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Solid-State and Solvatochromic Spectra of a Highly Regular Polythiophene

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Intense research has centered on development of highly conjugated polymers for commercial applications. Along with the polydiacetylenes (PDA's), polythiophenes have been at the forefront of interest because their essentially one dimensional rigid planar backbone allows significant π-conjugation with room temperature conductivities on the order of 100 S/cm.[1−3] However, this conjugation and strong interchain interactions render polythiophenes infusible and insoluble in common organic solvents.

Long alkyl side chains inserted at the monomer 3 position increase solubility. These cause steric effects and inhibit regiochemical control during polymerization. The 3-alkyl substituent results in two different regio−regularities: head to tail (HT) and head to head (HH) creating four possible regiobonding configurations in the polymer: HT−HT, HT−HH, TT−HT, and TT−HH. The HH bonding configuration greatly reduces planarity and subsequent conjugation of the polymer due to intrachain alkyl−alkyl and alkyl−sulfur interactions.[3] Current research has centered on controlling the regiobonding, since regularity and ordering in the polymeric structure are expected to lead to enhancements in physical properties.[4,5] Rieke et al. have recently produced regioregular poly-3-hexylthiophene (PHT) possessing >98% HT−HT type bonding and a unique regiorandom form that contains approximately 1:1:1:1 ratios of the four possible regiobonding configurations.[6] This presents an opportunity for characterizing a highly ordered regioregular PHT and contrasting its behavior to a regiorandom polymer of known configurational composition.

Most polyalkylthiophene (PAT) spectra are measured for solution-cast films using conventional UV−vis techniques.[2,3,5] To avoid complications due to high molar concentrations and large extinction coefficients, near-normal-incidence specular reflection spectroscopy is used.[7] A fast-Fourier transform is employed to obtain the absorption spectrum.[8]

The regioregular polymer lot used in all experiments had a $M_w = 37\,680$ and $M_n = 25\,500$, while that for the regiorandom polymer was $M_w = 24\,400$ and $M_n = 5650$. Solid-state samples of the regioregular and regiorandom polymers were prepared by refluxing glass substrates in dichloroethane and 2-propanol to remove impurities or moisture. Then 3% (w/w) chloroform solutions of both polymers were prepared and spin coated onto the glass substrates at 600 rpm. Regioregular polymer films were deep violet by transmission and metallic gold by reflection. The regiorandom films transmitted a dull red-orange with no significant reflectivity. The room-temperature reflection spectra[9] of the regioregular and regiorandom polymeric films were measured between 12 500 and 25 000 cm^{-1} with a bandwidth of 100 cm^{-1}. Spectra were measured and averaged for at least four different areas on each spun sample to establish reproducibility.

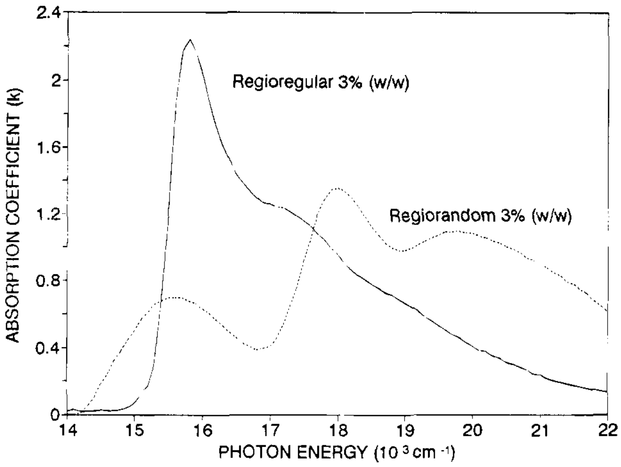

Figure 1. Fourier transformed, room temperature absorption spectra: regioregular (- -) and regiorandom (···) PHT films. The monomer repeat unit referred to in the text is shown in the inset.

The transformed absorption spectrum for the regioregular PHT spin-cast film (Figure 1) exhibits red-edge absorption at 15 700 cm^{-1} which is attributed to the 0−0 vibron of a $\pi^* \leftarrow \pi$ transition of the backbone. Distinct structure blue-shifted by 1600 cm^{-1} from the 0−0 transition is also present. This spectrum shows structure that is usually attributed to a Franck−Condon progression.

The transformed solid-state absorption spectrum of the 3% (w/w) regiorandom PHT shows dramatic change. The most red-shifted peak occurs at 15 600 cm^{-1} with an intense peak at 18 000 cm^{-1} followed by a broad structureless band with a maximum at roughly 19 700 cm^{-1}. The apparent difference in peak extinctions is not significant since the integrated intensities of the regioregular and regiorandom spectra are nearly equivalent.

The regioregular PHT's spectrum displays similarities to those of single crystal PDA's. Both exhibit intense 0−0 transitions occurring at approximately 15 600 cm^{-1} which are based on apparent 1600 cm^{-1} progressions.[10] In the PDA's, resonance Raman studies attribute this structure to a double bond vibron that couples strongly to the electronic structure of the PDA conjugated chain.[11] A like coupling in PHT is reasonable since it possesses a similar backbone double bond. This is

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consistent with the widely held notion that the electronic properties of organic conjugated polymers are governed primarily by the conjugated backbone with ancillary side group effects. These absorptions around 15 600 cm^{-1} are the lowest $\pi^* \leftarrow \pi$ transitions yet reported for the polythiophenes indicating that, in the solid-state, the polymer backbone has an extensive planar structure. HT–HT bonding should minimize steric repulsion resulting in extended π-conjugation with a concomitant red-shifted absorption.

Polymer order-disorder conformational changes in solution are well-known and have been treated theoretically and experimentally.[12–16] Unique to these are those of conjugated polymers which, because of the aforementioned strong coupling, undergo dramatic color changes as a function of temperature and solvent/nonsolvent ratio. Regioregular and regiorandom solute behavior is then of some interest.

Regioregular and regiorandom absorption spectra were obtained in pure chloroform using a Cary-210 spectrophotometer (Figure 2a). The spectra exhibit broad and structureless absorption bands which we attribute to a distribution of conjugation lengths. The peak absorption for the regiorandom form occurs at 23 000 cm^{-1} while that for the regioregular is red shifted by 1200 cm^{-1} to 22 100 cm^{-1}, implying the latter has more extensive conjugation.

For solvatochromism measurements, $\sim 2.5 \times 10^{-6}$ molar solutions were prepared by using spectrophotometric grade chloroform and titrating in the nonsolvent, absolute ethanol, to increasing mole fractions (Figure 2b). Solutions were sealed in the cuvette to prevent evaporation. Above a mole fraction of 0.64 ethanol the regioregular polymer gels, but the regiorandom does not.

These spectra show the growth of structure at 16 750, 18 300, and 19 400 cm^{-1} with concomitant diminution of the broad structureless peak at 22 100 cm^{-1}. The broadened isosbestic point at approximately 22 000 cm^{-1} indicates the presence of a mixture. Previous PHT thermochromic studies have attributed this to the presence of both a solubilized and microcrystalline suspension of polymer.[12] These spectra are strikingly similar to those reported for the solution thermochromic study of PHT and the solid-state thermochromism of poly(3-octyloxy)-4-methylthiophene, which also show the same sequence of structure (at nearly the same frequencies) as a function of decreasing temperature.[12,17] The agreement of energies, in spite of the variance of the substituents of the PHT's, suggests the electronic effects are solely a function of the backbone. Recent theory predicts that an ordered, rodlike conformation results from conformational transitions in solution that are induced by attractive dispersion interactions between delocalized electrons of the polymer backbone and the surrounding polarizable medium.[16]

Except for broadening and a shift in the peak absorption to 22 000 cm^{-1}, the addition of 0.64 mol of ethanol has little effect on the regiorandom absorption spectrum (Figure 2c). This indicates that the solute polymer maintains a rather broad distribution of short conjugation lengths.

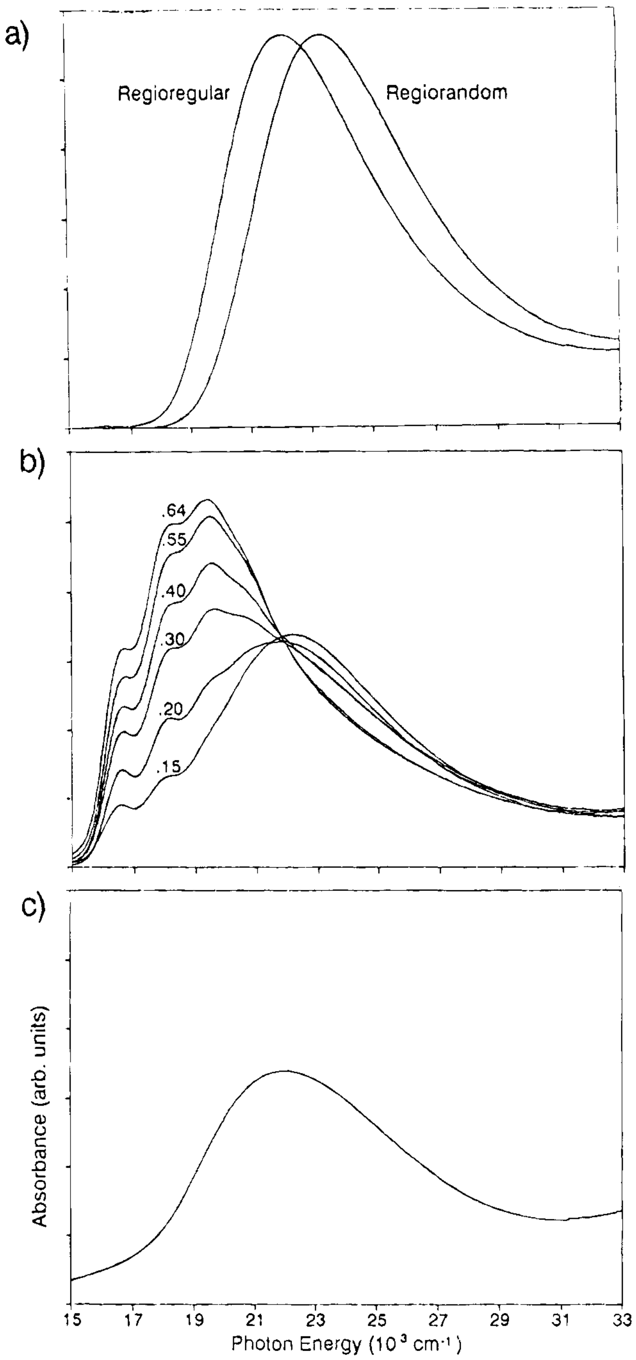

Figure 2. Room-temperature solution absorption spectra: (a) regioregular and random PHT in pure chloroform; (b) regioregular PHT as a function of increasing ethanol mole fraction; (c) Regiorandom PHT in 0.64 mole fraction of ethanol.

Kuhn's modified free-electron theory was applied to estimate the distribution of conjugation lengths in each of the above systems.[18–20] The single and double bond alternation was modeled by superimposing a sinusoidal potential on the square well. For the polymers in pure chloroform the model predicts that regioregular PHT

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conjugation lengths range from five to eleven thiophene repeat units (Figure 1) while the regiorandom falls between four and ten rings, thereby accounting for the blue-shift in the regiorandom spectrum. For the solvatochromism spectra, which exhibit an isosbestic at 22 000 $\mathrm{cm^{-1}}$, the low-lying transition at 16 750 $\mathrm{cm^{-1}}$ is consistent with an effective conjugation length of 19 thiophene repeat units. An estimate of the ratio between extended and short conjugation lengths is possible by deconvolution. For the 0.64 ethanol mole fraction solution, this ratio is 79/21 thus supporting the extensive conjugation model. The addition of ethanol to the regiorandom form only shows a broadening of the spectrum consistent with a distribution of four to eleven repeat units.

The solid-state regioregular spectrum exhibits a more ordered backbone as evidenced by the 1050 $\mathrm{cm^{-1}}$ red-shift of the lowest lying energy transitions when compared to the 0.64 mole fraction solvatochromism spectrum. Modified free-electron theory predicts that the lowest energy transition of the regioregular PHT (15 700 $\mathrm{cm^{-1}}$) is consistent with a conjugation length of 28 thiophene repeat units. However, the absorption envelope still has some reasonable intensity in the frequency region of short conjugation lengths. By following the deconvolution procedure for the solvatochromism spectrum and applying the shift criterion of 1050 $\mathrm{cm^{-1}}$ to account for the increased dielectric constant of the solid, we find a conjugation ratio of 97/3 indicating that almost all of the solid regioregular polymer possesses extended conjugation. This ratio is consistent with the estimates of regularity for this form.[6]

The regiorandom film has three absorption bands corresponding to conjugation length ranges of 21 to 30, 12 to 17, and 8 to 11 (from low to high energy) repeat units with area ratios of 30:25:45 (as percentages), respectively. Since the HT−HH and TT−HH configurations are expected to decrease backbone planarity the most and the broad, highest energy structure comprises 45% of the spectrum, we assign this structure to an admixture of these configurations. The intermediate energy band centered at 18 000 $\mathrm{cm^{-1}}$ (25%) is assigned to the TT−HT configuration based upon steric hindrance considerations. The low-frequency system at 15 600 $\mathrm{cm^{-1}}$ (30%) is of the HT−HT configuration since it is of the same energy as the regioregular films which are 98% HT−HT.

The new regioregular polymer has substantially more extended conjugation than any heretofore reported PHT. This also is true in solution where the regioregular solute is shifted by about 1000 $\mathrm{cm^{-1}}$ to the red of the regiorandom. Its solvatochromism shows essentially the same behavior as the solid-state thermochromism of poly(3-octyloxy)-4-methylthiophene films suggesting that, even as a solute, the regioregular form maintains more extended conjugation lengths than do other reported PAT's even as solids. This new regioregular PHT may represent the limit of the possible PHT conjugation length, and thus this system may serve as the prototype of these materials.

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