

## ARTICLES

## Enhancement of Room Temperature Electrical Conductivity of Polypyrrole by Chemical Modification

Swapan Chakrabarti,<sup>†,‡</sup> D. Banerjee,<sup>\*,†</sup> and R. Bhattacharyya<sup>§</sup>*Department of Physics, University of Calcutta, 92, Acharya Prafulla Chandra Road, Calcutta 700 009, India, and Department of Chemistry, Jadavpur University, Calcutta 700 032, India**Received: July 9, 2001; In Final Form: December 2, 2001*

Polypyrrole and polypyrrole–tetracyanoquinodimethane (TCNQ) have been prepared to see the energy band structure modification and associated change in the electrical and optoelectrical properties. The temperature-dependent electrical conductivity of the samples show interesting behavior, namely, higher room-temperature conductivity of polypyrrole–TCNQ and a crossover phenomenon which may be considered as a competition between two opposing factors, charge-transfer interaction and disorderness. CHN microanalysis, UV–vis absorption spectroscopy, and positron annihilation lifetime spectroscopy corroborate the findings.

## 1. Introduction

The mechanism for formation of a metallic state and charge conduction in conducting polymers has been the subject of intensive study since the 1980s.<sup>1,2</sup> The theoretical model coupled with experimental investigation suggest that polaron, bipolaron, or soliton type defects are the charge carriers in these polymer systems.<sup>3–5</sup>

Of the many conducting polymers identified so far, polypyrrole (PPy) and its derivatives have been studied extensively because of its many interesting properties.<sup>6</sup> Over the past two decades, several illustrative ideas have been put forth to modify the electronic and optoelectronic properties of PPy with a view to finding its potential worth in making microelectronics and molecular electronic devices.<sup>6</sup> However, it has been observed by the earlier researchers that both ring-substituted and N-substituted poly(alkyl-pyrrole) have poor electrical conductivity with respect to pure PPy.<sup>6</sup>

In the present work, we have initiated a systematic investigation aimed at improving the electrical properties of PPy. We prepared a charge transfer complex using pyrrole as the donor and TCNQ as an acceptor. After polymerization of the resulting complex, we have studied how the various electrophysical properties of PPy are influenced in the new procedure of synthesis. Early investigations on the electrochemically synthesized PPy–TCNQ system by Fourier transform infrared reflection absorption spectroscopy reveal the existence of charge transfer to take place from polymer backbone to the TCNQ molecule.<sup>7</sup> In another work, using ultraviolet photoemission spectroscopy, Takemura et al. showed how the valence band spectra of PPy are affected by the presence of TCNQ in the lattice.<sup>8</sup>

In the present study, we have observed higher room-temperature electrical conductivity of PPy–TCNQ and an

electrical crossover phenomenon while measuring the temperature-dependent electrical conductivity of PPy and PPy–TCNQ systems. Although electrical crossover phenomena have also been observed in the conducting polymer and their blends,<sup>9,10</sup> the present investigation is interesting because here the crossover phenomenon is observed in the systems comprised of a pure conducting polymer (PPy) and a chemically modified version of it (PPy–TCNQ).

To understand the transport mechanism in these samples we have used the following experimental techniques: (i) UV–vis spectroscopy, (ii) CHN microanalysis, (iii) temperature-dependent four probe conductivity, (iv) fluorescence spectroscopy, and (v) PAL spectroscopy.

## 2. Experimental Outline

**A. Materials.** Pyrrole (E. Merck, Germany) was purified twice by fractional distillation under nitrogen atmosphere immediately prior to use. Ammonium ferric sulfate  $[(\text{NH}_4)\text{Fe}(\text{SO}_4)_2] \cdot 12\text{H}_2\text{O}$  (E. Merck, Germany) was used as an oxidizing agent for PPy synthesis. To avoid moisture contamination during weighing of the sample, we have chosen this oxidizing agent. TCNQ (E. Merck, Germany) was procured as the highest grade obtainable and used without purification. Deionized water was used as the solvent to prepare the solutions.

**B. Synthesis.** PPy has been synthesized by mixing a pyrrole solution with a solution of the oxidizing agent,  $[(\text{NH}_4)\text{Fe}(\text{SO}_4)_2] \cdot 12\text{H}_2\text{O}$ . The temperature of the system is kept at 0 °C. Pyrrole is added to such an extent that the molar ratio of the oxidizing agent to the pyrrole is 50:1. This ratio is maintained to ensure complete conversion of pyrrole monomer to PPy.<sup>11</sup> The polymerization process is allowed to proceed for 1 h. PPy, formed as a black precipitate, is collected by filtration in a sintered bed crucible. The polymer thus obtained is rinsed thoroughly with water and dried for 24 h at room temperature under vacuum.

For the preparation of PPy–TCNQ, a charge transfer (CT) complex involving pyrrole as a donor and TCNQ as an acceptor

\* To whom correspondence should be addressed.

<sup>†</sup> University of Calcutta.

<sup>‡</sup> Presently at Department of Chemistry, University of Calcutta.

<sup>§</sup> Jadavpur University.

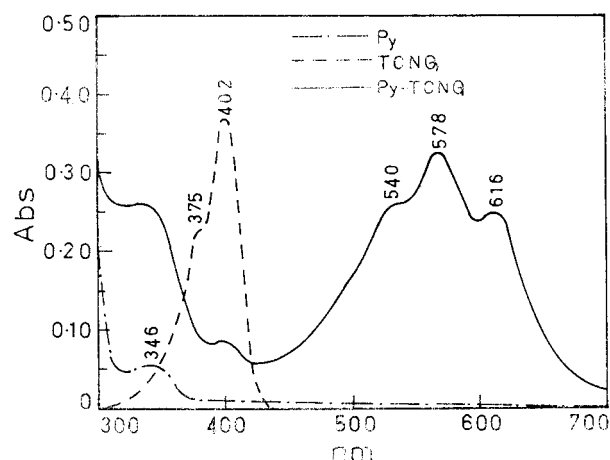


Figure 1. UV-vis spectra of pyrrole, TCNQ, and CT complex.

TABLE 1: Results of CHN Microanalysis

sample	C(%)	H(%)	N(%)
PPy	42.04	3.76	11.34
PPy-TCNQ	50.10	4.13	14.67

has been prepared in the molar ratio 1:1. Formation of CT complex is evident from the UV-vis absorption spectroscopy (Figure 1). Although pyrrole and TCNQ show absorption peaks at 346 and 402 nm, the complex shows a spectrum with an absorption maximum at 578 nm and two almost equidistant shoulders on both sides of it. The resulting complex was then polymerized and collected following the same method as in the case of PPy. In contrast to PPy, a dark black material, the color of the PPy-TCNQ system is gray. The weight percentages of CHN of PPy and PPy-TCNQ were determined, and the results are presented in Table 1. The results appear to provide a quite astonishing feature. The CHN data for PPy-TCNQ is different from what it ought to be. The only possibility is that in the resulting polymer TCNQ is randomly distributed as CT interactions are disrupted in some of the monomer moieties during synthesis.

Dried polymer powders obtained in both the cases are subjected to 6 ton/cm<sup>2</sup> pressure for 10 min to make the pellets which are subsequently used for four probe resistivity as well as positron annihilation lifetime measurements.

**C. UV-vis-Near-Infrared Spectroscopy.** UV-vis-near-infrared spectra of pyrrole, TCNQ, and the CT complex were recorded with a Hitachi U-3501 spectrophotometer.

**D. CHN Microanalysis.** The weight percentages of CHN of PPy and PPy-TCNQ were determined by means of elemental analysis using a CHN analyzer (2400 series II, Perkin-Elmer).

**E. Fluorescence Spectroscopy.** The front surface fluorescence measurements were carried out using a Perkin-Elmer LS 50B spectrophotometer, and 10/10 nm slits were used for this purpose.

**F. Positron Annihilation Lifetime Measurements.** The positron annihilation lifetimes have been measured with a fast-slow coincidence assembly. The detectors are 25 mm dia, 25 mm long cylindrical BaF<sub>2</sub> scintillators coupled to Philips XP2020Q photomultiplier tubes (PMT). The negative pulses from the anodes of the PMTs are fed directly to constant fraction differential discriminators and then to the inputs of a time-to-amplitude converter. The resolving time (fwhm), measured with a <sup>60</sup>Co source and with the windows of the slow channels of the fast-slow coincidence assembly set to select pulses corresponding to 300–550 keV in one channel and 700 keV to 1.32 MeV in the other, is 190 ps.

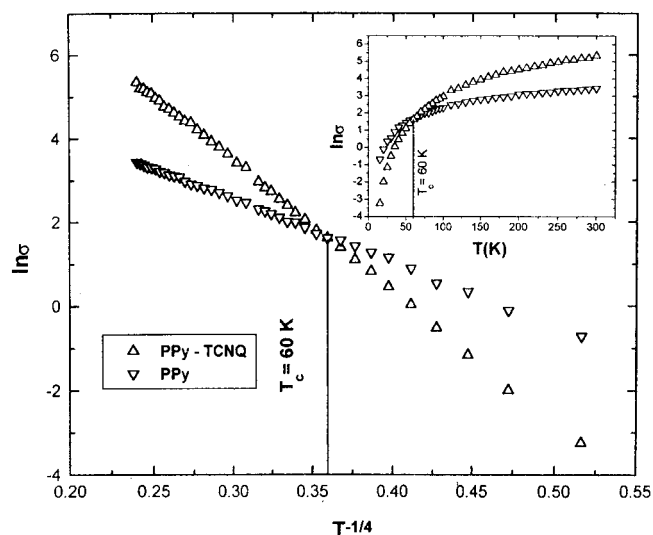


Figure 2. Plot of  $\ln \sigma$  vs  $T^{-1/4}$  for PPy and PPy-TCNQ.

The experimental positron source is prepared from a carrier free <sup>22</sup>NaCl solution in water by depositing a drop of the solution and then drying it on a thin nickel foil 2 μm thick to obtain a source strength of 10 μCi. A similar nickel foil is placed on the source to cover it.

The contribution of the source in the lifetime spectrum, which has been ascertained by referring to the measured value of the lifetime of positrons in an Al single-crystal sample, is ≤2%.

The lifetimes and their relative intensities have been extracted from the recorded spectra using the PATFIT-88 program.<sup>12</sup>

**G. Resistivity Measurements.** The four probe electrical resistivity of PPy and PPy-TCNQ were measured in the temperature range 15 ≤ T ≤ 300 K using Keithley electrometer (model 236). The low temperature measurement was performed using closed cycle helium cryostat. Electrical contacts were made with highly conducting silver paints.

### 3. Results and Discussion

The temperature dependence of d.c. electrical conductivity  $\sigma(T)$  of the samples show that the conductivity decreases with the decrease of temperature, indicating the semiconducting behavior in the whole range of temperature. The room-temperature conductivity of pure PPy is 32 Scm<sup>-1</sup>, but the conductivity changes to a somewhat higher value, 189 Scm<sup>-1</sup> for the PPy-TCNQ system.

We have plotted  $\ln \sigma$  vs  $T^{-1/n}$  for both of the systems, where  $n = 2, 3$ , and 4. It has been observed that the best fits (standard deviation 0.012) for both of the systems are obtained with  $n = 4$  in the temperature range 15 ≤ T ≤ 300 K. The striking feature of the plot in Figure 2 is the crossover phenomenon at  $T_c = 60$  K. It is also evident from the plots that

$$\sigma_{II} > \sigma_I \text{ at } T > T_c$$

$$\sigma_{II} = \sigma_I \text{ at } T = T_c$$

$$\sigma_{II} < \sigma_I \text{ at } T < T_c$$

where pure PPy and PPy-TCNQ are denoted by I and II, respectively.

Justification of such an observation certainly needs proper characterization of the samples, and identification of the variables those might responsible for the occurrence of  $T_c$ . In this regard, the front surface fluorescence technique has been

TABLE 2: PAL Spectroscopic Parameters

sample	pelletization pressure (ton)	$\tau_1$ (ps)	$\tau_2$ (ps)	$\tau_3$ (ns)	$I_2$ (%)	$I_3$ (%)
PPY	4	150 $\pm$ 3	331 $\pm$ 5		45 $\pm$ 1.5	
	6	150 $\pm$ 3	333 $\pm$ 5		45 $\pm$ 1.5	
	8	150 $\pm$ 3	334 $\pm$ 5		45 $\pm$ 1.5	
PPy-TCNQ	4	130 $\pm$ 2.8	290 $\pm$ 5.8	1.25 $\pm$ 0.09	52 $\pm$ 1.3	3.02 $\pm$ 0.4
	6	130 $\pm$ 2.8	292 $\pm$ 5.8	1.17 $\pm$ 0.09	51 $\pm$ 1.4	2.35 $\pm$ 0.3
	8	130 $\pm$ 2.8	291 $\pm$ 5.8	1.16 $\pm$ 0.07	50 $\pm$ 1.4	2.25 $\pm$ 0.3

employed to find out the energy band structure of the samples and microstructural features are excerpted from PAL measurements.

The fluorescence spectra of the samples are presented in Figure 3. Although 380 nm excitation is suitable for PPy, the PPy-TCNQ system requires 400 nm excitation. It has been observed that PPy gives a fluorescence spectrum having  $\lambda_{\max} = 584$  nm which may be surmised as antibipolaron to bipolaron band transition. For the PPy-TCNQ system, the nature of the spectrum is drastically different. It shows three distinct emission peaks with  $\lambda_{\max} = 535, 598$ , and 719 nm. The peak at 598 nm may be regarded as a slightly red shifted antibipolaron to bipolaron band transition, and the other two peaks are certainly associated with the charge transfer process. Thus incorporation of TCNQ in PPy lattice leads to the band structure modification of it. The presence of the extra levels apart from the normal bipolaron bands within the band gap in the PPy-TCNQ system are certainly responsible for the excess concentration of the charge carriers at the conduction band as is evident from the room-temperature conductivity data of the samples.

The positron annihilation lifetimes have been measured, and it has been observed that the positron lifetime spectrum for the PPy system is best fitted for two lifetime components, and for the PPy-TCNQ system, the best fit is obtained with three lifetime components. Three-component fit indicates the presence of a very long third component (1.16–1.25 ns) with a low intensity (2–3%). This is important, in spite of its low intensity, because one ends up with significantly different values of  $\tau_1$  and  $\tau_2$  and poorer fit on ignoring it. With microstructural voids as its possible origin,  $\tau_3$  can be attributed to positronium formation and subsequent *o*-Ps to *p*-Ps conversion. As described elsewhere,<sup>13</sup> explicitly, the first positron lifetime component,  $\tau_1$ , cannot be related with annihilation from a particular site unlike for the intermediate lifetime component,  $\tau_2$ , which arises from annihilation in the defect sites. Our recent investigation on microstructural lattice deformation of PPy indicates that  $\tau_2$  originates from positron annihilation at the dopant site with a polaronic or bipolaronic environment depending upon the nature of the oxidizing agent and its strength.<sup>13,14</sup> From Table 2, it

appears true that the presence of TCNQ in a PPy lattice alters the electron density distribution. The quenching of  $\tau_2$  and increase in the  $I_2$  value are manifested in the high room-temperature conductivity of PPy-TCNQ.

Thus, from PAL spectroscopy along with the CHN microanalysis study, it is imperative that PPy-TCNQ is structurally more disordered than pure PPy. The electrical properties of doped polymers are strongly dependent on the extent of disorder present in the material.<sup>15,16</sup> The term disorder is a vector of many aspects including (i) nonequivalence of conjugated fragments, (ii) presence of both crystalline and noncrystalline phases, (iii) impurities, (iv) substitution at the monomer unit, etc. Besides, conducting polymers are regarded as a randomly distributed polaron/bipolaron lattice which in fact gives the quantum picture of disorder. When disorder is introduced in a system, electronic states change fundamentally. Incorporation of disorder would lead to a scattering process that would decrease the amplitude for the electron to move from one end of the material to the other.<sup>17</sup>

In the present context, in order to bring a semblance of coherence in the internal multiplicity of arguments and facts, considering all of these experimental results, one can propose that at  $T > T_c$ , the higher  $\sigma_{II}$  over  $\sigma_I$  is due to an extra charge transport apart from the normal hopping transport through bipolarons. However, when  $T < T_c$ ,  $\sigma$  for PPy-TCNQ falls off more rapidly than pure PPy. It appears true that, at  $T < T_c$ , the charge transfer band transition which plays a significant role in the high temperature domain practically freezes and disorder induced localization of charge carrier dominates. Finally a detrimental effect of disorder and bolstering role of charge-transfer interaction on conductivity leads to the appearance of the cross over temperature ( $T_c$ ).

#### 4. Conclusions

In summary, we have presented detailed results from a series of experiments through which we have investigated the role of the charge-transfer agent in modifying the energy band structure of PPy and the concomitant change in the electrophysical properties of the same. The major findings of this experiment are (i) the room-temperature conductivity of the modified polymer is greater than that of pure PPy and (ii) the crossover phenomenon observed in the temperature dependence study of the electrical conductivity of the samples which suggests the possibility of the dominance of disorder rather than the extra charge-transfer process in the lower temperature region.

**Acknowledgment.** The authors wish to convey their appreciation to Dr. S. Bhattacharya and S. Kumar, Dr. K. Pramanik, and A. Das for various helps.

#### References and Notes

- (1) Diaz, A. Z.; Bargon, J. In *Handbook of conducting polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986; Vol. 1, pp 81–115.

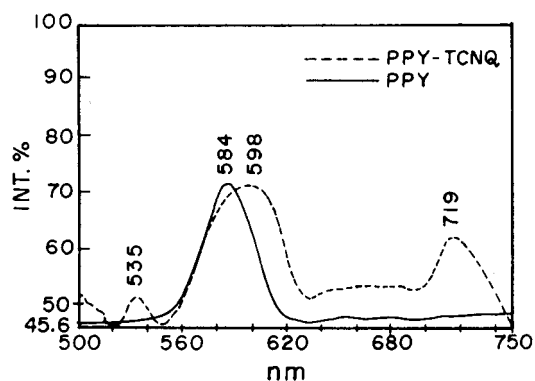


Figure 3. Fluorescence spectra of PPy and PPy-TCNQ.

- (2) Heeger, A. J.; Kivelson, S.; Schriber, J. R.; Su, W. P. *Rev. Mod. Phys.* **1988**, *60*, 781.
- (3) Kaufman, J. H.; Colaneri, N. *Phys. Rev. Lett.* **1984**, *53*, 1005.
- (4) Scott, J. C.; Pfluger, P.; Krounbi, M.; Street, G. B. *Phys. Rev. B* **1983**, *28*, 2140.
- (5) Pfluger, P.; Street, G. B. *J. Chem. Phys.* **1984**, *80*, 544.
- (6) Saunders, B. R.; Fleming, R. S.; Murray, K. S. *Chem. Mater.* **1995**, *7*, 1082.
- (7) Kato, H.; Nishikawa, O.; Matsui, T.; Honma, S.; Kokado, H. *J. Phys. Chem.* **1991**, *95*, 6011.
- (8) Takemura, S.; Kitagawa, Y.; Kato, H.; Nakajima, Y. *Appl. Surf. Sci.* **1996**, *100/101*, 107.
- (9) Subramaniam, C. K.; Kaiser, A. B.; Gilberd, P. W.; Wessling, B. *J. Polym. Sci. B: Polym. Phys.* **1993**, *31*, 1425.
- (10) Subramaniam, C. K.; Kaiser, A. B.; Gilberd, P. W.; Liu, C. J.; Wessling, B. *Solid State Commun.* **1996**, *97*, 235.
- (11) Lei, J.; Cai, Z.; Martin, C. R. *Synth. Met.* **1992**, *46*, 53.
- (12) Kirkegaard, P.; Pedersen, N. J.; Eldrup, M. Report of Riso National Laboratory (Riso-M-2740), 1989.
- (13) Chakrabarti, S. *J. Chem. Phys.* **1999**, *110*, 9305.
- (14) Chakrabarti, S.; Das, B.; Banerji, P.; Banerjee, D.; Bhattacharya, R. *Phys. Rev. B* **1999**, *60*, 7691.
- (15) Ghosh, M.; Barman, A.; Das, A.; Meikap, A. K.; De, S. K.; Chatterjee, S. *J. Appl. Phys.* **1998**, *84*, 806.
- (16) Chakrabarti, S.; Bhattacharya, S. N.; Banerjee, D.; Bhattacharya, R. *J. Chem. Phys.* **2000**, *113*, 7593.
- (17) Phillips, P.; Wu, H. L. *Science* **1991**, *252*, 1805.