# Synthesis and Processing of Heterocyclic Polymers as Electronic, Optoelectronic, and Nonlinear Optical Materials. 4. New Conjugated Rigid-Rod Poly(benzobis(imidazole))s

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*Received June 16, 1994*®

ABSTRACT: New conjugated rigid-rod poly(benzobis(imidazole))s incorporating varying lengths of *trans*-polyene segments and 1,4-phenylenebis(vinylene) linkages have been synthesized and characterized by infrared, $^1$H NMR, and electronic absorption spectra. Thin films of the polymers were prepared from their soluble coordination complexes. The $\pi-\pi^*$ optical band gap of thin films of the new polymers was in the range 1.8–2.3 eV which is smaller than the corresponding poly(benzobis(thiazole))s. In spite of the structural modifications which ensure strong interchain interactions in the new polymers, they still exhibit significant moisture sensitivity, absorbing equilibrium moisture of ~6–9 wt % which is however smaller than the well-known poly(1,3-phenylenebibenzimidazole) (PBI) which absorbs ~15 wt %. It is suggested that the moisture sensitivity of the poly(benzobis(imidazole))s is intrinsic to the N–H group and also partly explains the luminescence quenching in thin films. However, the poly(benzobis(imidazole))s are highly fluorescent in dilute solution.

## Introduction

Our studies exploring the heterocyclic rigid-rod polymers as electronic, optoelectronic, and nonlinear optical materials have included earlier reports on poly(benzobis(thiazole))s,[1] poly(quinoline)s,[2,3] and poly(anthrazoline)s.[2,3] These conjugated rigid-rod polymers have interesting photoconductive,[4,5] light-emitting,[6–8] and third-order nonlinear optical properties[9,10] that have potential for applications in optoelectronics and photonics. Apart from the potential device applications of these materials, our studies are also aimed at understanding the underlying structure–property relationships.[1–10] For example, comparative studies on poly(*p*-phenylenebenzobis(thiazole)) (PBZT) and poly(*p*-phenylenebenzobis(oxazole)) (PBO) and derivatives have explored the role of the heteroatoms (S, O) on the electronic, optoelectronic, and nonlinear optical properties, among other structural factors investigated. It was shown that the sulfur- and oxygen-containing polymers PBZT and PBO had very similar nonlinear optical properties throughout the spectral range investigated by third harmonic generation spectroscopy.[10a] The implication of these earlier results is that the analogous nitrogen-containing poly(benzobis(imidazole)) may have optical properties similar to those of PBZT and PBO. However, it is known that poly(1,3-phenylenebibenzimidazole) (PBI) is moisture sensitive, absorbing ~15 wt % water at equilibrium in a 100% relative humidity atmosphere.[11] Most of the earlier studies on PBI and other poly(benzimidazole)s thus focused largely on their development as fire resistant materials and for membrane applications.[11–13] Our synthesis and investigation of new conjugated poly(benzobis(imidazole))s is aimed at the detailed understanding of the effects of molecular structure on the properties of the heterocyclic poly(benzobis(azole))s, including the possible effects of moisture in the case of the benzobis(imidazole) polymers.

In this paper we report the synthesis, characterization, thin film processing, and optical properties of the conjugated poly(benzobis(imidazole))s shown in Chart 1. The series of polymers include the parent poly(benzobis(imidazole)) (PBBI), poly(benzobis(imidazole)–vinylene) (PBIV), poly(benzobis(imidazole)–divinylene) (PBIDV), poly(benzobis(imidazole)–1,4-phenylenebis(vinylene)) (PBIPV), and poly(bibenzimidazole–divinylene) (PBBIDV). The new nonconjugated polymer poly(benzobis(imidazole)–dodecamethylene) (PBIC12), as well as the previously reported poly(*p*-phenylenebenzobis(imidazole)) (PBZI),[14] were also synthesized for the purposes of comparative studies. A wide variation in optical absorption spectra was observed with the introduction of different linkages into the poly(benzobis(imidazole)) backbone, similar to what was observed in the benzobis(thiazole) polymers.[1] The moisture sensitivity of the new poly(benzobis(imidazole))s and the effect of the absorbed moisture on the steady state photoluminescence was also investigated.

## Experimental Section

**Materials and Purification.** 1,2,4,5-Tetraaminobenzene tetrahydrochloride (TABH) was obtained from Fluka Chemicals and was purified by decolorization and recrystallization under nitrogen atmosphere using the literature method.[15] TABH (20 g) was dissolved in 500 mL of deaerated 10 wt % hydrochloric acid solution. Activated charcoal (~8 g) was added and the suspension was stirred for 15 min. It was subsequently filtered through a fritted glass. The pure TABH was recrystallized from the clear filtrate by adding ~120 mL of concentrated hydrochloric acid. It was subsequently dried over phosphorus pentoxide in an Abderhalden drying apparatus by refluxing hexane for 24 h.

Fumaric acid (99.5+%, Fluka), oxalic acid (anhydrous, Aldrich), and 3,3′-diaminobenzidine (>99%, Aldrich) were used as received. *trans,trans*-Muconic acid (98%, Aldrich) was recrystallized from a large volume (5 g/250 mL) of boiling water.[16] The pure crystals were obtained as small prisms (mp 314 °C). 1,4-Phenylenediacrylic acid (98%, Aldrich) was recrystallized as reported previously.[8] Poly(phosphoric acid) (PPA) and 85% phosphoric acid (ACS reagent grade) were purchased from Aldrich Chemical and used as received to prepare 77% poly(phosphoric acid) used in the dehydrochlorination of TABH. Phosphorus pentoxide ($P_2O_5$) was obtained from Baker Inc. and used as received.

**Polymer Synthesis. Poly(benzobis(imidazole)) (PBBI).** TABH (4.0 g, 14.18 mmol) was dissolved in 12 g of 77% PPA

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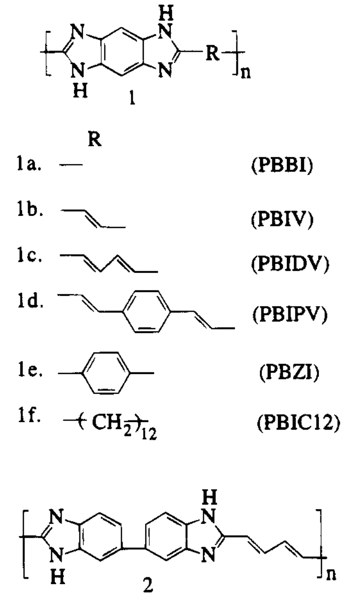
® Abstract published in *Advance ACS Abstracts,* January 1, 1995.

**Chart 1**



(deaerated) in a glass reactor fitted with a mechanical stirrer, two gas ports, and a side arm. The reaction vessel was purged with nitrogen for 20 min, and dehydrochlorination was carried out at 80 °C under vacuum for 24 h. After complete dehydrochlorination, the reaction mixture was cooled to 50 °C under a nitrogen atmosphere and 1.277 g (14.18 mmol) of oxalic acid was added. Fresh $P_2O_5$ (8 g) was added under positive pressure to compensate for the calculated water of condensation. The reaction temperature was increased to 120 °C and held at this temperature for 10 h. The reaction temperature was then raised to 140 °C and finally to 180–200 °C, and the reaction was allowed to proceed at the elevated temperatures (180–200 °C) for 36 h. The polymerization dope in PPA (blue-green in color) was cooled to room temperature and precipitated in water. It was purified by extraction of the PPA with water for 3 days. FTIR (KBr pellet, $cm^{-1}$): 3408, 3010, 1616, 1512, 1447, 1356, 1256, 1179, 1139, 1069, 841.

**Poly(benzobis(imidazole)–vinylene) (PBIV).** The polymerization was carried out using a 10 wt % polymer concentration. TABH (5.2 g, 18.3 mmol) was dehydrochlorinated in 16.5 g of deaerated 77% PPA. Fumaric acid (2.125 g, 18.3 mmol) and 12.2 g of $P_2O_5$ were added. The temperature was gradually raised to 120 °C over 6 h and then to 160 °C and finally to 180 °C. The polymerization mixture became yellowish-brown in color. Polymerization was allowed to proceed for 24 h at 180 °C before precipitating the polymer dope in water. The precipitated polymer was purified by extraction for 3 days with a large volume of water. FTIR (KBr pellet, $cm^{-1}$): 3300, 3010, 1629, 1388, 1297, 1238, 1151, 1015, 960, 841, 669.

**Poly(benzobis(imidazole)–divinylene) (PBIDV).** TABH (2.2 g, 7.75 mmol) was reacted with 1.1 g (7.75 mmol) of *trans,-trans*-muconic acid by following the same procedure as outlined for the PBIV synthesis. The polymer concentration was 8 wt %. The reaction temperature was raised to 85 °C over 2 h and held at this temperature for 6 h before finally increasing it to 120 °C. The viscosity of the reaction mixture rose rapidly, with the color changing from yellow to yellowish-green at 120 °C. The polymerization dope exhibited stir opalescence at this temperature. The reaction was allowed to proceed for 14 h at 120 °C. The polymerization dope was cooled to room temperature and precipitated in water. The fibrous polymer was shredded into small pieces with a blender to facilitate purification which consists of extraction with water for 3 days. FTIR (free standing film, $cm^{-1}$): ~3400, 3040, 1619, 1500, 1383, 1278, 1151, 1091, 984, 828. $^1H$ NMR ($CD_3NO_2/AlCl_3$, 300 MHz, TMS), ppm: $\delta$ 7.5 (d, 2H), 8.0 (d, 2H), 8.4 (d, 2H), 9.1 (s, 2H).

**Poly(benzobis(imidazole)–1,4-phenylenebis(vinylene)) (PBIPV).** TABH (2.0 g, 7.04 mmol) was reacted with 1.54 g (7.04 mmol) of 1,4-phenylenediacrylic acid by following the same procedure outlined for the PBIDV synthesis. The reaction was allowed to proceed for 24 h at 120 °C. The polymerization dope was cooled to room temperature and precipitated in water. The fibrous polymer (red in color) was shredded into small pieces with a blender to facilitate purification which consists of extraction with water for 3 days. FTIR (free standing film, $cm^{-1}$): ~3400–3384, 3203, 3045, 1636, 1595, 1567, 1521, 1420, 1399, 1287, 1002, 962, 842, 809, 726. $^1H$ NMR ($CD_3NO_2/AlCl_3$, 300 MHz, TMS), ppm: $\delta$ 7.6 (d, 2H), 8.0 (m, 2H), 8.2 (m, 2H), 8.4 (d, 4H), 9.2 (s, 2H).

**Poly(benzobis(imidazole)–dodecamethylene) (PBIC12).** TABH (1.76 g, 6.2 mmol) was reacted with 1.6 g (6.2 mmol) of dodecanedicarboxylic acid by following the same procedure outlined for the PBBI synthesis. The polymer concentration was 5 wt %. The polymerization was carried out for 15 h at 120 °C. The polymerization dope was cooled to room temperature and precipitated in water. The fibrous white polymer was shredded into small pieces with a blender to facilitate purification which consists of extraction with water for 2 days. FTIR (free standing film, $cm^{-1}$): ~3400–3300, 3058, 2924, 2852, 1619, 1570, 1448, 1344, 1230, 1150, 1059, 850. $^1H$ NMR ($CD_3NO_2/AlCl_3$, 300 MHz, TMS), ppm: $\delta$ 1.2–1.7 (m, 16H), 1.9 (t, 4H), 3.5 (t, 4H), 6.9 (br, 2H), 8.2 (s, 2H).

**Poly(bibenzimidazole–divinylene) (PBBIDV).** *trans,-trans*-Muconic acid (1.0 g, 7.04 mmol) was condensed with 1.508 g (7.04 mmol) of 3,3′-diaminobenzidine in 25 g of 83.3 wt % PPA under a nitrogen atmosphere. The polymerization reaction was carried out for a total of 30 h; 6 h at 100 °C and 24 h at 140 °C. The yellowish-brown polymerization dope was precipitated in water and purified in a manner similar to PBIV purification. FTIR (KBr pellet, $cm^{-1}$): ~3400, 3010, 1627, 1504, 1458, 1287, 1249, 1081, 995, 881. $^1H$ NMR ($CD_3NO_2/AlCl_3$, 300 MHz, TMS), ppm: $\delta$ 7.4 (s, 2H), 7.9–8.4 (broad peaks, 8H), 9.0 (s, 2H).

**Poly(*p*-phenylenebenzobis(imidazole)) (PBZI).** This polymer has previously been synthesized.[12] It was synthesized for our studies under conditions similar to those for the other polymers, e.g. PBIPV.

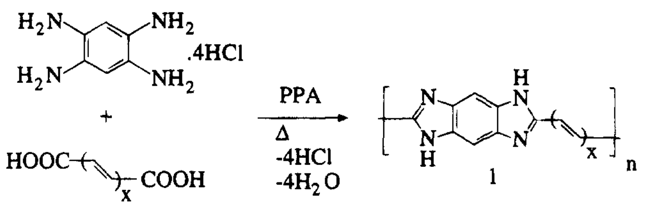
In all cases, the purified sample was treated further with an aqueous solution of 0.1 M NaOH and subsequently washed with a large volume of water to ensure that it was free of any residual acid polymerization medium (PPA).

**Preparation of Thin Films.** Thin films for optical absorption spectra and IR studies were prepared from the soluble Lewis acid complexes as described previously.[1,17] Thick free standing films of PBIDV were prepared from the polymerization dope either by shearing the dope at 70 °C between two glass slides and coagulating in water or by precipitating dilute methanesulfonic acid solution (0.25 g/dL) of PBIDV in water and filtering through a fritted glass to form an aggregate film upon drying. The resulting film was then extracted with water typically for 3 days to free it from any acid.

**Characterization.** The intrinsic viscosity $[\eta]$ of all the polymers was measured in methanesulfonic acid at 30 °C using a Cannon Ubbelohde capillary viscometer. Dilute solutions (0.1–0.3 g/dL) of the polymers in MSA were used for the intrinsic viscosity measurements. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were done using a DuPont 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 while DSC thermograms were obtained in nitrogen at a heating rate of 20 °C/min. Moisture absorption in the polymers was determined by using a thermogravimetric analyzer to monitor the weight gained by a dry sample of the polymers in the presence of a stream of saturated air (~100% relative humidity) until equilibrium was established. After absorbing equilibrium moisture, the polymers were heated at 10 °C/min in the presence of dry nitrogen to 200 °C and the weight loss was recorded. The weight loss was used as an independent check on the absorbed moisture.

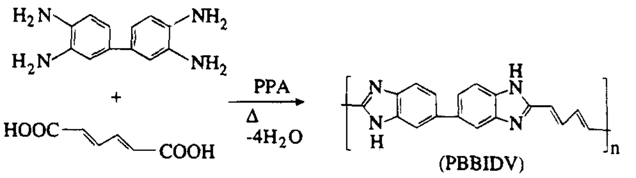
FTIR spectra were taken at room temperature using a Nicolet Model 20SXC Fourier transform infrared (FTIR) spectrometer under nitrogen purge. Free standing films were

**Scheme 1**



1a. x = 0 (PBBI)
1b. x = 1 (PBIV)
1c. x = 2 (PBIDV)

**Scheme 2**



used for obtaining the IR spectra of PBIDV, PBIPV, PBIC12, and PBZI, and KBr pellets were used for PBBI, PBIV, and PBBIDV. The $^1$H 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(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. Steady state photoluminescence studies were done on dilute solutions of the polymers and on thin films by using a Spex Fluorolog-2 spectrofluorometer as described previously.[8] X-ray powder diffraction of PBIDV was obtained at Oneida Research (Whitesboro, NY) on a Siemen D500 automated powder diffractometer equipped with a graphite monochromator as described previously.[1]

## Results and Discussion

**Polymerization and Polymer Structure.** The synthesis of the new poly(benzobis(imidazole))s was based on the $P_2O_5$ adjustment method of Wolfe,[14,18] and it involves the condensation polymerization of the appropriate diacid and tetraaminobenzene to form the benzobis(imidazole) ring in a polymer backbone, as shown in Scheme 1. The nonfused bibenzimidazole structure (PBBIDV) was synthesized using diaminobenzidine with *trans,trans*-muconic acid, as shown in Scheme 2. The yields of PBBI and PBIV were typically 70–80% and were much lower than the yields of PBIDV, PBIPV, and PBBIDV, which were essentially quantitative (>95%). The lower yields obtained in the PBBI and PBIV syntheses are due to the lower reactivity of the acids used. Our earlier finding with the synthesis of benzobis(thiazole) polymers[1] was that phosphorylation increases the reactivity of the diacids in the following order: *trans,trans*-muconic acid > fumaric acid > oxalic acid. In the synthesis of PBBI, the temperature had to be raised to 180–200 °C to ensure complete closure of the imidazole rings, whereas in the case of PBIDV and PBIPV, a maximum polymerization temperature of 120 °C was sufficient to achieve complete cyclization. On the other hand, because of the lower reactivity of 3,3′-diaminobenzidine compared to 1,2,4,5-tetraaminobenzene, a maximum temperature of 140 °C was used in the synthesis of PBBIDV. The synthesis of PBIDV was found to be unique among the benzobis(imidazole) polymers because the polymerization occurred in the liquid crystalline phase even at 8 wt % polymer concentration, whereas the lyotropic liquid crystalline phase could not be achieved in the other polymers at 10 wt % polymer concentration, apparently due to the lower molecular weight of the resulting polymers compared with PBIDV.

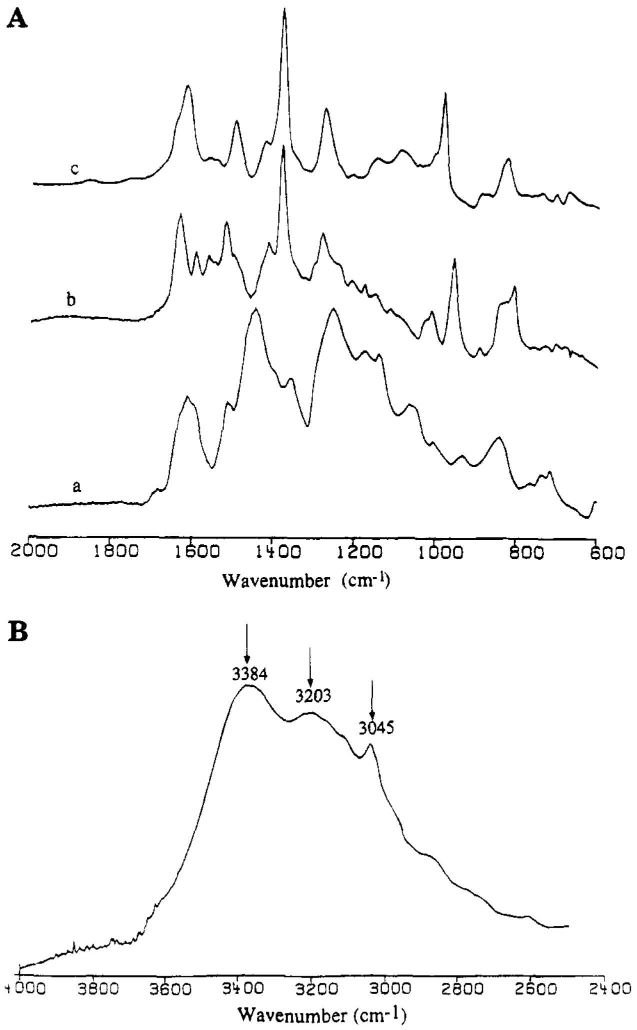


**Figure 1.** (A) FTIR absorbance spectra of (a) PBBI, (b) PBIPV, and (c) PBIDV. (B) FTIR absorbance spectrum of PBIPV showing the N–H stretching region.

The polymer structures were established primarily by FTIR and $^1$H NMR spectra. Figure 1 shows the FTIR spectra of PBBI, PBIDV, and PBBIDV. It is observed from this figure that there is no residual carbonyl (C=O) peak between 1720 and 1650 cm$^{-1}$ which suggests that cyclization to form the benzobis(imidazole) ring was complete in all the polymers. Notably, the C=N and the C–N bands characteristic of the benzobis(imidazole)s[12a,19] appear between 1616 and 1629 and 1377 and 1388 cm$^{-1}$, respectively, in all the polymers. The asymmetric stretching vibration of the C=C bonds in PBIV, PBIDV, PBIPV, and PBBIDV appear in the same region as the C=N stretching bands of the imidazole ring; however, the C–H out-of-plane bending in the vinylene and divinylene linkages appears at ~960, 984, 962, and 995 cm$^{-1}$ in PBIV, PBIDV, PBIPV, and PBBIDV, respectively. These bands are absent in PBBI, as shown in Figure 1A.

One of the structural features that distinguishes the poly(benzobis(imidazole))s from either the sulfur- or oxygen-containing poly(benzobis(azole))s, is the presence of the N–H group in the backbone of the former. Figure 1B shows a typical N–H stretching region of the poly(benzobis(imidazole))s, as exemplified by the FTIR

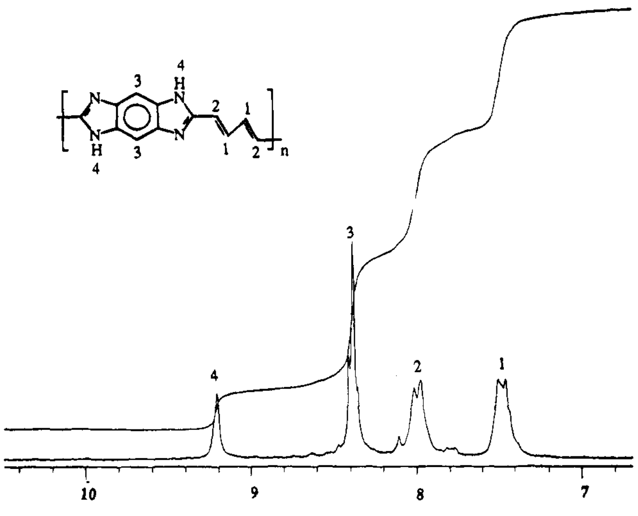


**Figure 2.** $^1$H NMR spectrum of PBIDV in $CD_3NO_2/AlCl_3$ and its assignment.

**Table 1. Summary of Intrinsic Viscosity [η], Thermal Stability, and Optical Properties of Poly(benzobis(imidazole))s**

| polymer | [η][a] (dL/g) | TGA[b] $T_d$ (°C) | $\lambda_{max}$[c] (nm) | π–π* gap[c] $E_g$ (eV) |
|---|---|---|---|---|
| PBBI | 0.26 | 530 | 529 | 1.80 |
| PBIV | 0.35 | 536 | 466 | 2.07 |
| PBIDV | 6.30 | 475 | 525 | 1.91 |
| PBIPV | 2.70 | 576 | 491 | 2.08 |
| PBBIDV | 0.65 | 420 | 420 | 2.30 |
| PBZI | 0.70 | 680 | 424 | 2.48 |
| PBIC12 | 1.5 | 440 | 295 | 3.75 |

[a] Obtained in methanesulfonic acid at 30 °C. [b] Onset of decomposition ($T_d$) in flowing nitrogen at 10 °C/min heating rate. [c] Values for thin films.

spectrum of PBIPV. The spectrum shows broad features between 3600 and 2900 cm$^{-1}$, indicating that the N–H groups are hydrogen bonded either to imine nitrogens on neighboring chains or to water. This feature is typical of most N–H group-containing molecules in the solid state. The asymmetric N–H stretch in PBIPV is observed at 3384 cm$^{-1}$ due to hydrogen bonding, while the symmetric stretching mode appears at 3203 cm$^{-1}$ for the same reason. The N–H stretching frequencies of the other polymers appeared between ~3408 and 3200 cm$^{-1}$.

The solubility of the poly(benzobis(imidazole))s in nitromethane containing Lewis acids provided a unique opportunity to obtain $^1$H NMR spectra to confirm their structures. Although several poly(benzimidazole)s have been synthesized in the past, their molecular structures were characterized primarily by FTIR spectra.[12,13] The $^1$H NMR spectrum of PBIDV in deuterated nitromethane containing aluminum trichloride which is shown in Figure 2 exemplifies the results. The assignment of the resonances is also shown in Figure 2, in agreement with the proposed structure, including the *trans,trans*-divinylene conformation. However, the integration of the amine (N–H) protons of the ring was not very accurate due to the rapid proton exchange.[20] The N–H proton resonance in the conjugated poly(benzobis(imidazole))s was at 9.0–9.2 ppm whereas the resonance of this proton in the nonconjugated PBIC12 was at 6.9 ppm. The $^1$H NMR spectra were all in good agreement with the proposed structures of the polymers in Chart 1.

**Intrinsic Viscosity and Molecular Weight.** A summary of the intrinsic viscosity [η] of the poly(benzobis(imidazole))s measured in methanesulfonic acid at 30 °C is given in Table 1. The values are in the range of 0.26 for PBBI to 6.30 dL/g for PBIDV. The intrinsic viscosity of PBIDV (6.3 dL/g) indicates that it is a relatively high molecular weight polymer. On the basis of the intrinsic viscosity–molecular weight relationship established for poly(*p*-phenylenebibenzimidazole)[12a] a rough estimate of the molecular weight of PBBIDV is ~18 000 and that of PBIDV is on the order of 100 000. The true molecular weight of these polymers could be quite different from these estimates. The intrinsic viscosities of the other polymers were quite low compared to that of PBIDV apparently due to the lower reactivity of oxalic acid and fumaric acid coupled with the possibility that the synthesis procedure may not have been fully optimized. In spite of the low intrinsic viscosity of PBBI and PBIV, thin films suitable for optical absorption and nonlinear optical characterizations were successfully fabricated by spin coating.

**Thermal Stability.** The thermal stability of the poly(benzobis(imidazole))s was assessed in TGA runs in nitrogen at a heating rate of 10 °C/min. The TGA thermograms of PBBI, PBIDV, and PBBIDV in a nitrogen atmosphere are shown in Figure 3. The thermal stability of these polymers is lower than that of PBZI (~680 °C), as would be expected, since the aromatic ring is much more stable than aliphatic moieties. A summary of the decomposition temperature of all the polymers is shown in Table 1. It is observed that PBBIDV shows the lowest thermal stability, with an onset of decomposition of 420 °C. This is apparently due to the *nonfused* bibenzimidazole linkage compared with the other polymers having a *fused* benzobis(imidazole) structure in their backbone. It is interesting that the thermal stabilities of PBIV and PBIDV are higher than those of the corresponding benzobis(thiazole) polymers reported earlier.[1] Poly(benzobis(imidazole))s are known to possess a high temperature resistance; hence they have been widely studied for fire resistant applications.[5,6] In spite of the lower thermal stability of the vinylene-linked poly(benzobis(imidazole))s compared to the widely investigated wholly aromatic PBI, the decomposition in nitrogen is comparable to other conjugated polymers which are currently being studied for device applications.[21] The DSC scans of the polymers did not show any measurable glass transition or melting point when heated from room temperature to 400 °C.

**Film Processing.** Thin films and coatings of the poly(benzobis(imidazole))s were prepared by the Lewis acid ($AlCl_3$, $GaCl_3$) complexation mediated solubilization technique[17] which provides a better way to process these polymers into high optical quality thin films compared with processing from the polymerization dope in poly(phosphoric acid). The otherwise intractable polymers are made solution processible from organic solvents by forming their Lewis acid–base coordination complexes in nitromethane, as described previously.[1,17] Aluminum(III) chloride or gallium(III) chloride in nitroalkanes were found to be effective in forming the soluble coordination complexes of the polymers. It was, however, difficult to dissolve the high molecular weight ([η] = 6.30 dL/g) PBIDV sample in strong acids such as methanesulfonic acid or in Lewis acid/nitromethane systems at high concentrations (e.g. 5 wt %). A much

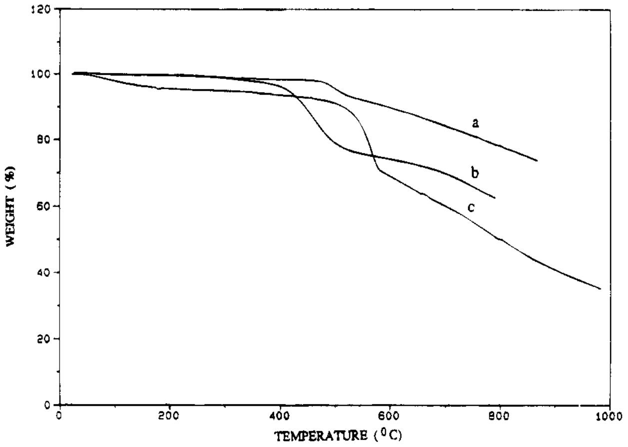


**Figure 3.** TGA thermograms of (a) PBIDV, (b) PBBIDV, and (c) PBBI.

lower molecular weight sample of PBIDV with an intrinsic viscosity of 0.65 dL/g could be readily dissolved at high concentrations in either nitromethane/Lewis acid systems or in protonic acids. We attribute this very high solvent resistance to the nature of chain packing and strong intermolecular interactions in this *trans,-trans*-divinylene-linked poly(benzobis(imidazole)). 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 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 by this proceedure.

Another route to processing PBIDV into thick flexible films is by the method of *aggregation*.[15] It was found that PBIDV could be precipitated from dilute methanesulfonic acid solution (~0.25 g/dL) using a fritted glass, to form microscopic sheets which coalesce into continuous strong metallic green film. This aggregate film forming phenomenon which was originally ascribed to ladder structures[15] as exhibited by the poly(benzimidazobenzophenanthroline) ladder (BBL) has previously been found to be also feasible with the nonladder polymer, *cis*-PBO.[14] Thus, a conceptual link was made between forming the ordered microscopic sheets and the rigid-rod conformation rather than the ladder configuration. However, not all the rigid-rod polymers form microscopic sheets upon coagulation from their dilute protonic acid solutions, for example, polyquinolines[2,3] and PBZT. Appreciable intermolecular interactions are required in the forming of a supermolecular aggregate in solution which translate to the high degree of interchain packing in the bulk when the polymers are precipitated from solution. The molecular geometry of the polymer backbone dictates the extent of chain packing in the bulk, and a linear polymer backbone is expected to give rise to efficient packing.[22] Thus, the film forming ability of PBIDV suggests very strongly that this polymer has the rigid-rod conformation with a linear backbone. The ordered chain packing as a result of the backbone rigidity, interchain hydrogen bonding and the high $\pi$-bond content also explain the appreciable solvent resistance of this polymer. The other polymers, PBBI, PBIV, PBIPV, and PBBIDV did not exhibit this aggregate film forming phenomenon, apparently due to the lower molecular weight of these polymers compared with PBIDV.

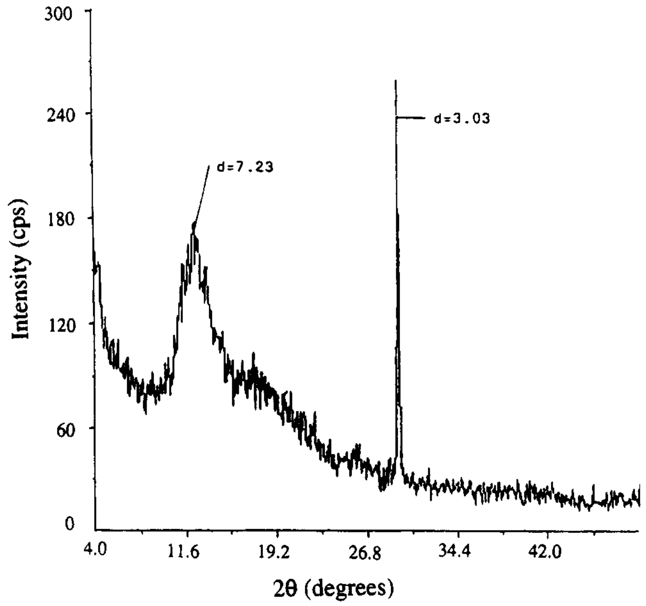


**Figure 4.** X-ray diffraction pattern of PBIDV film.

In order to fully understand the nature of packing in PBIDV and the related poly(benzobis(imidazole))s, an X-ray powder diffraction pattern was taken on a free standing film of PBIDV. As can be seen in Figure 4, the X-ray diffraction pattern of the PBIDV film shows two strong Bragg peaks with *d* spacings at 7.23 and 3.03 Å. This is very similar to the diffraction pattern of BBL which has only two peaks with *d* spacings at 7.5 and 3.3 Å.[23] The 3.3 Å X-ray reflection in BBL corresponds to the interchain spacing. The smaller interchain spacing of 3.03 Å in PBIDV suggests that there is stronger intermolecular interactions in PBIDV compared with BBL, hence the higher solvent resistance. The similarity between the X-ray diffraction patterns of PBIDV and BBL also explains the aggregate film forming ability of these two polymers.

**Optical Properties.** The series of polymers in Chart 1 provides an interesting set for exploring the effects of molecular structure on electronic structure and optical properties of the poly(benzobis(imidazole))s. The nonconjugated PBIC12 should give information on the benzobis(imidazole) ring as an isolated chromophore whereas PBBI facilitates knowing the extent of electronic delocalization between benzobis(imidazole) rings in a conjugated polymer. The different R linkages in the conjugated poly(benzobis(imidazole))s in Chart 1 should shed light on the relative extents of coplanarity and electronic delocalization between the benzobis(imidazole) ring and the R linkages. The effect of a *fused* benzobis(imidazole) ring on the electronic structure relative to the *nonfused* ring can be inferred from comparison of PBIDV and PBBIDV. Finally, conclusions on the effects of the heteroatoms on the electronic structure and optical properties can be drawn by comparing the present results on the poly(benzobis(imidazole))s to previous results on related poly(benzobis(thiazole))s.[1]

Figure 5 shows the optical absorption spectrum of a thin film of PBIC12. As expected for the isolated benzobis(imidazole) chromophore in a nonconjugated polymer, the lowest energy transition is in the UV with a $\lambda_{max}$ at 295 nm and an optical absorption edge of 3.75 eV. The origin of this transition, i.e. whether $n-\pi^*$ or $\pi-\pi^*$, is not clear. Also shown in Figure 5 are the thin film optical absorption spectra of PBBI, PBIV, and

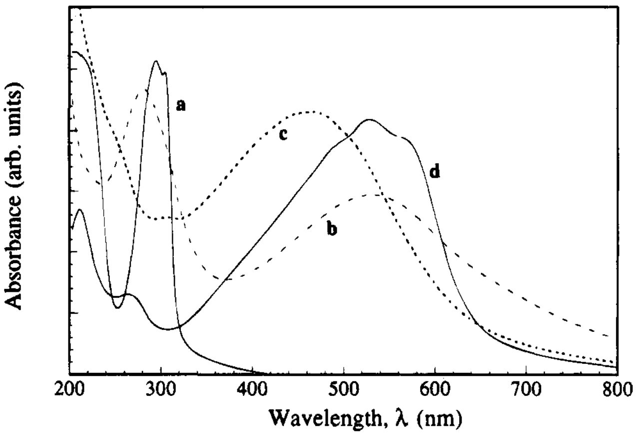


**Figure 5.** Optical absorption spectra of thin films of (a) PBIC12, (b) PBBI, (c) PBIV, and (d) PBIDV.

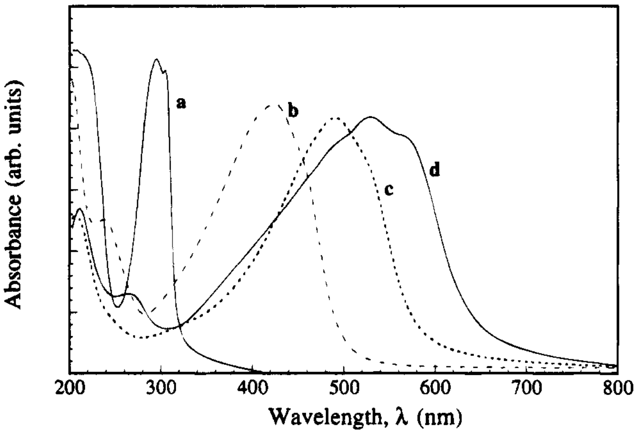


**Figure 6.** Optical absorption spectra of thin films of (a) PBIC12, (b) PBZI, (c) PBIPV, and (d) PBIDV.

PBIDV. All three conjugated polymers show a broad absorption band in the visible which can be assigned to the lowest energy $\pi$–$\pi^*$ transition. Compared to PBIC12, these three polymers dramatically show the effect of electronic delocalization along the polymer backbone. In the case of the parent conjugated poly(benzobis(imidazole)) PBBI, its absorption spectrum has a strong UV band at 281 nm, which is characteristic of the benzobis(imidazole) ring as seen in PBIC12, and a visible band with $\lambda_{\max} = 529$ nm. This shows that there is significant coplanarity between the benzobis(imidazole) rings that facilitates electronic delocalization beyond one repeat unit. It is noteworthy that the oscillator strength of the 281 nm band is about a factor of ~1.8 larger than that of the 529 nm band in PBBI. In contrast to PBBI, the 280 nm band which is characteristic of the benzobis(imidazole) ring has almost disappeared in PBIV and PBIDV which have strong visible absorptions with bands at 466 nm and 525 nm, respectively. Introduction of *trans*-vinylene and *trans,trans*-divinylene linkages clearly results in efficient $\pi$-electron delocalization which implies improved coplanarity between the benzobis(imidazole) ring and the linkages. The red shift of the absorption spectrum of PBIDV compared to that of PBIV is in accord with the increased number of delocalized $\pi$-electrons per repeat unit in going from PBIV to PBIDV.

In Figure 6 are shown the optical absorption spectra of PBZI and PBIPV in comparison to those of PBIC12 and PBIDV. A summary of the optical spectra parameters of the poly(benzobis(imidazole))s, i.e. lowest energy absorption maximun ($\lambda_{\max}$) and absorption edge ($E_g$), is presented in Table 1. The $\lambda_{\max}$ (424 nm) and $E_g$ (2.48 eV) values for PBZI indicate significant delocalization between benzobis(imidazole)s and *p*-phenylene rings. However, the large blue shift of the spectrum of PBZI from PBIDV shows that there is greater coplanarity and electronic delocalization between *trans,trans*-divinylene and the benzobis(imidazole) ring than between *p*-phenylene and the benzobis(imidazole) ring. This result is similar to what was observed in the corresponding benzobis(thiazole) polymers where the *p*-phenylene ring has been established to be twisted ~8–23° from coplanarity with the benzobis(thiazole) ring.[24] The 1,4-phenylenebis(vinylene) linkage in PBIPV improves coplanarity and electronic delocalization and hence the red shift of the absorption relative to PBZI (Figure 6).

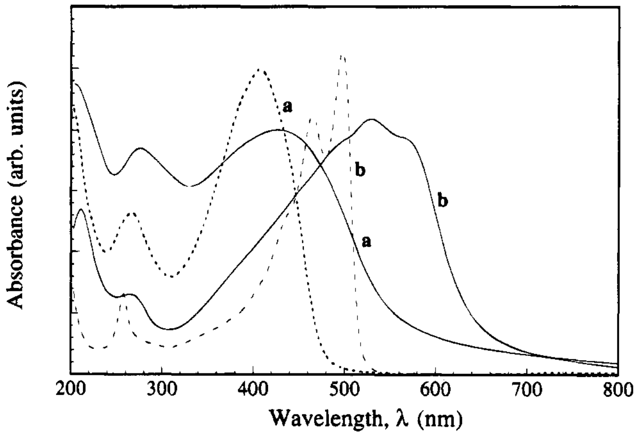


**Figure 7.** Optical absorption spectra of thin films and solutions of (a) PBBIDV and (b) PBIDV: (solid line) film spectra; (dashed line) solution spectra.

Figure 7 shows the solution and thin film optical absorption spectra of PBBIDV and PBIDV which both contain *trans,trans*-divinylene linkage. The effects of the *fused* benzobis(imidazole) ring compared with the *nonfused* bibenzobis(imidazole) ring on the electronic structure and optical properties are evident in the results of Figure 7 and Table 1. In solution as well as in the solid state, the optical spectrum of the nonfused ring polymer is significantly blue shifted from the corresponding fused ring PBIDV. The $\lambda_{\max}$ and $E_g$ values of PBBIDV are 420 nm and 2.3 eV, which are respectively 105 nm and 0.4 eV blue shifted from those of PBIDV.

The present results on the optical properties of the poly(benzobis(imidazole))s when compared to the corresponding poly(benzobis(thiazole))s[1] indicate that there is a significant effect of the heteroatom (S, O, N–H) on the electronic structure and linear optical properties. In general, there is greater electronic delocalization and hence larger $\lambda_{\max}$ and smaller $E_g$ in the poly(benzobis(imidazole))s. The likely reason for the enhanced electronic delocalization is the strong intermolecular hydrogen bonding. It will be interesting to see if the NH heteroatom in the poly(benzobis(imidazole))s and the consequent hydrogen bonding leads to any enhancement of the nonlinear optical properties compared to those of the sulfur- and oxygen-containing poly(benzobis(azole))s.[9,10]

**Moisture Sensitivity and Steady State Photoluminescence.** The poly(benzimidazole)s have been excluded from consideration for structural applications because of the moisture sensitivity of this class of polymers.[11,13] However, the moisture sensitivity can be advantageously used in other technological applications

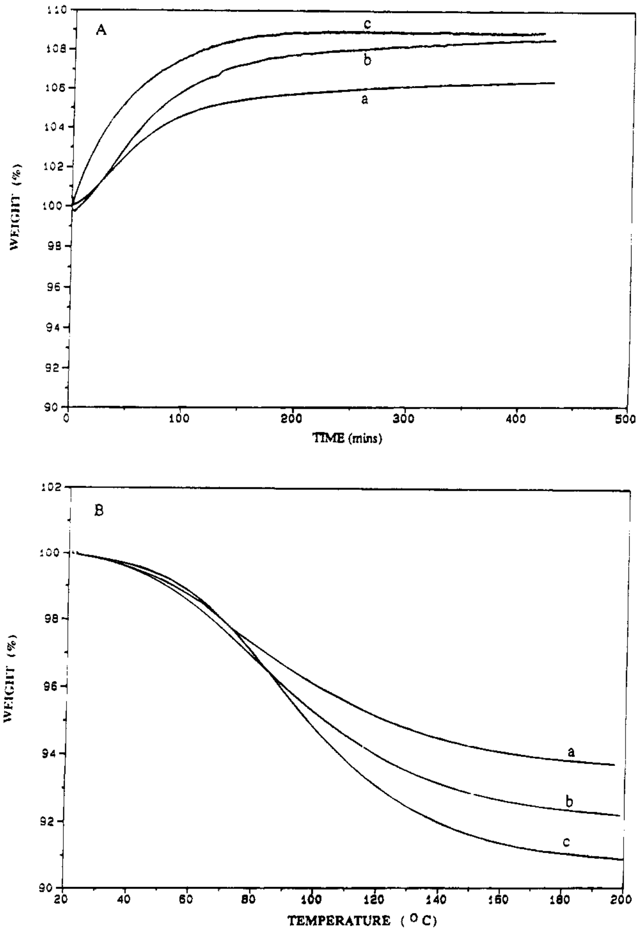


**Figure 8.** (A) Moisture uptake of (a) PBBI, (b) PBIV, and (c) PBZI as a function of time. (B) TGA thermograms showing weight loss versus temperature after equilibrium pickup by (a) PBBI, (b) PBIV, and (c) PBZI.

**Table 2. Equilibrium Moisture Uptake of the Poly(benzobis(imidazole))s**

| polymer | theor max equilibrium moisture (wt %) | exptl equilibrium moisture (wt %) |
|---|---|---|
| PBBI | 18.7 | 6 |
| PBIV | 16.5 | 8 |
| PBIDV | 14.8 | 8 |
| PBZI | 13.4 | 9 |

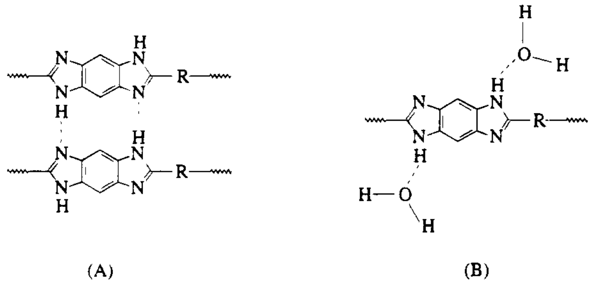


**Figure 9.** Molecular structure of poly(benzobis(imidazole))s showing (A) interchain hydrogen bonding and (B) H bonding of water molecules to the N−H groups.

such as humidity sensors. We investigated the moisture uptake of the poly(benzobis(imidazole))s in an atmosphere of saturated air (~100% relative humidity) by using a thermogravimetric analyzer (TGA) to monitor the weight gained as a function of time after first drying the samples in situ at 200 °C. The weight of the polymer samples at 200 °C was taken as the initial weight in order to take into account any absorbed moisture while cooling to room temperature. After absorbing equilibrium moisture at room temperature, the samples were heated at 10 °C/min under dry nitrogen flow in a TGA pan and the weight loss as a function of temperature was recorded. Figure 8A shows a typical plot of the observed moisture uptake by samples of PBBI, PBIV, and PBZI as a function of time. PBBI absorbs ~6 wt % equilibrium moisture, most of it within the first 2 h of exposure. However, PBIV, PBIDV, and PBZI absorb equilibrium moisture of 8, 8, and 9 wt %, respectively (Table 2). Figure 8B shows a typical plot of the corresponding TGA weight loss curves for PBBI, PBIV, and PBZI samples following equilibrium moisture absorption. The TGA thermograms indicate that all of the absorbed moisture is lost after heating to 200 °C. The amounts of water absorbed (Figure 8A) and water loss (Figure 8B) were similar. A summary of the results for the poly(benzobis(imidazole))s is given in Table 2. The theoretical maximum moisture uptake was calculated on the basis of one molecule of water being hydrogen bonded to each N−H site[19a] of the polymer backbone, as illustrated in Figure 9B. Clearly, the observed moisture sensitivity of the poly(benzobis(imidazole))s is quite high, 6−9 wt %, although lower than that of the well-known PBI which absorbs ~15 wt % equilibrium moisture at 100% relative humidity.[11] The smaller observed moisture absorption in these new polymers compared to PBI and to the theoretical maximum is apparently due to the stronger interchain interactions in the new poly(benzobis(imidazole))s. One would have expected that the *trans,trans*-divinylene- and *trans*-vinylene-linked poly(benzobis(imidazole))s would be less moisture sensitive than PBBI. However, it appears that most of the N−H groups in PBBI are preferentially hydrogen-bonded to the imine nitrogens on neighboring chains, rather than to water.

A recent solid $^1$H NMR study of absorbed water in poly(1,3-phenylenebibenzimidazole) (PBI) concluded that the majority of the absorbed water in PBI is effectively mobile and not bonded to the polymer.[11] Our previous study of the sulfur- and oxygen-containing members of the poly(benzobis(azole))s shows that they are not moisture sensitive.[1] Our results on moisture sensitivity of the new conjugated poly(benzobis(imidazole))s together with the FTIR spectrum of a free standing film of PBIPV shown in Figure 1B suggest that the presence of the N−H group in these polymers is the origin of their moisture sensitivity. In Figure 1B, there are no sharp O−H or N−H stretches which usually appear at ~3620 and 3420 cm$^{-1}$, respectively, for free water and the non-hydrogen-bonded N−H group. The broad features of the N−H stretching regions of the FTIR spectra suggest that polymer−polymer or polymer−water interactions via H-bonding are dominant.

We have previously shown that the conjugated rigid-rod poly(benzobis(azole))s have interesting luminescent properties in dilute solutions and in the solid state.[6−8] For example, dilute solutions of poly(*p*-phenylenebenzobis(thiazole)) and poly(benzobis(thiazole)−1,4-phenylenebis(vinylene)) have 100% fluorescence quantum efficiency in methanesulfonic acid solution ($\leq 10^{-6}$ M) whereas the corresponding solid state quantum efficiency is 6 and 4%, respectively.[7,8] Figure 10 shows the dilute solution ($10^{-6}$ M) emission spectra of PBZI and PBIDV. The spectra show well-resolved vibronic structures similar to the other previously reported poly(benzobis(azole))s. The corresponding fluorescence quantum efficiency in the dilute concentration range (~5 ×

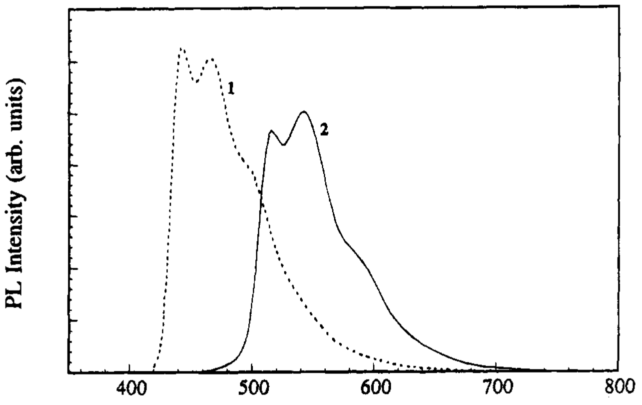


**Figure 10.** Solution emission spectra of (1) PBZI and (2) PBIDV in methanesulfonic acid (~$10^{-6}$ M).

$10^{-7}$ M) is 100%, using quinine sulfate as a fluorophore standard.[25] However, thin films of PBZI, PBIDV, and the other poly(benzobis(azole))s shown in Chart 1 were virtually nonemissive at ambient conditions. The estimated quantum efficiency in the solid state is on the order of $10^{-3}$%, which is about 4 orders of magnitude lower than those of the other sulfur- and oxygen-based poly(benzobis(azole))s.[6-8] Although the strong intermolecular hydrogen bonding in these materials could potentially lead to self-quenching of the excited state, we believe that the presence of absorbed moisture plays a significant role in excited state deactivation in these polymers. Thus, the effect of moisture or relative humidity on luminescence could be one approach to utilizing the poly(benzobis(imidazole))s as humidity sensors. Future studies will address this problem.

## Conclusions

A series of new rigid-rod poly(benzobis(imidazole))s has been synthesized and used to investigate the effects of molecular structure on the electronic structure and optical properties. Solution $^1$H NMR spectra, which are the first reported for any poly(benzobis(imidazole)), in conjunction with FTIR spectra were used to confirm the polymer structures. The soluble Lewis acid coordination complexes of the polymers were used to prepare thin films and coatings of good optical quality. The *trans,-trans*-divinylene-linked polymer, PBIDV, was found to form continuous tough films by aggregation when precipitated from its dilute solution. This result extends the polymers known to exhibit this phenomenon and most importantly confirms that a ladder structure is not essential to film formation by aggregation. The new poly(benzobis(imidazole))s were found to absorb up to 6–9 wt % moisture which partly accounts for the extremely poor luminescence of thin films. In dilute solution in MSA, however, the poly(benzobis(imidazole))s as with previously reported sulfur- and oxygen-based poly(benzobis(azole))s[6-8] are highly luminescent with a fluorescence quantum efficiency of 100%.

**Acknowledgment.** This research was supported by the National Science Foundation (CTS-9311741), the NSF Center for Photoinduced Charge Transfer (CHE-920001), and an Elon Huntington Hooker Fellowship to J.A.O.

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