonlinear optical applications.

Introduction

The synthesis and processing of conjugated polymers as electronic, optoelectronic, and nonlinear optical materials are of current interest because of the envisioned application of such materials in various areas of technology.[1,2] Ready processing of conjugated polymers to thin films or coatings is essential to their successful evaluation and use in these device applications. Although conjugated polymers are largely insoluble and intractible molecular materials, owing to their stiff chain structures and strong intermolecular interactions, significant progress is being made in developing new methods of solution processing of existing conjugated polymers. Most notable are the *soluble precursor*[3] approach to polyacetylene[3a] and vinylene-linked materials[3b] such as poly(*p*-phenylenevinylene) and poly(thiophenevinylene) and the *soluble coordination complexes*[4] approach to processing various heterocyclic and heteroaromatic conjugated polymers. It is therefore very important that processability and viable processing strategies be designed into the structures of new conjugated polymers. In this respect, new conjugated polymers containing heteroatoms are processable via their soluble coordination complexes.

The heterocyclic rigid-rod polybenzobisazole family, which includes poly(benzobisthiazoles), poly(benzobisoxazoles), and poly(benzimidazoles), has attracted much research interest in the past two decades because they exhibit high tensile strength, high modulus, and high thermal and environmental stability.[4-9] The high strength

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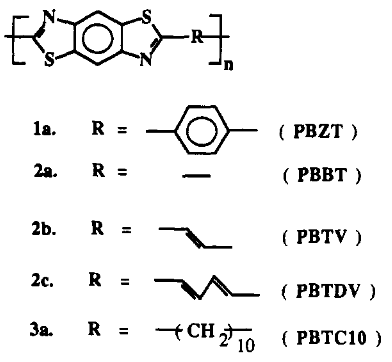
Chart I



of these polymers 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 and in Lewis acid/nitromethane[4] can exist in either optically isotropic or anisotropic liquid-crystalline phases, depending on the concentration, molecular weight, or temperature. Most of the initial research efforts aimed at establishing structure–property relationships in this class of polymers focused mainly on the mechanical properties of these polymers for structural applications.[5-10] The sulfur-containing polymer poly(*p*-phenylenebenzo[1,2-*d*:4,5-*d*′]bisthiazole-2,6-diyl) (PBZT, **1a**) has been found to be particularly interesting in the poly(benzobisazole) family. Consequently, structural modifications that have been made to improve the properties of this polymer have focused largely on maintaining the "para"-ordered rigid-rod geometry while modifying the structure with various pendant groups[9] on the *p*-phenylene ring. To improve the compressive strength of PBZT, for example, the effect of hydrogen bonding and thermal cross-linking have been explored by attaching 2,5-dihydroxy[9a] and 2,5-dimethyl[9b] pendant groups, respectively, on the *p*-phenylene ring. Other pendant groups such as 2-methyl,[9b] phenyl, and phenylbenzobisthiazole[9c] have been attached to the main chain with a view to improving the processability of the polymers in common organic solvents. However, these later efforts have not been successful in solubilizing the polymers in organic solvents.

Apart from the possible structural applications of the poly(benzobisazoles), recent advances in the study of polymers as materials for applications in electronic, photoelectronic, optoelectronic, and photonic devices suggest the need for new polymers with a wide range of optical and electronic properties. Such a wide property variation is needed to both understand the structure-property relationships and to optimize the materials. We[11] and others[12] have shown that the poly(benzobisazole) family with robust physical properties shows promise as nonlinear optical materials from studies of the third-order nonlinear optical susceptibility of PBZT[11,12] and PBO[13] and model compounds.[12b,c] To significantly improve the electronic, optical, and nonlinear optical properties of this class of polymers, a molecular design approach which does not involve merely attaching different pendant groups need to be considered. Consequently, we thought of retaining the benzobisthiazole unit and modifying the R portion in the polymer backbone as illustrated in Chart I. This kind of strategy can give rise to a totally visible transparent material when a nonconjugated R group is introduced (**3a**) or to a highly conjugated polymer when R is a conjugated segment (**1a, 2**). Others have recently explored this strategy of varying the R group.[10] Among the linkages that have been reported are thiophene oligomers,[10a] 4,9-diamantane,[10b] 1,4-bicyclo[2.2.2.]octane,[10c] and alkylenes.[10d,10e] One particularly interesting R group is the vinylene linkage. This has worked well in other polymers. For example, the optical bandgap of poly(*p*-phenylenevinylene) (E_g = 2.43 eV)[14a] is significantly reduced compared with poly(*p*-phenylene) (E_g = 2.8 eV)[14b] as is that of poly(thiophenevinylene) (E_g = 1.64 eV)[15a] compared with polythiophene (E_g = 2.0 eV).[15b] This idea has not been fully exploited in the benzobisthiazole polymers. Yokoyama et al.[16] have reported the synthesis of a polymer film they believed to be poly(benzobisthiazole-2,6-diylvinylene) (PBTV, **2b**) by interfacial polymerization (at the air/water interface) of 2,5-diamino-1,4-benzenedithiol with fumaric acid di-*n*-butyl ester and found that the optical absorption spectrum has a strong band in the UV (λ_{max} = 230 nm) and a weak band in the visible (λ_{max} = 420 nm) and a third-order optical susceptibility $\chi^{(3)}$ of (1.3–2.2) × 10^{-12} esu. We believe that these authors did not prepare the authentic PBTV, and we are sceptical about their findings since vinylene linkage has been shown to improve the optical and nonlinear optical properties of some other classes of polymers.[14c,15c-e] Our extensive measurement of the $\chi^{(3)}$ of PBZT by third harmonic generation spectroscopy over a wide wavelength range shows that its value is in the range 10^{-11}–10^{-10} esu.[11] We envisage that the more *trans*-polyacetylene segment that is introduced into the benzobisthiazole polymer backbone, the lower will be the optical bandgap of the resulting polymer since *trans*-polyacetylene is known to have a small bandgap (E_g = 1.5 eV).[17]

In this paper, we report the synthesis, characterization, processing, and optical properties of the conjugated poly(benzobisthiazoles): poly(benzobisthiazole) (PBBT,

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2a), poly(benzobisthiazole-2,6-diylvinylene) (PBTV, **2b**), and poly(benzobisthiazole-2,6-diyldivinylene) (PBTDV, **2c**). The synthesis and characterization of the model compound of PBTDV, 2,6-bis(hexa-2,4-dienyl)benzobisthiazole (BHBBT), is also reported. We compare the optical properties of these polymers with that of PBZT and show that PBTV and PBTDV are materials for potential electronic, photoelectronic, and nonlinear optical applications. The wide optical property variations obtained in going from the polymer containing only the benzobisthiazole unit to the vinylene- and divinylene-linked polymers provide a useful means of studying structure–property relationships in this class of polymers. We show that this is the first time that the authentic PBTV has been synthesized with optical properties that are dramatically different from those reported for the polymer obtained by interfacial polymerization.[16] The new polymers were found to be processable into optical-quality thin films by the approach of reversible soluble complexes in organic solvents, similar to the approach developed in our laboratory for processing other conjugated polymers, such as polyazomethines[4c] and polyquinolines[4e] having a heteroatom in their backbone.[4]

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.[6] DABDT (20 g) was dissolved in 500 mL of deaerated 10 wt % hydrochloric acid solution containing 1 wt % stannous chloride ($SnCl_2$) at 70 °C. The pure DABDT was recrystallized from solution by adding concentrated hydrochloric acid. It was subsequently dried in a vacuum oven at 60 °C overnight.

Fumaric acid (99.5+%) was purchased from Fluka Chemicals and was used as received. High-purity grade (>99%) 2,4-hexanedienoic acid and oxalic acid (anhydrous) were obtained from Aldrich Chemical and were used as received. *trans,trans*-Muconic acid (98%, Aldrich) was recrystallized from a large volume of boiling water.[18] The pure crystals were obtained as small prisms (mp 314 °C).

Polyphosphoric acid (PPA) and 85% phosphoric acid were purchased from Aldrich Chemical and used as received to prepare 77% polyphosphoric acid used in the dehydrochlorination of DABDT. Phosphorous pentoxide (P_2O_5) was obtained from Baker Inc.

Model Compound and Polymer Synthesis. *2,6-Bis(hexa-2,4-dienyl)benzobisthiazole (BHBBT)*. DABDT (4.55 g, 18.56 mmol) was dissolved in 44 g of 77% PPA (deaerated) in a glass reactor fitted with a mechanical stirrer, two gas ports, and a sidearm. The reaction vessel was purged with nitrogen for 15 min, and dehydrochlorination was carried out at 70 °C under vacuum. After complete dehydrochlorination, the reaction mixture was cooled to 50 °C, and 4.161 g (37.12 mmol) of 2,4-hexadienoic acid was added. P_2O_5 (24 g) was added under positive pressure to compensate for the calculated water of condensation. The reaction temperature was slowly increased to 85 °C and then to 120 °C over 8 h. The reaction was kept between 120 and 140 °C overnight. The yellow product was cooled to room temperature and precipitated in water. It was purified by refluxing in large volume of water for 2 days. The yield was ~90%.

Poly(benzobisthiazole) (PBBT). DABDT (3.87 g, 15.78 mmol) was dissolved in 14.66 g of deaerated 77% PPA. After dehydrochlorination at 70 °C under vacuum, 1.42 g (15.78 mmol) of oxalic acid was added together with 12 g of fresh P_2O_5 under positive pressure. The reaction temperature was raised gradually to 120 °C over 10 h, then to 140 °C, and finally to 180–200 °C. The reaction was allowed to proceed at the elevated temperatures (180–200 °C) for 24 h. The polymerization dope in PPA was precipitated in water and purified by extraction of the PPA with water for 2 days.

Poly(benzobisthiazole-2,6-diylvinylene) (PBTV). In the first attempt to synthesize this polymer, 3.4 g (13.87 mmol) of DABDT was dehydrochlorinated in 15 g of deaerated 77% PPA. After complete dehydrochlorination at 70 °C, 1.61 g (13.87 mmol) of fumaric acid was added together with ~11 g of fresh P_2O_5 to compensate for the water of condensation. The temperature was raised to 120 °C in 6 h. Within a few hours of raising the temperature to 120 °C, there was a rapid increase in the viscosity of the polymer dope which eventually balled-up the mechanical stirrer. After ~6 h, the highly viscous polymerization dope in PPA was precipitated in water, shredded into small pieces with a blender and purified by refluxing in water for 2–3 days.

A second polymerization was carried out using a dilute polymer concentration (5 wt %). 1.667 g (6.8 mmol) of DABDT was dehydrochlorinated in 18.5 g of deaerated 77% PPA. Fumaric acid (0.789 g, 6.8 mmol) and P_2O_5 (9 g) were added. The temperature was gradually raised to 120 °C over 6 h, then to 160 °C, and finally to 180 °C. The polymerization mixture became shiny dark green in reflection. It was allowed to proceed for 8 h at 180 °C before precipitating the polymer dope 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.

Poly(benzobisthiazole-2,6-diyldivinylene) (PBTDV). DABDT (4.31 g, 17.57 mmol) was reacted with 2.5 g (17.57 mmol) of *trans,trans*-muconic acid following the same procedure outlined for PBTV synthesis. The polymer concentration was 5.5 wt %. The reaction temperature was raised to 80 °C and held for 6 h at this temperature before finally increasing it to 120 °C. The reaction was allowed to proceed overnight for a total of 16 h. The polymerization dope was precipitated in water and purified in a similar way to PBTV purification.

Preparation of Thin Films. Thin films for optical absorption spectra and IR studies were prepared from both the polymerization dope and from dilute solutions of the polymers in aluminum chloride or galium chloride/nitromethane. Film preparation from the PPA dope involved shearing the dope at 70 °C between two glass slides and coagulating the film in water. The resulting film is then extracted with water for typically 2–3 days to free the film of acid. In the case of processing from the soluble Lewis acid complexes,[4] typically, a 0.5–1 wt % polymer solution in $AlCl_3$ or $GaCl_3$/nitromethane was prepared in a drybox, with the Lewis acid in slight excess of the stoichiometric amount to facilitate ready dissolution of the polymers at 40 °C. The nitromethane solutions were spin coated onto fused silica substrates using a Solitec Spinner. The thin films of the polymer–Lewis acid complex were immersed in deionized water to be decomplexed, typically for 2 days.

Characterization. Intrinsic viscosities $[\eta]$ of all the polymers were 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 a Model 951 TGA and a Model 910 DSC units. The TGA data were obtained in flowing nitrogen at a heating rate of 10 °C/min while 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. Free-standing films were used for obtaining the IR spectra of PBTV and PBZT, while KBr pellets were used for PBTDV and PBBT. 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 containing aluminum chloride.

Optical absorption spectra of thin films and solutions of the polymers as well as the solution spectra of the model compound were obtained with a Perkin Elmer Model Lamda 9 UV-vis–near-IR spectrophotometer in the wavelength range 190–3200 nm.

X-ray powder diffraction of PBTDV was obtained at Oneida Research (Whitesboro, NY) on a siemen D500 automated powder diffractometer equipped with a graphite monochromator. The instrument was set up with a Cu radiation (λ = 1.54 Å) X-ray

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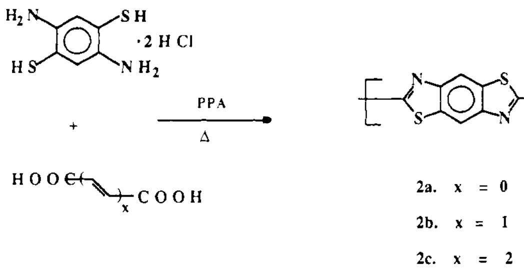
Scheme I



source operating at 50 kV and 40 mA. The 2θ scan range was set to be 4–80° using a step scan window of 0.05°/1.0 s step. Beam slits were set at 1°, 1°, 1°, 0.15°, and 0.15° widths. 2θ calibration was performed using an NBS mica standard (SRM 675). Data were collected and reduced with the use of a Micro VAX II computer.

Results and Discussion

Polymerization and Polymer Structure. As a check on the purity of the 2,5-diamino-1,4-benzenedithiol monomer, we first used it to synthesize poly(*p*-phenylenebenzobisthiazole) (PBZT) using the method of Wolfe et al.[5,6] and obtained a high molecular weight polymer with an intrinsic viscosity of 32 dL/g. The FTIR and optical absorption spectra of the PBZT sample were found to be identical with those reported in the literature.[11,19] These results proved the high purity of the DABDT monomer and the PBZT sample was also used in comparative studies with the new benzobisthiazole polymers.

The synthesis of PBBT, PBTV, and PBTDV was based on the same chemistry as that of PBZT synthesis; that is, the condensation polymerization of a diacid and diaminobenzenedithiol to form the benzobisthiazole ring in a polymer backbone as shown in Scheme I. Although PBBT has been previously synthesized[8] using a different chemistry, which involves the reaction of 2,6-dicyanobenzobisthiazole with 2,5-diamino-1,4-benzenedithiol, we chose the reaction of a simple dicarboxylic acid, oxalic acid, in the present synthesis. Also although Yokoyama et al.[16] have claimed to have synthesized poly(benzobisthiazolevinylene) at the air/water interface, we believe that their reaction did not go to completion, hence the poor optical absorption spectrum and $\chi^{(3)}$ they obtained. We infer this from our first attempt at the synthesis of PBTV. The reaction was quenched prematurely at 120 °C because of the high viscosity of the polymerization dope. The optical absorption spectrum of the thin film of this polymer is identical to that reported by Yokoyama et al.[16] as shown in Figure 1. The absorption spectrum did not change even after heating the film in the oven at 200 °C, in agreement with the results of Yokoyama et al. However, as can be seen from the IR spectrum in the insert of Figure 1, it is clear that there is a strong amide band (-NHC(O)-) at 1670 cm^{-1}, which indicates that complete closure of the thiazole rings was not achieved, though the IR spectrum shows some bands which are similar to the authentic poly(benzobisthiazolevinylene) synthesized at 180 °C. There was also a band in the -NH- stretching region ~ 3400–3500 cm^{-1}, indicating the presence of amide groups.

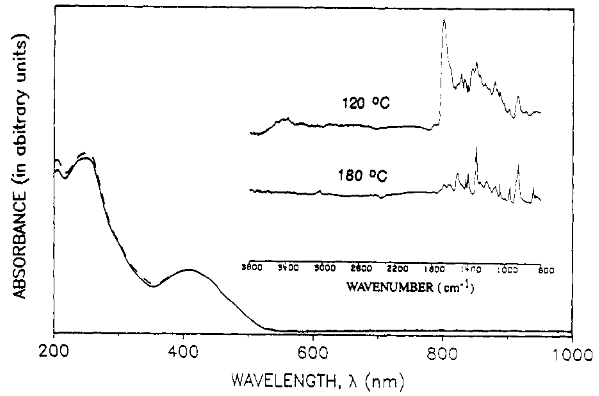
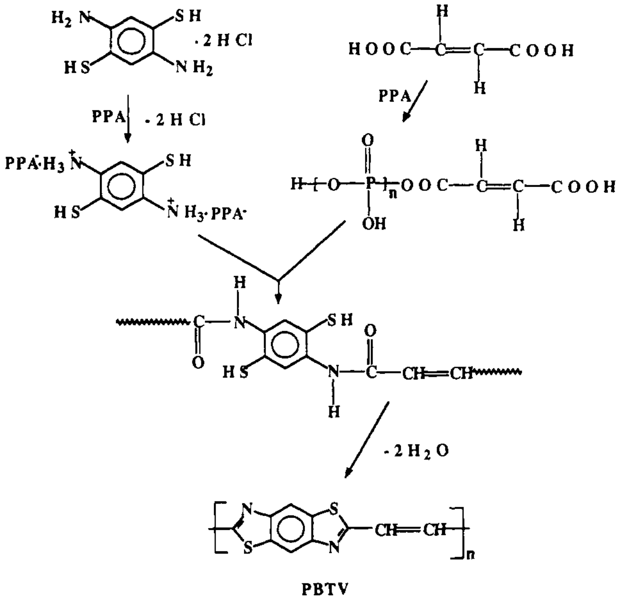


Figure 1. Optical absorption spectrum of polymer synthesized by condensation of DABDT with fumaric acid in PPA at 120 °C before (solid line) and after (dashed line) heat treatment at 200 °C and the corresponding FTIR absorption spectrum (insert) compared with the authentic PBTV (180 °C).

Scheme II



PBTV

In the second and successful synthesis of PBTV we used a 5 wt % polymer concentration and carried on the reaction in PPA to 180 °C. This resulted in a dramatic change in both the optical and IR spectra of the polymer. The amide band (1670 cm^{-1}) in the IR spectrum disappeared completely (Figure 1, insert) consistent with what is expected of the authentic PBTV. We infer from these results that the mechanism of condensation polymerization of diaminobenzenedithiol with fumaric acid to produce PBTV involves a polyamide intermediate shown in Scheme II. Formation of the polyamide intermediate occurs at a relatively low condensation temperature (120 °C) while the cyclicization step to form the thiazole ring takes place at higher temperatures (180 °C). In addition to temperature, another critical factor in the synthesis of authentic PBTV is the role of the polymerization medium. In the presence of polyphosphoric acid, the polymer chain growth relies on the phosphorylation (activation of functional groups) of both the amine and the acid groups. Phosphorylation of aliphatic acids makes the functional groups very reactive even at low temperatures. Although the polymer synthesized at the air/water interface was heated up to 180 °C in order to complete the cyclicization reaction, the results show that the reaction was not complete, probably due to the absence of functional group activation by polyphosphoric acid. This suggests that the ring closure is catalyzed by the phosphoric acid medium.

The synthesis of PBTDV was carried out at a much lower temperature (120 °C) compared with PBBT and PBTV, yet the ring closure was found to be complete from the FTIR and ^{1}H NMR characterization of this polymer. The choice of a lower temperature for the synthesis of this

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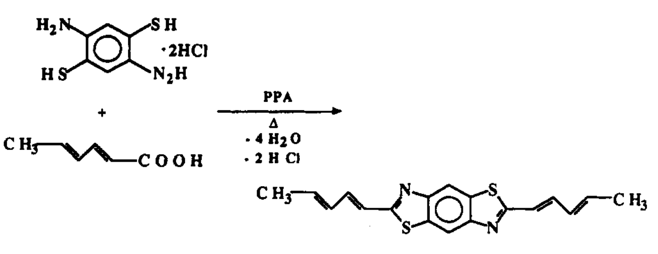
Scheme III



(BHBBT)

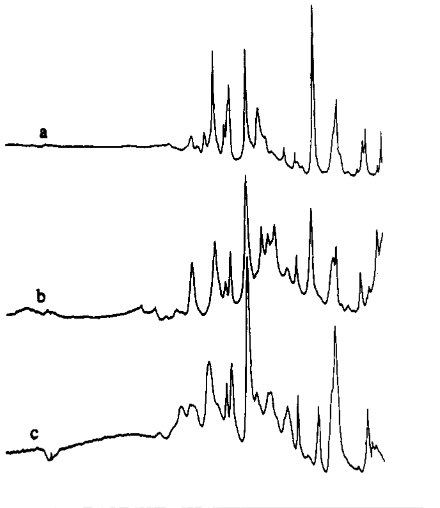


Figure 2. FTIR absorption spectra of (a) PBZT, (b) PBTDV, and (c) PBTV.

Table I. Summary of IR Spectra of Benzobisthiazole Polymers

	frequency (cm^{-1})			
assignment	PBBT	PBTV	PBTDV	PBZT[a]
sym C═C str (w)		1663		
asym C═C str		1600	1601	
heteroring str (vs)	1467	1515	1480	1485
heteroring str (s)	1406	1400	1400	1406
heteroring str (vs)	1313	1313	1315	1314
trans-vinylene		1052	1053	
heteroring "breathing" (vs)	889	944	974	960
1,2,4,5-C_6H_2 (s)	860	856	845	860
heteroring out-of-plane def	685	689	680	689

[a] Following the assignment of PBZT in ref 19.

polymer was suggested by the model compound studies. The model compound of PBTDV, 2,6-bis(hexa-2,4-dienyl)benzobisthiazole (BHBBT) was first synthesized (Scheme III) under conditions later used for the polymer synthesis and characterizated by both FTIR and ^{1}H NMR. The much lower temperature required for the synthesis of PBTDV implies that phosphorylation increases the reactivity of the diacids in the following order *trans,-trans*-muconic acid > fumaric acid > oxalic acid.

The polymer structures were established primarily by FTIR and ^{1}H NMR spectra. Figure 2 shows a comparison of the FTIR spectra of PBZT, PBTDV, and PBTV. The characteristic peaks of the benzobisthiazoles are listed in Table I. On the basis of previous[19] assignments of the IR bands in PBZT, the heteroring stretch associated with the thiazole ring shows intense bands at 1485 and 1314 cm^{-1}, while the heteroring "breathing" and the out-of-plane ring deformation are at 960 and 689 cm^{-1}, respectively. These bands which are slightly shifted (Table I) are also intense in the IR spectra of both PBTDV and PBTV as shown in Figure 2. In addition, the bands associated with the vinylene or divinylene C═C linkage in PBTV and PBTDV appear between 1663 and 1600 cm^{-1} together with the characteristic *trans*-vinylene band at 1052 cm^{-1}. However, these bands are absent in PBZT and PBBT as expected. The symmetric *trans*-vinylene stretch in PBTDV is practically IR inactive as expected for a conjugated diene system.[20] Thus the FTIR spectra show that the vinylene and butadiene linkages in PBTV and PBTDV, respectively, are trans and trans,trans.

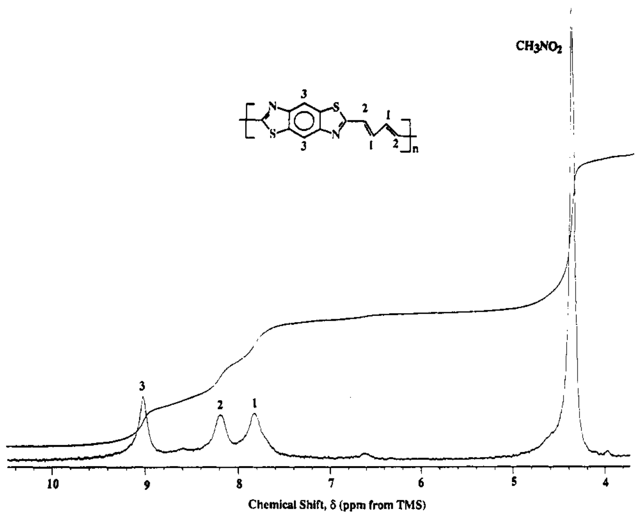


Figure 3. ^{1}H NMR spectrum of PBTDV in $CD_3NO_2/AlCl_3$ and its assignment.

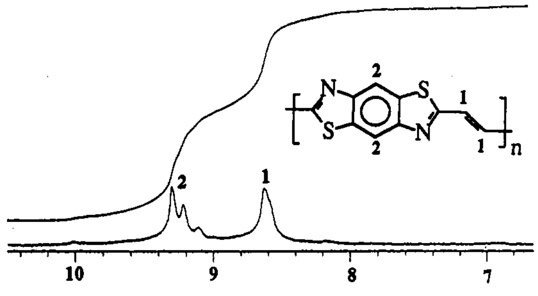


Figure 4. ^{1}H NMR spectrum of PBTV in $CD_3NO_2/AlCl_3$ and its assignment.

The ^{1}H NMR spectra of PBTDV, PBTV, PBBT, and the model compound BHBBT were obtained in deuterated nitromethane containing aluminum trichloride. Figures 3 and 4 show the ^{1}H NMR spectra of PBTDV and PBTV, respectively, and their assignment. The number of protons corresponding to each resonance are in good agreement with the proposed structure. The assignment of the chemical shift in PBTDV was based on the model compound studies in both deuterated dimethyl sulfoxide (DMSO) and in deuterated nitromethane containing $AlCl_3$. Because of the limited solubility of the model compound in DMSO, a solution concentration of ~1 wt % suitable for a well-resolved ^{1}H NMR spectrum could not be prepared, but we were able to compare the chemical shift obtained in dilute solution with that obtained from $AlCl_3$/nitromethame-d_3 in order to see the effect of complexation on the chemical shifts. Complexation resulted in a slight chemical shift of ~0.15 ppm downfield due to

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(20) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectroscopic Identification of Organic Compounds*, 4th ed.; Wiley: New York, 1981; p 109.

Table II. Summary of ^{1}H NMR Spectra of Model Compound BHBBT and Benzobisthiazole Polymers

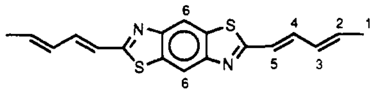
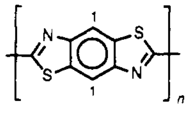
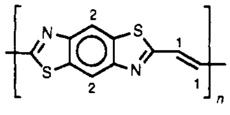
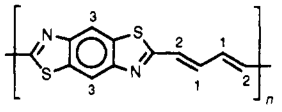
structure	proton no.	chem shift, ppm
	1	2.03
	2	6.65–6.67
	3	6.79–6.84
	4	7.04–7.10
	5	7.85–7.91
	6	8.80
	1	8.90–9.20
	1	8.65
	2	9.2–9.33
	1	7.82
	2	8.21
	3	9.02

Table III. Summary of Intrinsic Viscosity and Optical Absorption Spectra of Thin Films of Poly(benzobisthiazoles)

polymer	intrinsic viscosity $[\eta]^a$ (dL/g)	λ_{max} (nm)	absorption threshold (nm)	optical bandgap E_g (eV)
PBBT	0.4	428	530	2.34
PBTV	3.2	470	560	2.21
PBTDV	2.2	500	600	2.07
PBZT	32	438	500	2.48
PBTC10	3.3	295	344	3.65

[a] In methanesulfonic acid at 30 °C.

an electron deshielding effect. The effect of complexation on the chemical shifts of the polymers may not be more than a ~0.2 ppm chemical shift downfield. A singlet resonance was expected for the benzobisthiazole protons in PBTV; however, a multiplet of resonances was observed (Figure 4). The possible explanation of the multiplets or nonequivalency of protons includes incomplete closure of some of the rings or the result of asymmetric coordination of $AlCl_3$ to the nitrogen and sulfur heteroatoms. However, the FTIR could not detect any amide bands to support the former explanation. A summary of the assignment of the ^{1}H NMR spectra of the polymers and model compound is given in Table II. The NMR spectra of PBTV and PBTDV show that the vinylene and divinylene (butadiene) linkages in these polymers are trans and trans,trans, respectively.

Intrinsic Viscosity and Molecular Weight. A summary of the intrinsic viscosity $[\eta]$ of poly(benzobisthiazoles) measured in methanesulfonic acid at 30 °C is given in Table III. The intrinsic viscosity data show that PBTV and PBTDV have fairly high molecular weights. The first batch of PBTV synthesized with $[\eta]$ = 8.2 dL/g demonstrated that when the key variables such as polymer concentration, reaction temperature, reaction time, and P_2O_5 content are optimized, these polymers can be synthesized to very high molecular weights, comparable to other poly(benzobisthiazoles). The intrinsic viscosity of PBBT (0.4 dL/g) obtained through the oxalic acid synthetic route is quite low, compared with an intrinsic viscosity of 15 dL/g reported in the literature[8] for PBBT synthesized using 2,6-dicyanobenzobisthiazole. The rather low molecular weight of PBBT is due to the low reactivity of oxalic acid. In spite of this low $[\eta]$ value, thin films suitable for optical absorption and nonlinear optical characterizations were successfully fabricated. Although a Mark–Houwink relation has not been established for these polymers, a rough estimation of the molecular weight can be made from the intrinsic viscosity data using the relation[6,21] for class 1 (PBZT) and class 2 poly(2,6-benzothiazole) (2,6-PBT) rigid-rod polymers to establish a lower and upper bound for the molecular weight. Accordingly, we estimate that the intrinsic viscosities of the two PBTV samples (3.2 and 8.2 dL/g) translate to a molecular weight of 11 200 in the lower limit and 65 300 in the upper limit.

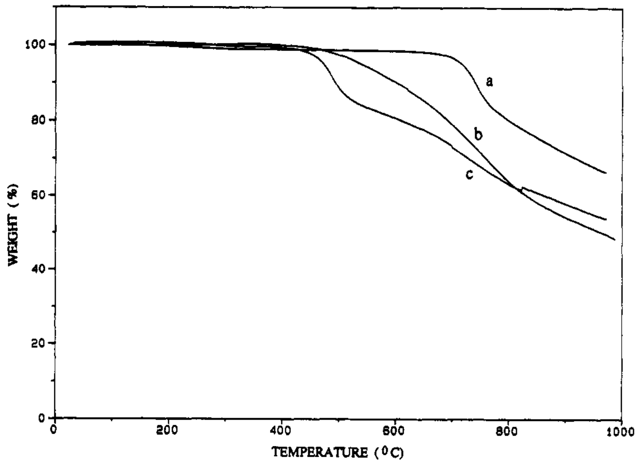


Figure 5. TGA thermograms of (a) PBZT, (b) PBTV, and (c) PBTDV heated in nitrogen.

Thermal Stability. The TGA thermograms of PBTV and PBTDV in nitrogen atmosphere are shown in Figure 5 together with that of PBZT for comparison. As can be seen from Figure 5, the thermal stability of these polymers is lower than that of PBZT as would be expected, since aromatic ring is much more stable than aliphatic moieties. In spite of this, the polymers have reasonably good thermal stability. The decomposition in nitrogen starts at ~460 °C and is comparable to other conjugated polymers which are currently being studied for device applications.[4c] It should be noted that there is no weight loss between 200 and 260 °C which usually occurs when there is residual PPA left in a polymer prepared in it. DSC scans did not show any measurable glass transition or melting point in the range of up to 400 °C.

Film Processing. Thin films for optical and spectroscopic studies can be prepared either directly from the polymerization dope in polyphosphoric acid (PPA) or by using the Lewis acid ($AlCl_3$ or $GaCl_3$) complexation-mediated solubilization technique[4] which provides a better way to process these polymers into optical-quality thin films. The otherwise intractable polymers can be made solution processible from organic solvents by forming their Lewis acid–base coordination complexes in nitromethane as illustrated in Scheme IV. Aluminun(III) chloride and galium(III) chloride in nitroalkanes were found to be effective in forming the soluble coordination complexes of the polymers. It should be noted that the dissolution of PBTV and PBTDV in high concentrations, say 3 wt % or higher, takes a while to achieve compared to PBZT and PBBT. It was also difficult to dissolve high molecular weight PBTV and PBTDV in strong acids such as methanesulfonic acid at high concentration. We attribute this solvent resistance to the nature of chain packing and strong

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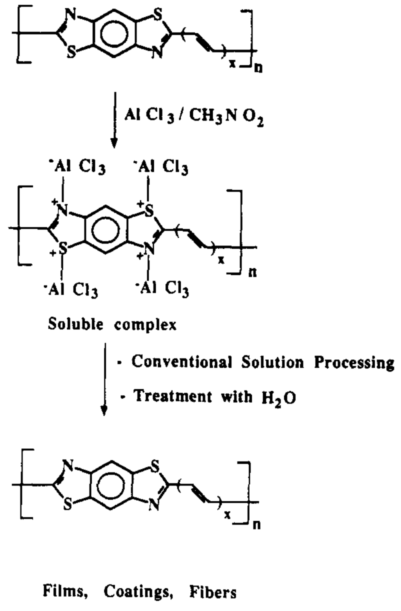
[21] (a) Berry, G. C.; Metzger, P. C.; Venkatraman, S.; Cotts, D. B. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1979**, *20* (1), 42. (b) Berry, G. C. *Mater. Sci. Eng.* **1985**, *52*, 82, and references therein.

Scheme IV



intermolecular interactions in these vinylene-linked poly(benzobisthiazoles). Once solutions of the polymers in nitromethane were prepared, they were processable by conventional polymer solution processing techniques. For example, thin films and coatings of the polymers were prepared by spin coating of solutions onto substrates and followed by treatment of the polymer complex with water or methanol which is a stronger Lewis base than the polymer. The pure polymers in the form of films or coatings are obtained in the process (Scheme IV).

Films of the vinylene-linked polymers PBTV and PBTDV are typically orange-red in transmission and metallic green in reflection. Although the crystal structure of these polymers (PBBT, PBTV, and PBTDV) has not been fully studied, the X-ray powder diffraction pattern of PBTDV showed two broad peaks similar to the diffraction pattern of PBZT.[22] The two broad diffraction peaks in PBTDV were at *d* spacings of 5.47 and 3.49 Å. These correspond to *d* spacings of 5.85 and 3.54 Å in the diffraction patterns of PBZT[22] which have been attributed to e_1 and e_2 reflections, respectively. The results indicate that the chains in the divinylene polymer PBTDV are more closely packed than those in PBZT and also that the intermolecular interactions in PBTDV are greater.

Optical Properties. Although the parent conjugated poly(benzobisthiazole) (PBBT) has previously been synthesized, its optical and electronic properties have not been reported nor compared to the widely studied PBZT which has an optical bandgap (E_g) of 2.48 eV.[4a] Figure 6 shows the optical absorption spectrum of a thin film of PBBT. This polymer has a strong visible absorption with a π–π^* transition (λ_{max}) at 428 nm. The corresponding optical bandgap of PBBT is 2.34 eV (Table III) which is smaller than PBZT. This result suggests that the known[23] ~23° twist of the *p*-phenylene ring from the benzobisthiazole plane in PBZT molecule accounts for only ~0.14 eV of the band gap of PBZT. The E_g value (2.34 eV) of PBBT compares favorably to the bandgap of other well-known conjugated ring polymers: poly(*p*-phenylene) (~3.1 eV); polypyrrole (~3.2 eV); poly(2,6-(4-phenylquinoline)) (2.65 eV); and polythiophene (~2.2 eV).

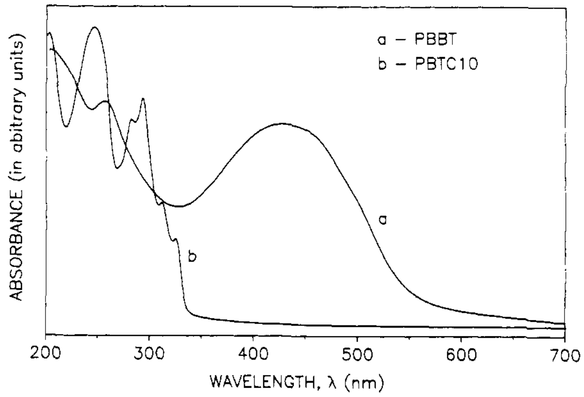


Figure 6. Optical absorption spectra of thin films of (a) PBBT and (b) PBTC10.

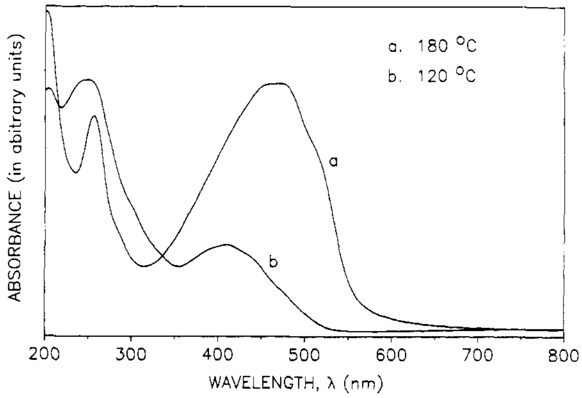


Figure 7. Effect of polymerization temperature on the optical absorption of PBTV: (a) 180 °C; (b) 120 °C.

To explore the extent of π-delocalization beyond the repeat units of these benzobisthiazole polymers, we have prepared the nonconjugated derivative poly(benzobisthiazole-2,6-diyldecamethylene) (PBTC10). The detailed synthesis, characterization, thermotropic liquid crystallinity, and physical properties of PBTC10 and related polymers will be reported elswhere.[24] As would be expected, the absorption spectrum and optical bandgap (E_g = 3.65 eV) of PBTC10 are dramatically blue shifted from the conjugated PBBT by a large 1.31 eV (Figure 6). This result suggests that there is a strong electronic delocalization beyond the benzobisthiazole polymer repeat units.

Figure 7a shows the optical absorption spectrum of a thin film of the authentic PBTV synthesized at 180 °C in PPA medium. Figure 7b shows the optical absorption of a thin film of an incompletely cyclicized sample of PBTV synthesized in PPA at 120 °C. The optical absorption spectrum of Figure 7b is identical to the spectrum of a film obtained by carrying out the polymerization at the air/water interface.[16] We have demonstrated earlier on that this spectrum (Figure 7b) does not represent the authentic PBTV. It should be noted that not only is the visible band stronger than the band in the UV, the λ_{max} (470 nm) is 50-nm red shifted from the incompletely cyclicized sample. These results show that the reaction temperature and polymerization medium have profound effects on the optical properties of poly(benzobisthiazole-2,6-diylvinylene).

The optical bandgap (E_g) of PBTV is 2.21 eV, which is smaller than the parent homopolymer PBBT (2.34 eV) and

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[22] (a) Cohen, Y.; Thomas, E. L. *Mol. Cryst. Liq. Cryst.* **1987**, *153*, 375. (b) Roche, E. J.; Takahashi, T.; Thomas, E. L. In *Fiber Diffraction Methods*; French, A. D., Gardner, K. H., Eds.; ACS Symp. Series No. 141; American Chemical Society: Washington, DC, 1980; p 303. (c) Odell, J. A.; Keller, A.; Atkins, E. D. T.; Miles, M. J. *J. Mater. Sci.* **1981**, *16*, 3309.

[23] Wellman, M. W.; Adams, W. W.; Wolff, R. A.; Wiff, D. R.; Fratini, A. V. *Macromolecules* **1981**, *14*, 935.

[24] Osaheni, J. A.; Jenekhe, S. A. manuscript in preparation.

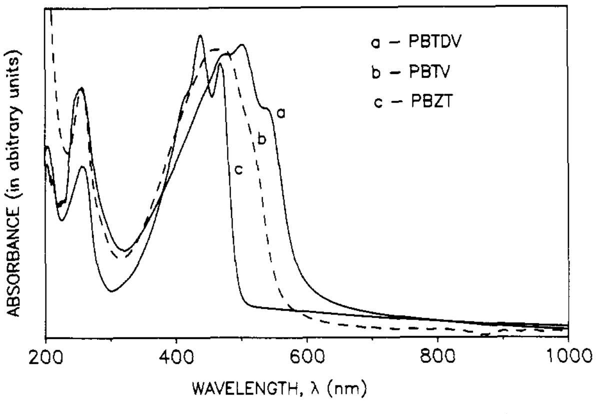

Figure 8. Optical absorption spectra of thin films of (a) PBTDV, (b) PBTV, and (c) PBZT.

the well-known PBZT (2.48 eV).[4a] This result is in accord with other studies that showed that vinylene-linked conjugated polymers such as poly(*p*-phenylenevinylene) (PPV)[14a] and poly(thiophenevinylene) (PTV)[15a] have smaller optical bandgaps than the corresponding parent polymers. It is interesting that PBTV has a smaller bandgap than PPV (2.43eV).

Figure 8 shows the optical absorption spectrum of the divinylene-linked polymer PBTDV along with those of the other benzobisthiazole polymers. The optical bandgap and the λ_{max} of π–π^* transition in PBTDV are 2.07 eV and 500 nm, respectively (Table III). Clearly, from Figure 8 and Table III, one sees a progressive reduction in the bandgap and red shift of the λ_{max} in progressing from *p*-phenylene linkage in PBZT to the vinylene (PBTV) and divinylene linkage (PBTDV). Of particular significance is the further reduction in the bandgap observed in going from vinylene to divinylene (*trans,trans*-butadiene) linkage. This is a consequence of increasing the *trans*-polyacetylene (E_g = 1.5 eV)[17] segment in the backbone. Although the *trans,trans*-butadiene segment is not expected to have properties approaching *trans*-polyacetylene, its presence on the PBTDV backbone makes PBTDV more of a block copolymer compared to PBTV which is best thought of as an alternating copolymer.

Observation of the optical absorption spectra of the conjugated benzobisthiazole polymers in Figure 8 shows that the bandwidth of the π–π^* transition is in the decreasing order PBTDV > PBTV > PBBT > PBZT. On the other hand, the optical bandgap is decreasing in the order PBZT > PBBT > PBTV > PBTDV. These results suggest that the divinylene- and vinylene-linked polymers (PBTDV, PBTV) have better electronic delocalization than the *p*-phenylene-linked polymer (PBZT). The implication of this is that it may be a result of better coplanarity of the vinylene and divinylene moieties with the benzobisthiazole or the effects of stronger intermolecular interactions previously evidenced in the solubility of the polymers or both. To shed light on the role of intermolecular interactions on the optical properties of these benzobisthiazole polymers, the optical absorption spectra have been obtained in solution. Figure 9 shows the optical absorption spectra of PBTDV and its model compound BHBBT in methanesulfonic acid (MSA) solution. Both spectra in Figure 9 exhibit similar features, as expected. The optical absorption maximum (λ_{max}) of the polymer (λ_{max} = 495 and 525 nm) is significantly red shifted from the model compound (λ_{max} = 412 nm), reflecting the greater electronic delocalization beyond the repeat unit of PBTDV. The bandwidth, λ_{max}, and optical absorption threshold of PBTDV in solution are reduced relative to the solid-state spectrum. Thus, interchain interactions contribute to the observed optical properties of the conjugated benzobisthiazole polymers. However, the progressive trend in the optical band gap or λ_{max} observed in the solid state spectra are also seen in the solution spectra as shown in Figure 10. This suggests that *intramolecular* effects still dominate the intrinsic electronic properties of this class of polymers.

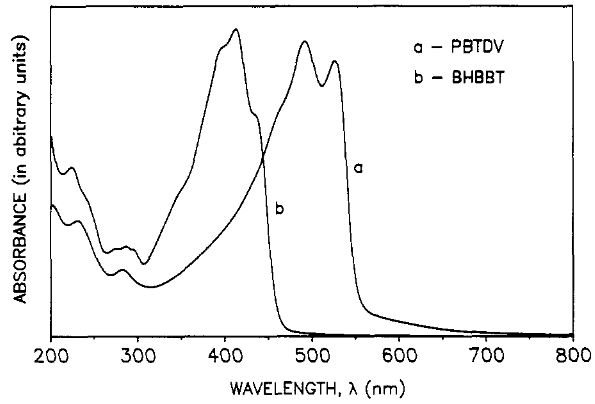

Figure 9. Optical absorption spectra of PBTDV and model compound BHBBT in methanesulfonic acid solution.

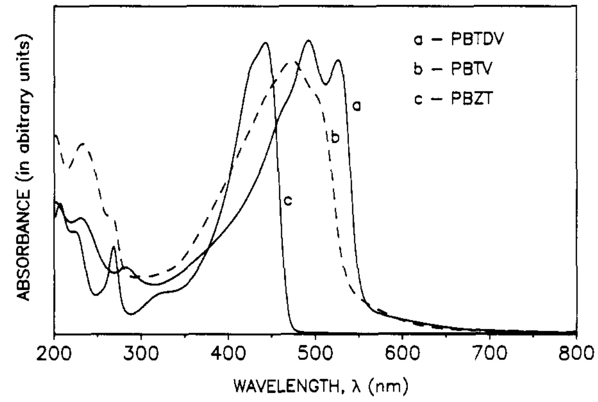

Figure 10. Solution optical absorption spectra of (a) PBTDV, (b) PBTV, and (c) PBZT in methanesulfonic acid.

Prospects for Enhanced Electronic, Optoelectronic, and Nonlinear Optical Properties. One of the main reasons for our synthesis and investigation of the present new conjugated polymers is to explore the molecular engineering approach as a means of the structural basis for the optimization of the desired solid-state properties. For example, applications of conjugated polymers in optoelectronics require spectral tunability of the luminescent properties in the blue-green as well as in the red.[25,26] This requires tunability of the optical bandgap of the polymers over a wide range. The results of the present study show that the optical bandgap of the benzobisthiazole polmers in Chart I varies from ~2 to 3.65 eV. Also, our prior studies of the third-order nonlinear optical susceptibility $\chi^{(3)}(-3\omega;\omega,\omega,\omega)$ of PBZT in the wavelength range 0.8–2.5 μm revealed that the $\chi^{(3)}$ was large (10^{-10}–10^{-11} esu).[11] The present results on the electronic structure and optical properties of PBBT, PBTV, and PBTDV suggest that they can be expected to have improved nonlinear optical

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[25] (a) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Mark, R. N.; Mackay, K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539. (b) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.

[26] Jenekhe, S. A., Ed. *Macromolecular Host-Guest Complexes: Optical, Optoelectronic, and Photorefractive Properties and Applications*; Materials Research Society Proceedings; Materials Research Society: Pittsburgh; Vol. 277, 1992.

properties. Preliminary measurement of the steady-state photoconductivity of PBZT shows that it is large. We can thus also expect enhanced and spectrally tunable photoelectronic properties in the new benzobisthiazole polymers. The detailed electronic, photoelectronic, and nonlinear optical properties of these polymers are currently under investigation.

Conclusions

We have successfully synthesized, characterized, and processed new vinylene- and divinylene-linked conjugated rigid-rod benzobisthiazoles which are materials for potential electronic, optoelectronic, and nonlinear optical applications. The soluble coordination complexes of these rigid-rod polymers with Lewis acids ($AlCl_3$, $GaCl_3$) in organic solvents provide both a means to process the materials into optical-quality films and coatings and a unique opportunity to characterize their molecular structures by NMR spectra. The results show that the longer the *trans*-polyacetylene segment introduced into the polybenzobisthiazole backbone, the lower the optical bandgap of this class of polymers, demonstrating the correctness of the molecular design approach. By replacing the *p*-phenylene ring in PBZT with a *trans*-divinylene moiety in the polymer repeat unit (PBTDV), there is a 0.4-eV decrease in the optical bandgap. The new synthesis and results on the optical and spectroscopic studies of PBTV correct an earlier report[16] on the adverse role of the vinylene linkage in the benzobisthiazole polymers that resulted from an unsuccessful synthesis of this polymer at the air/water interface. The enhanced solvent resistance of PBTV and PBTDV compared to PBZT also make them attractive for applications in hostile environments.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-912-0001) and by Amoco Foundation. We thank a reviewer who brought ref 10 to our attention.

Registry No. **2a** (copolymer), 143104-73-8; **2a** (SRU), 90940-20-8; **2b** (copolymer), 143104-74-9; **2b** (SRU), 143104-77-2; **2c** (copolymer), 143104-75-0; **2c** (SRU), 143104-78-3; DABDT, 15657-79-1; BHBBT, 143104-72-7; $AlCl_3$, 7446-70-0; 2,4-hexadienoic acid, 110-44-1.

Low-Temperature Pyrolytic Transformations of Tri-*tert*-butoxysiloxy Derivatives of Aluminum to Aluminosilicate Materials

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The tri-*tert*-butoxysiloxy complex $\{Me_2Al[\mu\text{-}OSi(O^tBu)_3]\}_2$ (**1**) was prepared by the reaction of $[AlMe_3]_2$ with $HOSi(O^tBu)_3$. Crystals of **1** are tetragonal ($P4_2nm$) with $a = 14.684$ (3) Å, $c = 9.463$ (2) Å, $V = 2041.8$ (9) Å^3, $Z = 4$, and $R_F = 5.77\%$. Molecules of **1** in the crystal have a folded Al_2O_2 core (156.2°), probably because of steric interactions involving the bulky siloxy groups. A trimeric derivative, $[Me(^tBuO)AlOSi(O^tBu)_3]_3$ (**2**), was obtained by addition of *tert*-butyl alcohol to **1**. Compounds **1** and **2** were investigated as precursors to aluminosilicate materials. In the solid state, **1** undergoes thermolysis at low temperatures (150–200 °C) by cleanly eliminating isobutylene (6 equiv), along with methane and water. Clean conversion to a $Al_2O_3\cdot 2SiO_2$ material is observed by thermal gravimetric analysis (TGA) and elemental analysis. Differential thermal analysis (DTA) and X-ray powder diffraction (XRD) show that mullite crystallizes at about 1000 °C, and at 1200 °C, mullite particles of about 15 nm are produced (as calculated from the Scherrer equation). Compound **2** exhibits similar pyrolytic conversions, except that much higher surface areas are observed for the aluminosilicates produced. For example, thermolysis of **2** at 200 °C gives a sample with a BET surface area of 270 m^2 g^{-1}, compared to a surface area of only 30 m^2 g^{-1} for a sample obtained similarly from **1**. Compound **2** also cleanly decomposes by elimination of isobutylene (12 equiv). The network-forming thermolyses of **1** and **2** are facile enough to be conveniently carried out in solution. For example, **1** is pyrolyzed in refluxing toluene, resulting in a polymerization that resembles the sol–gel process. A gel powder obtained from this procedure had a surface area of 210 m^2 g^{-1} and was composed of small particles (ca. 500 nm in diameter) consisting of much smaller grains (by transmission electron microscopy, TEM). Heating this sample to 800 °C increased the BET surface area to 280 m^2 g^{-1}, and further heating to 1200 °C produced mullite particles (average size 18 nm, by XRD) that were densely packed into an amorphous silica matrix (by TEM).

Introduction

Aluminosilicates are technologically important as catalysts,[1] catalyst supports,[2] and structural materials.[3] Development of new chemical and physical properties for such materials will rely heavily on discovery of new routes to aluminosilicate networks. Low-temperature routes, such as those based on hydrolysis of alkoxides in solution (the sol–gel process), are particularly attractive since they offer the possibility for providing new (metastable) structures. Sol–gel routes to Al_2O_3–SiO_2 systems based on cohydrolysis

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