Polarons and Bipolarons on a Conducting Polymer in Solution

M. J. Nowak, S. D. D. V. Rughooputh, S. Hotta,[†] and A. J. Heeger*

Institute for Polymers and Organic Solids and Department of Physics, University of California, Santa Barbara, Santa Barbara, California 93106. *Received September 19, 1986*

ABSTRACT: Electron spin resonance (ESR) measurements and spectroscopic studies have been carried out on the soluble conducting polymer poly(3-hexylthienylene) *doped in solution* with $(NO)^+(PF_6)^-$. From the ESR and spectroscopic data, we have determined the nature of the charge-storage configurations as a function of doping level and as a function of doped polymer concentration. The results indicate that the spinless bipolaron is the lowest energy charge-storage configuration on single poly(3-hexylthienylene) macromolecules in dilute solution. Polarons are formed either as a result of an odd number of charges on a single polymer chain or as a result of interchain interactions (in the semidilute regime).

Introduction

Because of the near degeneracy of the different valence-bond configurations that characterize the ground states of conjugated polymers, the dominant "electronic" excitations are strongly coupled by the electron–phonon interaction to nonlinear chain distortions. Thus, rather than the electrons and holes characteristic of a rigid lattice, one expects that solitons, polarons, and bipolarons will be the fundamental nonlinear excitations and the dominant charge-storage configurations in conducting polymers.[1] *trans*-Polyacetylene represents a special class of one-dimensional semiconductors; the twofold degeneracy of the ground state leads to nonlinear excitations in the form of topological solitons.[2] For polymers such as *cis*-polyacetylene, polypyrrole, polythiophene, and the poly(3-alkylthienylenes), the nondegenerate ground state leads to confinement of soliton–antisoliton pairs into spinless bipolarons.[1c,3,4]

Polarons (spin $^1/_2$) are known to be valid excitations both for degenerate ground-state systems and for polymers where the ground state is not degenerate.[3] When the degeneracy is lifted, the energy for creation of a confined soliton pair (bipolaron) remains less than that for two polarons.[3] Thus, $P^+ + P^+ \Rightarrow B^{2+}$, where P^+ and B^{2+} denote polarons and bipolarons, respectively.

Addition of the Coulomb interaction to the model changes the creation energies and reduces the polaron–bipolaron *energy difference*. Since the bipolaron has a double charge and each polaron has a single charge, the Coulomb interaction favors the formation of polarons. Thus, the polaron and bipolaron creation energies could become comparable, or polarons could even be energetically favored, depending on the relative strengths of the electron–phonon and electron–electron interactions.

The energy level diagram for a spinless positive bipolaron[1,3] is sketched in Figure 1. The two gap states are empty for a positive bipolaron (charge 2*e*) and filled for a negative bipolaron (charge −2*e*). In the polaron case,[1,3] the gap states are partially filled (e.g., one electron in the lower level for a positive polaron), implying a spin $^1/_2$ configuration and leading to a third subgap absorption subsequent to polaron formation.

Although there is evidence that upon doping[5] or photoexcitation[6] charge is stored in spinless bipolarons, polaron formation has been reported as well.[7] Therefore, the question of whether the polaron or the bipolaron is the lowest energy configuration in nondegenerate conducting polymers continues to be of fundamental importance.

Experimental results have demonstrated electron–hole symmetry and weak confinement in polythiophene,[5,6] making this polyheterocycle a nearly ideal example of a model system in which the degeneracy has been lifted. With the addition of alkyl side groups to the thiophene ring (see Figure 1), soluble poly(3-alkylthienylenes) (P3ATs) have been synthesized and characterized as conducting polymers.[8–10] Since these polythiophene derivatives are soluble in common organic solvents (e.g., chloroform and tetrahydrofuran), the P3ATs open the way to studies of the charge-storage configurations of doped isolated macromolecules in dilute solution.

The addition of the alkyl side group serves to increase the solubility without significantly changing the π-electron structure.[9] It is not surprising that the *saturated* alkyl chain has little effect on the electronic structure of the π-system of polythiophene. One might anticipate, however, a decrease in interchain coupling because of the bulky side group. Although detailed structural data are not yet available, the excellent optical and electrical properties would seem to imply a face-to-face interchain stacking arrangement that facilitates interchain electron transfer and that leads to extensive delocalization.

In this paper we report the results of ESR and spectroscopic studies, *carried out in solution*, of the conducting polymer P3HT, poly(3-hexylthienylene), doped with $NO^+PF_6^-$. We have determined the nature of the *charge-storage configurations* as a *function of doping level* and as a function of doped polymer concentration. The results indicate that the spinless bipolaron is the lowest energy charge-storage configuration on single P3HT macromolecules in dilute solution. Polarons are formed either as a result of an odd number of charges on a single polymer chain or as a result of interchain interactions (in the semidilute regime).

Preparation and Characterization of Polymer Solutions

Details of the electrochemical synthesis and the polymer characterization have been reported.[9] The soluble P3ATs have relatively high molecular weight[9] ($\bar{M}_w \approx 48\,000$ against polystyrene standards) and high purity. Infrared studies[9] characterized these materials as 2,5-linked linear polythienylene chains. The *n*-butyl [P3BT] and the *n*-hexyl [P3HT] derivatives can be prepared as free-standing films with high electrical conductivities[9,10] (≈30–100 S cm^{-1}). Solution-cast films have spectral features essentially identical with those of as-grown films, both in the neutral state and after doping.[9]

Solutions were prepared by dissolving P3HT in spectral-grade quality chloroform; all samples were prepared under inert atmosphere. The dopant ($NOPF_6$) was purified by sublimation under vacuum and then dissolved in distilled acetonitrile. Doped polymer solutions were prepared by adding the appropriate amount of the dopant solution (4 mg of $NOPF_6$ in 1 mL of acetonitrile) to previously prepared chloroform solutions of P3HT. For the dilution experiments, the doping was carried out with a polymer concentration of 1 mg/mL (or greater), and the doped

---

[†] Permanent address: Central Research Laboratories, Matsushita Electric Industrial Co., Ltd., Moriguchi, Osaka 570, Japan.

0024-9297/87/2220-0965$01.50/0

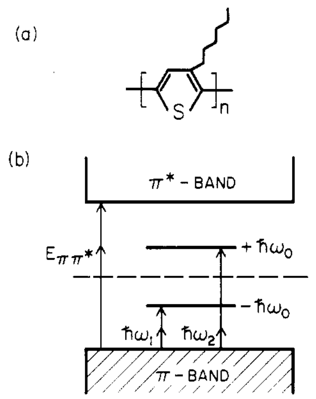

Figure 1. (a) Structure of poly(3-hexylthienylene), P3HT. (b) Bipolaron band diagram showing the two gap states and the $\pi-\pi^*$ ($E_{\pi\pi^*}$) and subgap ($\hbar\omega_1$ and $\hbar\omega_2$) transitions. In the polaron case, the gap states are partially filled (e.g., one electron in the lower level for a positive polaron), leading to a third subgap absorption subsequent to polaron formation.

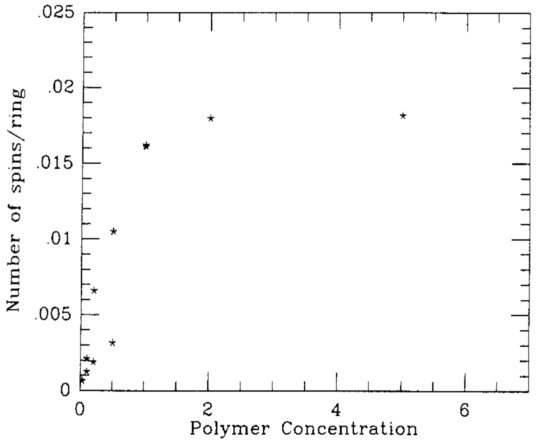

Figure 2. Number of spins per thiophene ring as a function of doped P3HT concentration (in chloroform) at a fixed dopant level ($y \approx 0.08$). The polymer concentration is given in units of c_0, where c_0 = 1 mg/mL (6×10^{-3} M).

polymer solution was diluted by addition of pure chloroform. In this way any desired concentration (c) of polymer in chloroform could be doped to any desired dopant level, $[(3HT)^{y+}(PF_6^-)_y]_x$. The quoted y values are nominal and assume that the doping reaction has gone to completion, with each NO^+ ion yielding a transfer of one electron from a P3HT macromolecule.[11] Volumetrically accurate amounts of solutions were sealed in optical cells or in ESR tubes to ensure against loss of volatile solvents during the course of the measurements. Although we observed no obvious signs of degradation or instability, all of our studies routinely utilized freshly prepared samples.

P3HT (both neutral and partially oxidized by doping) appears to exist as macromolecular chains in solution in chloroform. Quasi-elastic light scattering from neutral polymer solutions yields a hydrodynamic diameter of ≈300 Å, implying that the dilute regime is restricted to polymer concentrations $c \ll c_0$ = 1 mg/mL (6×10^{-3} M); for $c > c_0$, intermolecular interactioins can be expected to be of importance. The dilute solutions (both of the neutral polymer and after doping) were clear and stable over long times with no indication of cloudiness or precipitation. Visual evidence of intermolecular aggregation was observed only at concentrations greater than about (5–10)c_0. Our initial conclusion, therefore, is that for polymer concentrations well below c_0 we are dealing with the properties of single P3HT macromolecules in solution and that intermolecular interactions play an increasingly important role at higher concentrations.

Electronic Structure of Doped P3HT in Solution

Figure 2 shows the number of spins per thiophene ring (y_s) as a function of polymer concentration at a fixed dopant level of $y = 0.08$. The ordinate represents the number of spins per thiophene ring; i.e., the change in polymer concentration has been taken into account. For polymer concentrations below c_0, the number of spins decreases, reaching a limiting value of ≈(1-2) × 10^{-3} per ring ($y_s/y \approx 2 \times 10^{-2}$). Since the mean molecular weight is equivalent to about 300 monomer rings,[9] this limiting value is consistent with spins (polarons) being generated *only* when there are an odd number of charges per chain (typically half the chains will have an odd number of charges and half an even number). Thus in the dilute limit, $c \ll c_0$, the ESR data indicate that $P^+ + P^+ \Rightarrow B^{2+}$ except when this is inhibited by the presence of an odd number of polarons on a finite macromolecular chain.[12]

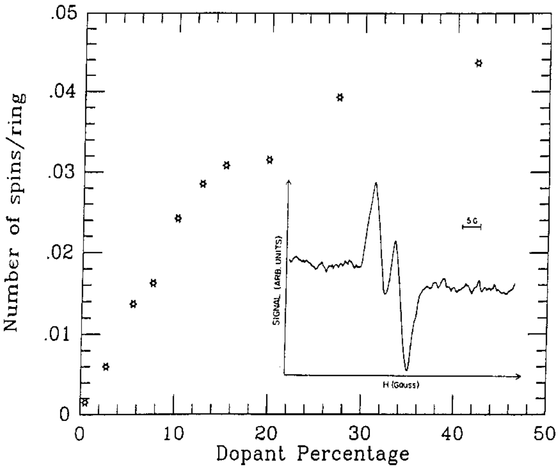

Figure 3. Number of spins per thiophene ring as a function of dopant level (y) at a fixed doped polymer concentration, $c = c_0$ (in chloroform). The inset shows an ESR spectrum that exhibits a hyperfine splitting (see text).

The number of spins increases as c approaches c_0 and saturates for higher concentrations at a value of about 0.02 spins per ring. The increase in the relative number of spins per ring as c approaches c_0 implies that interchain interactions are responsible for the stabilization of polarons relative to bipolarons.

The number of spins per ring (y_s) is plotted in Figure 3 as a function of the dopant level (y) at a fixed polymer concentration of $c = c_0$. The initial slope corresponds to $y_s/y \approx 1/5$, consistent with the data from the semidilute regime on Figure 2; for higher y, the ratio is even smaller.

The hyperfine splitting due to the interaction between the π-electron on the thiophene ring and the adjacent proton has been resolved (see inset to Figure 3), thus enabling a more detailed determination of the spatial extent of the polaron wavefunction.[3] A splitting of approximately 4.5 G was observed under two distinct experimental conditions: (1) at dilute concentrations ($<0.2c_0$) of lightly doped polymer and (2) at high concentrations of the neutral polymer. With the use of the McConnel relations,[13] the observed splitting implies a *maximum* spin density of about 0.2, consistent with delocalization of the polaron spin over a number of carbons on the pseudopolyene backbone. The additional splittings due to more distant protons are not resolved but contribute to the width of the two resolved lines. Since the two carbons at the 3 and 4 positions of the thiophene ring are equivalent by symmetry, the polaron wave function is localized primarily on a single thiophene ring with only a small spin density on the neighboring rings on either side. The hyperfine splitting in solution, therefore, implies a somewhat more tightly localized wavefunction than expected from calculations based upon a straight-chain conformation for the neutral polymer.[14]

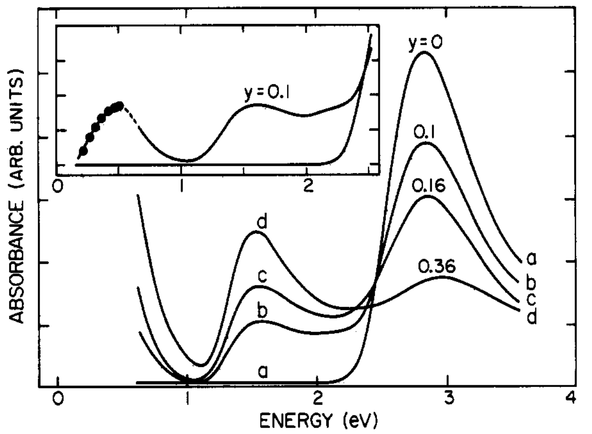

Figure 4. Absorption spectra of the neutral and doped polymer ($y \approx 0.1$, and 0.16 and $y \approx 0.36$) at a P3HT concentration of $c_0/100$ (in chloroform). The inset shows an extended-range IR spectrum (obtained with $c \approx c_0$ in chloroform).

The absorption spectra of the neutral and the doped polymer ($y \approx 0.1$ and 0.16 and $y \approx 0.36$) are compared in Figure 4 for a polymer concentration of $c_0/100$. The effect of doping is characteristic of conducting polymers:[1] the π–π^* transition is depleted with the oscillator strength shifted into two principal subgap features in the infrared. That the low-energy feature is indeed a peak (implying *two* localized gap states) is demonstrated in the inset where the broad-band mid-IR absorption and the near-IR spectrum (obtained with two different instruments) are superposed. The data in the inset were obtained with a polymer concentration of $c \approx c_0$. Note that an additional weak absorption can be seen in the inset at $\hbar\omega \approx 2.15$ eV; excess absorption is also observed at this energy in the spectrum taken with $c_0/100$ (this feature shows up clearly in difference spectra). The two principal subgap absorption bands with maxima at $\hbar\omega_1 \approx 1.55$ eV and $\hbar\omega_2 \approx 0.5$ eV in the doped polymer are consistent with charge storage predominantly in bipolarons. The π–π^* transition energy (onset at $\approx$2.2 eV, peak at $\approx$2.8 eV) is, however, greater than $\hbar\omega_1 + \hbar\omega_2 \approx 2.05$ eV.

The additional absorption near 2.15 eV is not the result of a (third) polaron mode. Detailed examination of difference spectra shows that this feature decreases in relative strength at high y an at high c, whereas the magnetic data indicate in both cases a monotonic increase in the number of polarons per ring.

A series of visible–near-IR spectra taken at successively higher doping levels (polymer concentration of $0.4c_0$) is shown in Figure 5. The well-defined isosbestic point at 505 nm (2.45 eV) implies the coexistence (and interconversion) of two regions on a doped P3HT chain: neutral regions where the π–π^* transition is unchanged and localized regions surrounding the charge-storage configuration (bipolarons). As the doping level is increased, the subgap absorption grows at the expense of the π–π^* transition; at high doping levels in dilute solution (see inset to Figure 5) nearly all the π-electron oscillator strength has been shifted into the two intense infrared bands.

Implications of the Magnetic and Spectroscopic Data

The magnetic resonance data demonstrate that charge is stored predominantly in a spinless configuration for doped P3HT in solution. For dilute solutions ($c \ll c_0$), virtually all the charge is stored in bipolarons; polarons are formed only as a result of an odd number of charges on a single macromolecule. Interchain interactions at higher concentrations cause a significant increase in the number of spins. Even at c_0 and above, however, only a small fraction of the charge is stored in polarons (see Figure 2).

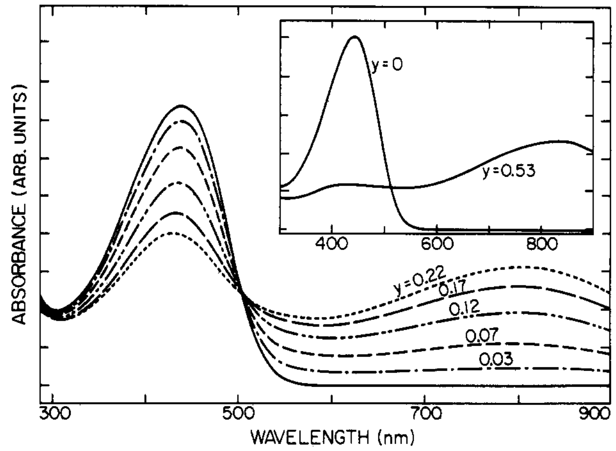

Figure 5. Series of visible–near-infrared absorption spectra taken at successively higher doping levels (P3HT concentration $0.4c_0$ in chloroform). The inset compares the spectra for the neutral polymer solution with that for maximum doping ($y \approx 0.53$) at $c \approx c_0/100$.

The two principal subgap absorption bands (Figure 4) with maxima at $\hbar\omega_1 \approx 1.55$ eV and $\hbar\omega_2 \approx 0.5$ eV in the doped polymer are consistent with charge storage predominantly in bipolarons, as shown in the energy level diagram of Figure 1. For heavily doped P3HT macromolecules even in dilute solution, see inset to Figure 5, essentially all the π-electron oscillator strength has been shifted into the bipolaron transitions, implying a close-packed array of bipolarons[15] (interspersed with a relatively small number of polaron defects). Since the isosbestic point is independent of polymer concentration (from $10^{-3}c_0$ to c_0) and since only subtle changes are observed in the spectra (fixed y, as a function of c), the same qualitative picture is valid as the polymer concentration is increased but with an increasing (but always relatively small) number of polaron defects appearing in the bipolaron "lattice".

In contrast to Figure 1, however, the π–π^* transition energy (onset at $\approx$2.2 eV, peak at $\approx$2.8 eV) is greater than the sum of the two doping induced transition energies $\hbar\omega_1 + \hbar\omega_2 \approx 2.05$ eV. As noted in earlier studies,[16] there is a blue-shift of the π–π^* transition for P3HT in solution as compared with either (partially) crystalline films or macromolecular aggregates. The straight-chain conformation characteristic of the solid state has a π–π^* transition that onsets at 1.9 eV (peak at about 2.4 eV),[9] whereas in dilute solution (see Figure 4) the onset is at $\approx$2.2 eV (peak at about 2.8 eV). This shift implies a conformational change in solution, presumably to a more disordered flexible conformation. We suggest that in the vicinity of a bipolaron on a doped chain in dilute solution the straight-chain conformation is restored. This is implied by the similarity of the subgap absorptions for P3HT in solution,[16] for P3HT films,[17] and for P3AT films more generally.[9,18] Moreover, the quinoid-like regions associated with the bipolaron would be expected to be more rigid against inter-ring rotations. Thus, doping introduces changes in the electronic spectrum and simultaneously introduces changes in the local chain conformation. In this case one should compare the sum ($\hbar\omega_1 + \hbar\omega_2$) to the π–π^* transition energy ($E_{\pi\pi^*}$) for the straight-chain conformation[9,16] (2.05 eV), rather than to the π–π^* transition of the neutral polymer in solution.

When the electron–electron repulsion associated with the double charge on the bipolaron and the electron–ion attraction (E_B) associated with the binding of the charged bipolaron to the counterion[5b,6] are included, the two bipolaron transitions satisfy the following relation:

$$\hbar\omega_1 + \hbar\omega_2 = E_{\pi\pi^*} - 2(U_B - E_B)$$

where U_B is the difference in the Coulomb energy between initial state (double charge) and final state (single charge). Since $\hbar\omega_1 + \hbar\omega_2 \approx 2.05$ eV, $U_B \approx E_B$. The resulting values are nearly identical with those obtained for polythiophene.[5,6] Thus, as for polythiophene, the spectroscopic data for P3HT in dilute solution imply relatively weak Coulomb interactions.

The implied change in local conformation in the vicinity of the bipolaron provides an explanation for the excess absorption near 2.15 eV in the doped samples. If the doping-induced straight-chain region extends somewhat beyond the coherence length of the bipolaron, doping would shift oscillator strength from the π–π^* transition of the neutral polymer in solution to near that of the neutral straight chain, in agreement with the experimental results.

Summary and Conclusion

In summary, we find that the spinless bipolaron is the lowest energy charge-storage configuration on single P3HT macromolecules in dilute solution. Polarons are formed either as a result of an odd number of charges on a single polymer chain or as a result of interchain interactions (in the semidilute regime). The conclusion that the bipolaron is the lowest energy charge-storage configuration together with the results of detailed analysis of the absorption spectra indicate that electron–electron Coulomb correlations are relatively weak, even for isolated conducting polymer chains in dilute solution. More generally, the results demonstrate that the novel concepts developed in the study of the solid-state properties of conducting polymers are directly applicable to such polymers in solution.

Acknowledgment. We thank N. Colaneri for generously helping with the absorption spectra and for discussions of the implications of these data. We are grateful to Prof. F. Wudl for making facilities available for sample preparation and characterization and to Dr. R. H. Friend for comments and discussions. This research was supported in part by the Office of Naval Research; the ESR studies were supported by the National Science Foundation (DMR 85-21392).

Registry No. P$_3$HT, 104934-50-1; (NO)$^+$(PF$_6$)$^-$, 16921-91-8.

References and Notes

(1) (a) Skotheim, T. J., Ed. *Handbook of Conducting Polymers*; Marcel Dekker: New York, 1986. (b) Etemad, S.; Heeger, A. J.; MacDiarmid, A. G. *Annu. Rev. Phys. Chem.* **1982**, *33*, 443. (c) Bredas, J. L.; Street, G. B. *Acc. Chem. Res.* **1985**, *18*, 309.

(2) (a) Su, W. P.; Schrieffer, J. R.; Heeger, A. J. *Phys. Rev. Lett.* **1979**, *42*, 1698; *Phys. Rev. B: Condens. Matter* **1980**, *22*, 2099. (b) Schrieffer, J. R. *Highlights of Condensed Matter Theory*; Society Italiana di Fisica: Bologna, 1985. (c) Rice, M. J. *Phys. Lett. A* **1979**, *71A*, 152. (d) Takayama, H.; Lin-Liu, Y. R.; Maki, K. *Phys. Rev. B: Condens. Matter* **1980**, *21*, 2388.

(3) (a) Brazovskii, S. A.; Kirova, N. *JETP Lett.* **1981** *33*, 4. (b) Campbell, D. K.; Bishop, A. R. *Phys. Rev. B: Condens. Matter* **1981**, *24*, 4859; *Nucl. Phys. B* **1982**, *200*, 297.

(4) (a) Heeger, A. J. *Comments Solid State Phys.* **1981**, *10*, 53. (b) Lauchlan, L.; Etemad, S.; Chung, T.-C.; Heeger, A. J.; MacDiarmid, A. G. *Phys. Rev. B: Condens. Matter* **1981**, *29*, 3701.

(5) (a) Chung, T.-C; Kaufman, J. H.; Heeger, A. J.; Wudl, F. *Phys. Rev. B: Condens. Matter* **1981**, *30*, 702. (b) Chen, J.; Heeger, A. J. *Solid State Commun.* **1986**, *58*, 251.

(6) Vardeny, Z.; Ehrenfreund, E.; Brafman, O.; Nowak, M.; Schaffer, H.; Heeger, A. J.; Wudl, F. *Phys. Rev. Lett.* **1986**, *56*, 671.

(7) (a) Harbeke, G.; Meier, E.; Kobel, W.; Egli, M.; Kiess, H.; Tosatti, E. *Solid State Commun.* **1985**, *55*, 419. (b) Kaneto, K.; Kohno, Y.; Yoshino, K. *Solid State Commun.* **1984**, *51*, 267. (c) Genoud, F.; Guglielmi, M.; Nechtschein, M.; Genies, E.; Salmon, M. *Phys. Rev. Lett.* **1985**, *55*, 118.

(8) Jen, K. Y.; Oboodi, R.; Elsenbaumer, R. L. *Polym. Mater Sci. Eng.* **1985**, *53*, 79; *Synth. Met.* **1986**, *15*, 169.

(9) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.

(10) Sato, M.; Tanaka, S.; Kaeriyama, K. *Chem. Commun.* **1986**, 873.

(11) The doping-induced spectral changes for P3HT in solution at c_0 saturate with no additional shifts in oscillator strength above a nominal y of about 0.5. Since the maximum charge storage in thin films is about one per two to three rings, we infer that the actual doping level is close to the nominal level.

(12) Moraes, F.; Chen, J.; Chung, T.-C.; Heeger, A. J. *Synth. Met.* **1985**, *11*, 271. Moraes, F.; Davidov, D.; Kobayashi, M.; Chung, T.-C.; Chen, J.; Heeger, A. J.; Wudl, F. *Synth. Met.* **1985**, *10*, 169.

(13) Carrington, A.; McLachlan, A. *Introduction to Magnetic Resonance*; Harper and Row: New York, 1967. The hyperfine splitting is 22.5 G per spin for C_6H_6 and 29.9 G per spin for C_5H_5.

(14) See ref 1c and references therein.

(15) Saxena, A.; Gunton, J. D., preprint.

(16) Rughooputh, S. D. D. V.; Hotta, S.; Heeger, A. J.; Wudl, F. *J. Polym. Sci., Polym. Phys. Ed.*, in press.

(17) Colaneri, N., to be published.

(18) Sato, M.-A.; Tanaka, S.; Kaeriyama, K. *Synth. Met.* **1986**, *14*, 289.

Protonic Conduction in Poly(ethylenimine) Hydrates

Masayoshi Watanabe,* Ryoichi Ikezawa, Kohei Sanui, and Naoya Ogata*

Department of Chemistry, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102, Japan.
Received September 9, 1986

ABSTRACT: The ionic conductivity of crystalline hydrates of linear poly(ethylenimine) (PEI) was investigated as a function of temperature and water content. The main carriers were likely protons. The temperature dependence of the ionic conductivity obeyed the Arrhenius equation, and the activation energies were 18–20 kcal/mol irrespective of the composition of the hydrates. The ionic conductivity reached 10^{-5} S cm^{-1} at 30 °C in the hydrate with [H$_2$O]/[EI unit] = 1.5. A comparison to the conducting behavior of partially amorphous PEI hydrates, which were made by a cross-linking reaction, suggested that the ionic conduction in the linear PEI hydrates occurred in the crystalline phases and that the network structure of hydrogen bonds played an important role in the ionic conduction.

Introduction

The study of ionic conductivity of polymers is of considerable significance in terms of the fundamental understanding of dynamic process proceeding within polymers and of the major functions of energy storage and conversion. Studies have been performed on various kinds of ion-containing polymers in the presence and absence of solvents. An example of the former is highly protonic

0024-9297/87/2220-0968$01.50/0