

Poly(alkylbithiazoles): A New Class of Variable-Bandgap, Conjugated Polymer

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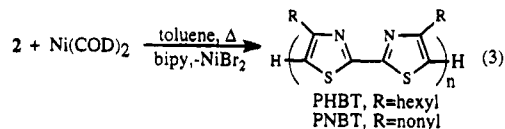
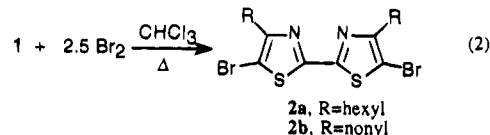
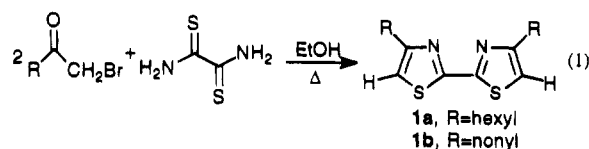
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Highly conjugated polymers have been a subject of intense research activity since the discovery by Shirakawa et al. of the high conductivity of doped poly(acetylene).¹ Since then, these electronically delocalized materials have found application in field effect transistors,² Schottky diodes,^{3,4} electrochromic displays,⁵ light emitting diodes,⁶⁻⁸ solar cells,⁹ EMF shields,¹⁰ push-pull amplifiers,¹¹ batteries,¹² and NLO devices.¹³ Recently, the bandgap behavior and conductivity as a function of the solid-state morphology has received increased attention.¹⁴⁻¹⁶ Here we report a new class of conjugated polymers, poly[5,5'-(4,4'-dialkyl-2,2'-bithiazole)] (PABT), that exhibit a rare type of variable bandgap behavior related to the degree of crystallinity in the solid state.

4,4'-Dialkyl-2,2'-bithiazoles (**1**) are readily prepared from the reaction of halomethyl ketones and dithiooxamide (eq 1).¹⁷ Compounds **1** are readily brominated according to eq 2,¹⁷ and the resulting 5,5'-dibromides



(**2**) may be coupled by a variety of methods. The method of choice for highest molecular weight polymer is the dehalogenative coupling with Ni(0) in refluxing toluene (eq 3).^{17,18} Two previous attempts to prepare homopolymers of bithiazoles were unsuccessful,^{19,20} although several copolymers made by oxidatively coupling 5,5'-bis(thienyl)bithiazoles have been prepared as well as nonconjugated copolymers connected through the 4,4' positions.²⁰⁻²²

Due to the favorable solubilities of the nonyl-substituted intermediates and polymer, most work to date has been performed on the compounds with R = nonyl. As prepared according to eq 3, poly[5,5'-(4,4'-dinonyl-2,2'-bithiazole)] (PNBT) precipitates from hot toluene during the course of the reaction. The PNBT whose properties are described below had values of M_n and M_w of 22 000 and 44 000, respectively, measured by GPC vs poly(styrene) standards (DP = 52, i.e., (NBT)₅₂). The freshly precipitated polymer has a spongy consistency and is deep red by transmitted light. The red polymer dissolves readily in hot CHCl₃ or hot toluene to give an initially red solution that rapidly fades to yellow. In CHCl₃, the $\lambda_{\text{max}}(\text{abs}) = 429 \text{ nm}$. This solution fluoresces a bright yellow-green under long-wavelength UV and has a $\lambda_{\text{max}}(\text{em}) = 523 \text{ nm}$.

Thin films (ca. 1000 Å) with a $\lambda_{\text{max}}(\text{abs}) = 438 \text{ nm}$ have been made by spin-coating the yellow solutions on glass substrates. Surprisingly, when these films are held at a temperature in the range 100–280 °C under vacuum or nitrogen atmosphere, the λ_{max} increases to 527 nm, and an isosbestic point (Figure 1) is observed as the color of the film turns from yellow to red. Upon cooling to room temperature, the film retains the red color and λ_{max} remains unchanged. The red film abruptly turns yellow at 300 °C, a temperature that corresponds to an endotherm in the DSC curve and is ascribed to the melting point (T_m) of the polymer. Slow cooling below the T_m restores the red film, whereas rapid quenching gives predominately the yellow form.

A third polymorph is obtained when solutions of PNBT in high boiling solvents, e.g., toluene and *p*-

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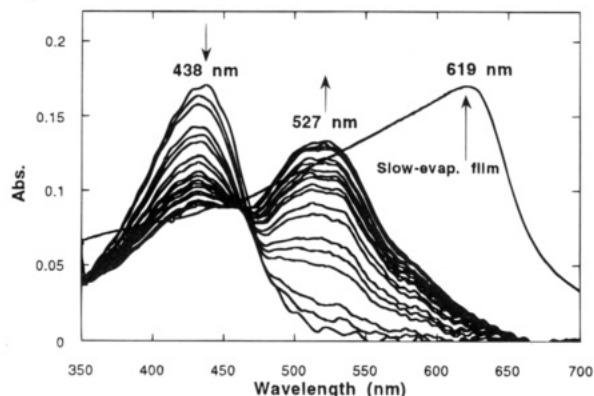


Figure 1. UV-vis spectra as a function of time of a film of PNBT held at 160 °C in an N₂ atmosphere.

xylene, are slowly evaporated. In this instance, a shiny, coppery-green film is obtained that exhibits the absorption curve labeled "slow-evap. film" in Figure 1. This curve has $\lambda_{\text{max}} = 619$ nm and a shape reminiscent of the absorption curves of intrinsic semiconductors.²³ The optical band gaps, determined by extrapolating the low energy edge of the absorption peak to zero absorption, are 2.52, 1.99, and 1.79 eV for the yellow, red, and green films, respectively. For comparison, the band gap calculated for the planar hexamer of bithiazole by the EHMO method is 2.66 eV.²⁴

These color changes are correlated to changes in the crystallinity of the films. As shown in Figure 1S (supporting information), the yellow film is essentially amorphous although there is a small amount of lamellar structure that gives a weak, diffuse peak at $2\theta = 4.2$ – 4.3° . The lamellar structure becomes more pronounced in the red film and new peaks appear at $2\theta = 7.0$, 10.8 , and 24.5° . The green film is the most crystalline, as evidenced by the sharpness of the peaks and their intensity relative to the broad, amorphous halo that extends from about 15° to 27° . The d spacings corresponding to the observed diffraction peaks from the green film are 24.5, 11.9, 8.0, and 3.6 Å. The first three are assigned to the 100, 200, and 300 (lamellar) interplanar distances, but 8.0 Å also corresponds to the 2-ring, (001) repeat distance along the bithiazole chain. The 3.6 Å peak corresponds to the π -stacking, (010) repeat distance perpendicular to the plane of the backbone.

Figure 2a shows one of the low-energy conformations of the nonylbithiazole dimer.²⁴ The chain backbone is calculated to be strictly planar with the nonyl groups in the extended, trans conformation and subtending a (C_β – C_α – C_4 – C_3) dihedral angle of 105° with the planar thiazole ring. The 24.5 Å distance observed in the X-ray diffraction pattern corresponds precisely to the wingtip-to-wingtip distance of the pendant alkyl groups, and 3.6 Å is the distance computed for π -stacking by lying one chain on top of another at the van der Waals contact distance (Figure 2b). Figure 2S is a computer-generated packing diagram that shows the unit cells as calculated

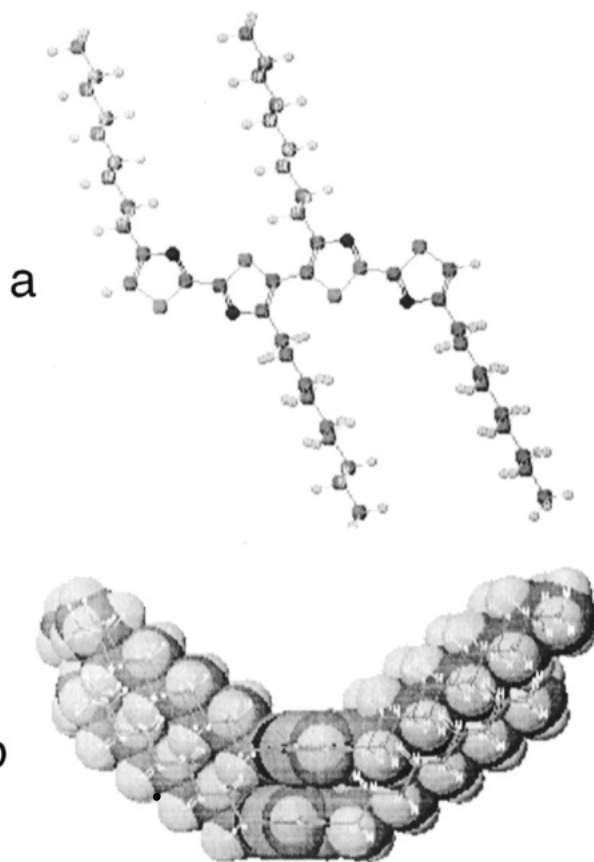


Figure 2. (a) View perpendicular to the planar chain backbone of a low-energy conformation of (NBT)₂ (atom spheres drawn at 20% of their van der Waals radii). (b) View along the chain axis of two molecules of (NBT)₂ stacked at 3.6 Å (atom spheres drawn at their van der Waals radii).

from the MM2 geometry and the X-ray diffraction data.²⁵

The optical changes observed for the polymer as the degree of crystallinity increases may be interpreted with the help of additional data obtained on well defined oligomers.^{17,26} (NBT)_x ($x = 1, 2, 3, 5$) oligomers, containing 2, 4, 6, and 10 monothiazole rings, exhibit bathochromic shifts of 0, 45, 65, and 75 nm, respectively, in the UV-vis absorption maximum on going from solution to solid state. On the basis of two crystal structures (see below) and thermal behavior, we believe that these oligomers have planar backbones in the solid state. Thus, heating solid films of the oligomers causes *hypsochromic* shifts in λ_{max} , indicative of a shortening of the conjugation length, and a plot of the transition energy at λ_{max} vs the reciprocal of the chain length is strictly linear (Figure 3), a behavior that is in accordance with theoretical expectations and other experimental observations.^{27,28}

The plot in Figure 3 may be used to estimate the conjugation lengths in the three polymorphs of (NBT)₅₂.

(25) At the current level of resolution, the diffraction data may be fit equally well with either of two unit cells. In the one with cell constants, $a = 27.7$ Å, $b = 3.7$ Å, $c = 7.64$ Å, $\beta = 59^\circ$ (monoclinic), the pendant nonyl groups of the bithiazole units are all cis with respect to the plane of the backbone. In the other, $a = 30$ Å, $b = 3.7$ Å, $c = 7.64$ Å, $\alpha = 90^\circ$, $\beta = 59^\circ$, $\gamma = 70^\circ$ (triclinic), the alternate nonyl groups are trans.

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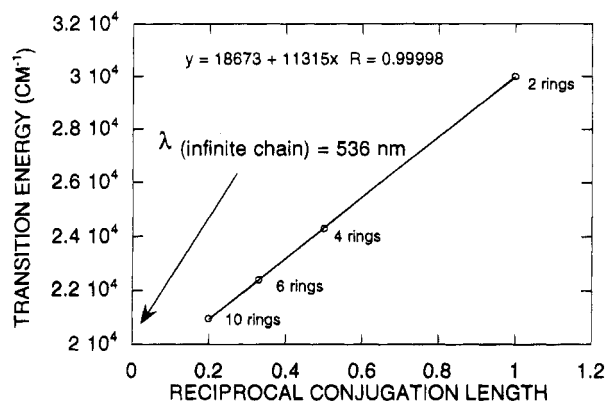


Figure 3. Graph of the transition energy ($1/\lambda_{\max}$, cm^{-1}) vs the reciprocal of the conjugation length ($1/x$) in bithiazole oligomers, (NBT) $_x$, $x = 1, 2, 3, 5$.

The yellow solution and yellow film have conjugation lengths of about 2.7 bithiazole groups (=5.4 rings), i.e., a conjugation length of 22 Å (8 Å per bithiazole). The red film has an apparent conjugation length of 34 bithiazole groups or 272 Å. According to this interpretation, 34/52 = 65% of the rings in the main chains of the red film are coplanar.

The green film with $\lambda_{\max} = 619$ nm is "off the scale" of Figure 3. Extrapolation to $1/n = 0$, i.e., infinite conjugation length, gives $\lambda_{\max} = 536$ nm, a value less than that observed in the green film. Hence, either the correlation simply breaks down for long conjugation lengths, or other factors are at work in the green film that contribute to its "extra" conjugation length. We propose that the green film is so ordered that π - π interactions become sufficiently strong that a cooperative, solid-state electronic transition contributes to the optical absorption of the green film. Such cooperative states, known as "*J*-aggregates", have been observed previously in crystalline dyes and LB films of aromatic compounds, and the effect of π -stacking on the electronic band structure has received theoretical attention.^{29,30}

The complete 3-D crystal structures of two bithiazoles, the *tert*-butyl- and nonyl-substituted derivatives, have been determined.³¹ In both structures, the thiazole rings are strictly coplanar and both exhibit a stepped π -stacked molecular packing (see Figures 3S–5S). The nonyl groups subtend a dihedral angle of 113° to the plane of the thiazole ring (cf. a MM2 computed angle of 105°). There appears to be a relatively strong S...S interaction as evidenced by the S...S distance of 3.49 Å, which is less than the sum of the van der Waals radii for S (3.6 Å). These S...S interactions may also con-

tribute to the cooperative electronic transition observed in the crystalline phase of PNBT.

The thermochromic behavior of PNBT is unlike that usually observed for structurally similar polythiophenes. Their normal behavior is a decrease in λ_{\max} with increasing temperature due to thermally induced disorder that decreases the conjugation length.^{16,32} Although red shifts have been observed previously,^{33,34} we believe this report is the first in which the red shift is correlated with structural results derived from X-ray diffraction. The highly extended conjugation length observed for PNBT also would not be anticipated on the basis of the widely held belief that head-to-head (HH) coupling of alkyl-substituted monomer units leads to twisting of the polymer backbone.^{35,36} The results described here demonstrate that HH coupling need not disrupt conjugation;³⁷ the more important factor is a *regular* structure that promotes crystallinity. The electrochemical, electrical, and luminescence properties of the PABTs described here are under investigation and will be reported in due course.

Note: While this paper was in review, Yamamoto et al. published a synthesis of PABTs similar to that reported here.³⁸ These authors apparently did not observe the thermochromism associated with PNBT. Our CV, doping, conductivity, and photoluminescence results are in accord with those reported by Yamamoto et al.

Acknowledgment. The authors thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. J.I.N. also thanks the Plastics Institute of America for a Supplemental Fellowship.

Supporting Information Available: Experimental procedures, figures of the X-ray diffraction pattern and unit cell of PNBT, and the molecular packing of NBT and ^tBuBT (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions. CM950423D

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