INSULATOR-TO-METAL TRANSITION IN POLYANILINE: EFFECT OF PROTONATION IN EMERALDINE

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Abstract

The emeraldine base form of the polymer can be varied from insulating $(\sigma \sim 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1})$ to conducting $(\sigma \sim 10^{0} \text{ ohm}^{-1} \text{ cm}^{-1})$ states through protonation. Based upon extensive magnetic, optical and transport data, we demonstrate that the resulting emeraldine salt is metallic with a finite density of states at the Fermi energy. The roles of a novel bipolaron-to-polaron lattice transition and phase segregation into conducting and non-conducting regions are discussed.

Introduction

The polyaniline family of polymers provides a means of systematically studying the electronic structure of polymers as a function of *both* the number of electrons and the number of protons on the polymer chain [1, 2]. Though polyaniline has been known for the past century [3], there has been increased interest recently [4 - 6] due to achievement of a highly conducting polymer as a function of the degree of protonation and oxidation/ reduction. The emeraldine base form of polyaniline is proposed [2] to have equal numbers of reduced $[-(C_6H_4)-(NH)-(C_6H_4)-(NH)-]$ and oxidized $[-(C_6H_4)-N=(C_6H_4)=N-]$ repeat units, Fig. 1(a). Upon treatment with acids of varying pH, protons are added to a fraction of the formerly unprotonated nitrogen sites [2 - 21]. For example, treatment of the emeraldine base with aqueous HCl of pH = 0.0 yields nearly complete protonation, *i.e.*, the emeraldine salt [2]. As a result of this treatment, the d.c. conductivity



Fig. 1. (a) Emeraldine base polymer (unprotonated); (b) schematic bipolaron lattice; (c) schematic polaron lattice.

increases from 10^{-10} ohm⁻¹ cm⁻¹ to 10^{0} ohm⁻¹ cm⁻¹ [2, 21, 22], despite the fact that the number of electrons on the chain has not been altered. Hence the protonation must lead to a significant change in the electronic structure of the polymer [23 - 29]. The conducting form of emeraldine can also be synthesized through the electrochemical oxidation of the fully-protonated leucoemeraldine form of polyaniline [1, 2, 21]. The determination of the appropriate description of the resulting conducting state and its relationship to the concepts of non-linear phenomena in polymers [30, 31] with differing repeat units (the '—A=B—' polymer [32]) and non-degenerate ground states [33 - 35] is an objective of this study.

In this report we summarize the results of magnetic, transport and optical studies of the emeraldine form of polyaniline as a function of protonation. Our experimental results show the development of a metallic density of states with protonation, together with phase segregation into small metallic particles. Results of temperature and electric field-dependent transport experiments are consistent with charging energy-limited tunneling [36] among the small metallic particles. It is proposed that the observed transition to the metallic state is a transition from isolated bipolarons to a polaron lattice.

Experimental techniques

The preparation of emeraldine and its protonation are described elsewhere [2, 21]. Experiments were performed in an anhydrous atmosphere or in vacuum. The magnetic susceptibility was measured via a Faraday technique [37] and electron spin resonance. The reflectance for emeraldine was measured with a Michelson interferometer in the far infrared and a grating monochromator in the infrared and visible [38]: the frequency-dependent conductivity was determined by Kramers-Kronig analysis. The temperature-dependent d.c. conductivity and its electric field dependence were measured together with the thermoelectric power in a previously described apparatus [39].

Experimental results

The temperature-dependent static magnetic susceptibility, $\chi^{\rm M}$, of representative samples of emeraldine as a function of protonation, Fig. 2, can be decomposed into a sum of a temperature-independent term, $\chi^{\rm core} + \chi^{\rm Pauli}$, and a temperature-dependent term, $\chi^{\rm Curie} = n_{\rm s}(T)C/T$, where C is the Curie constant and $n_{\rm s}(T)$ is the number of localized spins. After subtraction of $\chi^{\rm core}$ [40], the variation of $\chi^{\rm Pauli}$ and $n_{\rm s}(T)$ as a function of degree of protonation (expressed as $y = {\rm Cl/N}$) was obtained, Figs. 3 and 4. At the highest protonation level (y = 0.5) a $\chi^{\rm Pauli}$ of $+110 \times 10^{-6}$ emu/mole per two rings is observed, more than twice the $\chi^{\rm Pauli}$ reported [37, 41] for the metallic phase of polyacetylene.

The conductivity increases with protonation, although the functional dependence of the conductivity upon temperature changes little for y > 0.3, Fig. 5. Parametrizing as $\sigma_0 \exp(-(T_0/T)^{1/2})$, the T_0 term is found to vary little



Fig. 2. Magnetic susceptibility vs. temperature for emeraldine at representative protonation levels.



Fig. 3. Pauli susceptibility vs. y (number of protons added per two rings).



Fig. 4. 'Curie' spin concentration vs. y at 300 K (\bullet), $T_{\rm m}$ (\blacktriangle), and 4.2 K (\blacksquare), where $T_{\rm m}$ is the temperature for maximum concentration.



Fig. 5. Log σ vs. $T^{-1/2}$ as a function of protonation level.

for y > 0.3 (Fig. 6), while a strong dependence of the sample resistance upon applied electric fields is observed (see inset to Fig. 6). The room-temperature thermopower is small and negative for y > 0.3. At high protonation levels, the band gap absorption remains at energies greater than 3.5 eV, and two new in-gap absorptions appear at 1.5 eV and 2.9 eV, Fig. 7.

Discussion

The nearly linear increase in χ^{Pauli} ($\mu_{\text{B}}^2 N(E_{\text{F}})$ where $N(E_{\text{F}})$ is the density of states at the Fermi energy) with y is suggestive of phase segregation into metallic and non-metallic regions. The concentration dependence of the absolute conductivity and its temperature dependence are in accord with a percolation threshold among these particles at $y \sim 0.3$. For y > 0.3, barriers between these particles appear to continue to dominate the transport behavior with $\sigma(T) \propto \exp(-(T_0/T)^{1/2})$ at low electric fields and $\sigma(E) \propto \exp(-E_0/E)$ at high electric fields (E_0 is a constant), consistent with charging energy-limited tunneling [36] between the small metallic polyaniline particles.



Fig. 6. T_0 vs. y for data of Fig. 5 assuming $\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}]$. The inset is log resistance vs. E^{-1} for the y = 0.5 sample at 50 K.

The presence of a finite density of states at the Fermi energy for the protonated polymer reflects a change in the electronic structure of the polymer upon protonation. Addition of two protons at the (previously unprotonated) nitrogen sites on either side of the quinoid rings results in a spinless bipolaron defect, Fig. 1(b), inconsistent with the measured magnetic susceptibility. It has been proposed [22, 40, 42] that there is a transition to an ordered array of polarons, as shown schematically in Fig. 1(c). X-ray photoemission spectroscopy results [43] support the idea that the polarons are centered on alternate nitrogen sites. The transition from bipolarons to a polaron lattice is not energetically favored [35, 44], though it may be stabilized by the energy gained through reduced Coulomb interaction and delocalization [44]. In addition, three-dimensional coherent ordering [45], Coulomb interaction with the interstitial dopants and dielectric screening may stabilize the polaron lattice. From the measured $N(E_{\rm F})$, a polaron bandwidth $W^{\rm P}$ of 0.37 eV is obtained. Using the results of the continuum model expression for W^{P} (assuming Coulomb repulsion = 0, all C and N are identical and that both phases of bond alternation have the same energy) [44], we obtain [40] a polaron decay length of 0.4 of the N–N spacing.

The two new absorptions in the optical spectrum are in agreement with those expected [34] for a polaron lattice. There is relatively little change in the infrared vibrational spectrum upon protonation, in qualitative agreement with predictions [46] for a polaron lattice.



In addition to χ^{Pauli} , the number of 'Curie' spins increases with protonation. For each protonation level the number of 'Curie' spins increases as the temperature is lowered, reaching a maximum at a temperature $T_{\rm m} \sim 50$ K then decreasing as T is further decreased, Fig. 4. It has been suggested [40] that this is due to localization at low temperatures of polarons at the surface of the small metallic particles formed upon protonation of emeraldine. Below $T_{\rm m}$, pairs of these polarons, if in sufficient proximity, may combine to form spinless bipolarons.

Summary

The protonation of emeraldine results in a transition to a metallic polymer. The magnetic, optical and transport studies support the idea that the transition is to a polaronic metal with phase segregation of the metallic regions from the insulating regions. Charge transport is limited by the electron transitions between the small conducting polymer regions.

Acknowledgements

This research was supported in part by NSF-DMR-8416511 (H.S.W. and D.B.T.), DMR-8216718 (M.A. and W.S.H.) and Office of Naval Research (A.F.R.).

References

- 1 W. R. Salaneck, I. Lundström, W.-S. Huang and A. G. MacDiarmid, Synth. Met., 13 (1986) 291.
- 2 J.-C. Chiang and A. G. MacDiarmid, Synth. Met., 13 (1986) 193.
- 3 A. G. Green and A. E. Woodhead, J. Chem. Soc., (1910) 2388.

- 4 R. de Surville, M. Josefowicz, L. T. Yu, J. Perichon and R. Buvet, *Electrochim. Acta*, 13(1968) 1451.
- 5 J. Langer, Solid State Commun., 26 (1978) 839.
- 6 A. G. MacDiarmid, J.-C. Chiang, M. Halpern, W.-S. Huang, J. R. Krawczyk, R. J. Mammone, S. L. Mu, N. L. D. Somasiri and W. Wu, Polym. Prepr., 25 (1984) 248.
- 7 A. G. MacDiarmid, J.-C. Chiang, M. Halpern, W.-S. Huang, S.-L. Mu, N. L. D. Somasiri, W. Wu and S. I. Yaniger, *Mol. Cryst. Liq. Cryst.*, 121 (1985) 173.
- 8 P. M. McManus, S. C. Yang and R. J. Cushman, J. Chem. Soc., Chem. Commun., (1985) 1556.
- 9 J. P. Travers, J. Chroboczek, F. Devreux, F. Genoud, M. Nechtschein, A. Syed, E. M. Genies and C. Tsintavis, *Mol. Cryst. Liq. Cryst.*, 121 (1985) 195.
- 10 E. M. Genies, J.-M. Pernant, C. Santier, A. A. Syed and C. Tsintavis, Solid State Sci., 63(1985)211.
- 11 W. R. Salaneck, I. Lundström, B. Liedberg, M. A. Hasan, R. Erlandsson and P. Konradsson, Solid State Sci., 63 (1985) 218.
- 12 H. Kuzmany, E. M. Genies and A. Syed, Solid State Sci., 63 (1985) 223.
- 13 E. M. Genies and C. Tsintavis, J. Electronal. Chem. Interfacial Electrochem., 195 (1985) 109.
- 14 E. W. Paul, A. J. Ricco and M. S. Wrighton, J. Phys. Chem., 89 (1985) 1441.
- 15 G. E. Wnek, Polym. Prepr., 27 (1986) 277.
- 16 M. Kaya, A. Kitani and K. Sasaki, Chem. Lett., (1986) 147.
- 17 M. Nechtschein, C. Santier, J. P. Travers, J. Chroboczek, A. Alix and M. Ripert, Synth. Met., 18 (1987) 311.
- 18 E. M. Genies, M. Lapkowski, C. Santier and E. Vieil, Synth. Met., 18 (1987) 631.
- 19 Y. Cao, S. Li, Z. Xue and D. Guo, Synth. Met., 16 (1986) 305.
- 20 H. Kuzmany and N. S. Sariciftci, Synth. Met., 18 (1987) 353.
- 21 A. G. MacDiarmid, J.-C. Chiang, A. F. Richter and A. J. Epstein, Synth. Met., 18 (1987) 285.
- 22 A. J. Epstein, J. M. Ginder, F. Zuo, R. W. Bigelow, H. S. Woo, D. B. Tanner, A. F. Richter, W.-S. Huang and A. G. MacDiarmid, Synth. Met., 18 (1987) 303.
- 23 B. Thémans, J. M. André and J. L. Brédas, Solid State Sci., 63 (1985) 107.
- 24 S. Stafström and J. L. Brédas, Synth. Met., 14 (1986) 297.
- 25 R. R. Chance, D. S. Boudreaux, J. F. Wolf, L. W. Shacklette, R. Silbey, B. Thémans, J. M. André and J. L. Brédas, Synth. Met., 15 (1986) 105.
- 26 S. Stafström, J. L. Brédas, A. J. Epstein, H.-S. Woo, D. B. Tanner and W.-S. Huang, submitted.
- 27 C. B. Duke, E. M. Conwell and A. Paton, Chem. Phys. Lett., in press.
- 28 L. A. Burke and M. Kertesz, to be published.
- 29 C. B. Duke, A. Paton, E. M. Conwell, W. R. Salaneck and I. Lundström, 131 (1986) 82.
- 30 See, for example, T. Skotheim (ed.), Handbook of Conducting Polymers, Vols. 1 and 2, Dekker, New York, 1986.
- 31 A. J. Epstein, J. M. Ginder, A. F. Richter and A. G. MacDiarmid, in L. Alcacer (ed.), Proc. NATO Workshop on Conducting Polymers, Riedel, Dordrecht, in press.
- 32 M. J. Rice and E. J. Mele, Phys. Rev. Lett., 49 (1982) 1455.
- 33. W. P. Su and J. R. Schrieffer, Proc. Nat. Acad. Sci. U.S.A., 77 (1980) 5526.
- 34 K. Fesser, A. R. Bishop and D. K. Campbell, Phys. Rev. B, 27 (1983) 4804.
- 35 Y. Onodera, Phys. Rev. B, 30 (1984) 775.
- 36 P. Sheng, B. Abeles and Y. Arie, Phys. Rev. Lett., 31 (1973) 44.
- 37 A. J. Epstein, H. Rommelmann, M. A. Druy, A. J. Heeger and A. G. MacDiarmid, Solid State Commun., 38 (1981) 683.
- 38 X. Q. Yang, D. B. Tanner, A. Feldblum, H. W. Gibson, M. J. Rice and A. J. Epstein, Mol. Cryst. Liq. Cryst., 117 (1985) 267.
- 39 A. J. Epstein, H. Rommelmann, R. Bigelow, H. W. Gibson, D. M. Hoffman and D. B. Tanner, Phys. Rev. Lett., 50 (1983) 1866.
- 40 J. M. Ginder, A. F. Richter, A. G. MacDiarmid and A. J. Epstein, Solid State Commun., 63 (1987) 97.
- 41 T. C. Chung, F. Moraes, J. D. Flood and A. J. Heeger, Phys. Rev. B, 29 (1984) 2341.
- 42 J. M. Ginder, A. J. Epstein, R. W. Bigelow, A. F. Richter and A. G. MacDiarmid, Bull. Am. Phys. Soc., 31 (1986) 582.
- 43 W. R. Salaneck, I. Lundström, T. Hjertberg, C. B. Duke, E. Conwell, A. Paton, A. G. MacDiarmid, N. L. D. Somasiri, W.-S. Huang and A. F. Richter, Synth. Met., 18 (1987) 291.
- 44 S. Kivelson and A. J. Heeger, Phys. Rev. Lett., 55 (1986) 308.
- 45 H. B. Schüttler, to be published.
- 46 H.-Y. Choi and E. J. Mele, to be published.