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Interfacial polarization in semiconducting polypyrrole thin films

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Abstract. Semiconducting polypyrrole (PPY) thin films have been found to exhibit interesting dielectric properties when sandwiched between blocking electrodes. Dielectric relaxation studies have been carried out on metal–PPY–metal capacitors with and without an application of external bias. The relaxation spectra observed in the frequency range 1 kHz–1 MHz have been attributed to space charges and dipoles. The data have also been used to estimate the mobility of charge carriers inside PPY by application of simple space-charge theories. This phenomenon has been studied at several temperatures in the range 200–400 K. Interestingly, the mobility of charge carriers has been found to have a negative temperature coefficient, in agreement with theoretical calculations found in the literature for the mobility of charged polarons and kinks in conjugated polymers.

1. Introduction

The emergence of quasi-one-dimensional polymers as a new class of materials that can be doped to vary from the semiconducting to the conducting state has offered new concepts and mechanisms for electrical conduction. The charge transport mechanism in conjugated polymers such as polyacetylene (PA), polypyrrole (PPY) and polythiophene (PT) has been extensively studied [1–13]. In polymers such as PPY which have non-degenerate ground states, polarons and bipolarons are believed to be responsible for charge transport. Many accurate experiments such as ESR and NMR have been carried out to determine the types of charge carrier in these materials. The optical properties of these materials have also been studied in great detail. Nevertheless, the charge transport in these materials is yet to be firmly established as they possess a high degree of disorder and exhibit both semiconducting and metallic behaviour.

In this paper, we report the use of dielectric spectroscopy in understanding the charge-transport phenomena in doped PPY. Such studies have been useful in understanding the transport phenomena in inorganic semiconductors [14–16]. Space-charge relaxation studies can be useful in understanding the charge mobility in thin films of inorganic compounds as the space-charge region in thin films can have a well defined boundary. This distinction is further enhanced by an application of external bias.

Doped PPY is a well-known p-type semiconductor with a work function close to that of gold. Hence a metal with a work function less than that of PPY forms a rectifying or blocking contact. It has been found that the metal Al forms a blocking contact [17].

Hence it is possible to create a space-charge region by containing all the free charge carriers inside a PPY thin film by fabricating Al-PPY-Al capacitors. The dielectric studies on Al-semiconducting PA-Al capacitors has been extensively studied and discussed by Kanicki [18]. Interfacial polarization has been observed in this system and this has been attributed to the formation of space charges due to the formation of a Schottky barrier. We take advantage of this fact in our studies and construct a model for studying the relaxation phenomena of space charges. It is seen that dielectric relaxation studies on this system can give valuable information on the transport properties of charge carriers in PPY and this can be extended to other conjugated polymers as well.

2. Theory

The current-voltage (I-V) and capacitance-voltage (C-V) characteristics of a polymeric semiconductor are similar to those of a conventional inorganic semiconductor. Such characteristics have been obtained for various metal-PPY junctions [17].

Figure 1(a) depicts the resulting Al-PPY-Al capacitor. In the presence of a strong bias across the sample, the ions in the sample align towards their respective electrodes. As the electrodes are blocking, no injection or extraction of charges into and from PPY takes place. Thus a space charge is created near the electrodes, resulting in a field gradient across the sample. A depletion region is also created inside the sample. The resulting electric field and charge distribution inside the sample are shown in figures 1(b) and 1(c), respectively.

We now provide the theoretical basis for the interpretation of the dielectric data. Owing to the blocking nature of our electrodes and an external bias, we are justified in assuming a well defined space-charge region as shown in figure 1. We now write the equations of motion for the space-charge boundary when an alternating voltage is superposed on the existing bias.

As a simplifying assumption we consider the movement of the space-charge boundary at the cathodic region (this choice is arbitrary). Further, the width of the anodic space-charge region is also ignored as an approximation. The analysis and derivation of polarization based on such an approximation have been discussed in [19].

Let the space-charge region be limited to $0 < x < \xi$ as shown in figure 1. The electric intensity E , in the region $\xi < x < L$, is approximately given by [20]

$$E(\xi) = (1/L) [V_s - (ne/2\epsilon\epsilon_0) \xi^2] \quad (1)$$

where ϵ_0 is the permittivity in free space, e is the magnitude of the electronic charge, ϵ is the high-frequency permittivity, V_s is the static bias across the sample and n is the concentration of charge carriers.

The equation governing the movement of the space-charge boundary made of charges with mobility μ can be written as

$$d\xi/dt = -\mu E(\xi). \quad (2)$$

For a constant static bias $V = V_s$, the final position of the boundary ξ_s is given by

$$\xi_s = [(2\epsilon\epsilon_0/ne) V_s]^{1/2}. \quad (3)$$

In a situation where a steady bias is superposed by a small AC component $v = v_0 \exp(i\omega t)$ the capacitance C is given by

$$C = C_\infty [(\alpha^2 + \beta^3)/(\alpha^2 + \beta^2)] \quad (4)$$

where $C_\infty = \epsilon\epsilon_0 A/L$ and A is the area of the electrode.

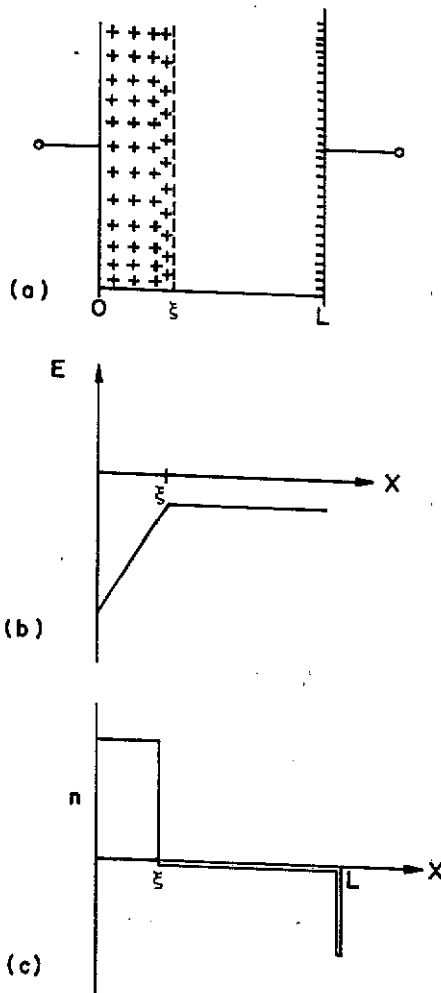


Figure 1. Charge distribution and electric field inside Al-doped PPY-Al capacitor: (a) space charge in the sample; (b) field distribution; (c) charge density.

The dielectric loss tangent $\tan \delta$ is given by

$$\tan \delta = \beta(\beta - 1)\alpha/(\beta^3 + \alpha^2) \tag{5}$$

where α and β are dimensionless variables defined as

$$\alpha = \omega L^2/2\mu V_s \tag{6}$$

and

$$\beta = (ne L^2/2\epsilon\epsilon_0 V_s)^{1/2} = L/\xi_s. \tag{7}$$

From equation (5) it is clear that $\tan \delta$ has a maximum when

$$\alpha^2 = \beta^3. \tag{8}$$

Finally, from equation (8), the mobility μ of the charge carriers can be written as

$$\mu = (\omega_m^4 \epsilon^3 \epsilon_0^3 L^2/n^3 e^3 V_s)^{1/4} \tag{9}$$

where ω_m is the frequency at which the dielectric loss is maximum and V_s is the static bias across the film.

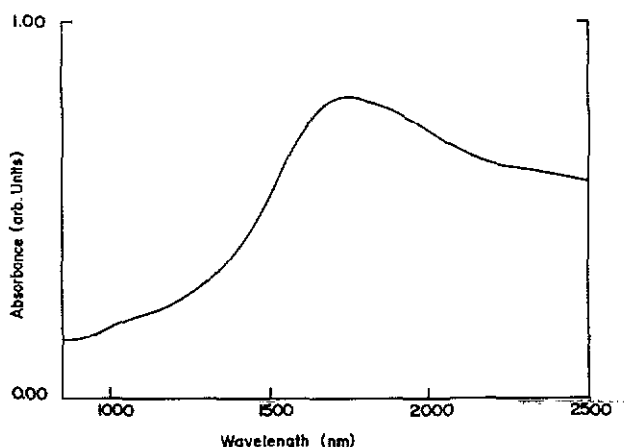


Figure 2. Optical absorption spectrum of a doped PPY thin film in the range 1000–2500 nm.

3. Experimental details

PPY films were prepared by the isothermal electrochemical deposition technique in a solution containing 0.1 M pyrrole as the monomer, and 0.1 M tetraethyl ammonium tetrafluoroborate as the solvent. The reaction vessel consisted of a three-electrode structure with an indium tin oxide glass plate as the anode, a platinum foil as the cathode, and a standard calomel electrode. Ultra-pure reagents and solvents were obtained from Fluka Chemie AG. The entire electrochemical deposition was carried out in an inert atmosphere under isothermal conditions. Current densities of the order of 5 mA cm^{-2} (at 15 V) were used during the electrodeposition. Self-supporting PPY films were obtained. Blocking contacts were made by depositing Al on PPY films by vacuum evaporation. The percentage of dopant was estimated to be of the order of 25%.

Dielectric measurements were carried out using an HP 4192-A impedance analyser within a frequency range 5 Hz–13 MHz on the PPY films with vacuum-evaporated blocking contacts. The undoping of PPY films was achieved by treating the films with aqueous ammonia.

4. Results and discussion

The conductivity of the doped PPY films as measured with a four-point probe was in the range $5\text{--}15 \Omega^{-1} \text{ cm}^{-1}$. The absorption spectrum of a doped PPY film is shown in figure 2. This is typical of PPY. The broad peak in this energy range is presumably due to the polaron and bipolaron levels.

All the dielectric measurements were done at a signal voltage of 0.1 V with 0, 50, 100 and 200 mV as bias. The thickness of the films was of the order of $10 \mu\text{m}$.

In the following discussions we restrict ourselves to the observations made in the frequency range 100 kHz–1 MHz where the relaxations observed are due to space charges and dipoles.

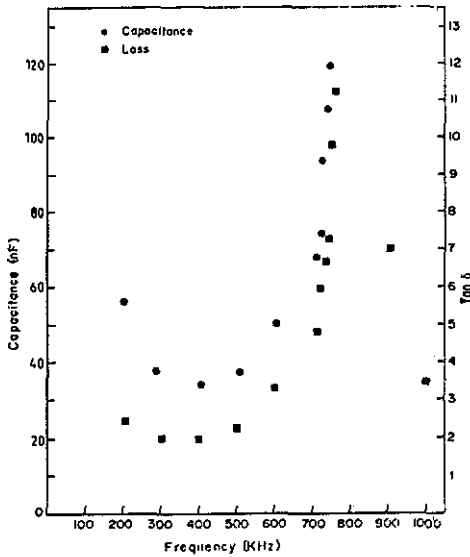


Figure 3. Variations in the differential capacitance and dielectric loss with frequency at zero bias.

4.1 Effect of frequency

The variations in differential capacitance and dielectric loss for the Al-PPY-Al capacitors at room temperature (290 K) and at zero bias are shown in figure 3. Interestingly the features of space-charge relaxation, interfacial polarization and dipole relaxation are seen in the capacitance data. The increase in the capacitance as the frequency decreases is indicative of interfacial polarization arising from the formation of space charges near the electrodes. The loss decreases with increase in the frequency and is a maximum at a frequency of around 800 KHz. The capacitance shows a strong resonance at around the same frequency. Clearly, the resonance is due to the formation of dipoles in PPY thin films when blocking electrodes are used on either side in conjunction with an external static bias. The relaxation observed here is typical of the relaxation expected from the damping of dipole oscillators. The loss peak can therefore be attributed to the movement of charge carriers inside the PPY sample. Also the relaxation seen here is found to be of non-Debye type. The origin of such relaxation lies in the fact that PPY is a highly disordered material and the charge transport occurs both along the chain and between the chains. An estimate of the relaxation times of 0.25 and 0.03 s is made from the $\log \omega$ versus $\log \epsilon''$ plot shown in figure 4.

The distribution of relaxation times is also evident from the Cole-Cole plot (figure 5). The deviation from the semicircular graph is clearly due to the presence of charge carriers and their conductivity σ . Accordingly the complex permittivity ϵ^* can be written as

$$\epsilon^* = \epsilon_\infty + (\epsilon_s - \epsilon_\infty)/(1 + i\omega\tau) - i\sigma/\omega$$

where ϵ_s is the static dielectric constant and τ is the relaxation time.

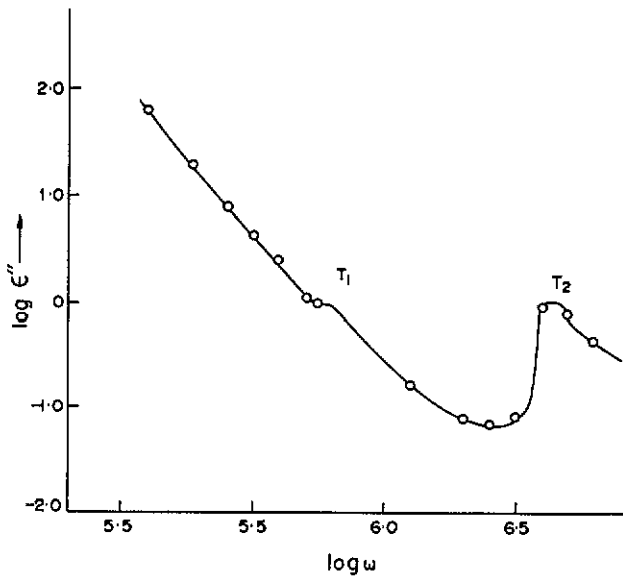


Figure 4. $\log \omega$ versus $\log \epsilon''$ for a doped PPY thin film at 290 K.

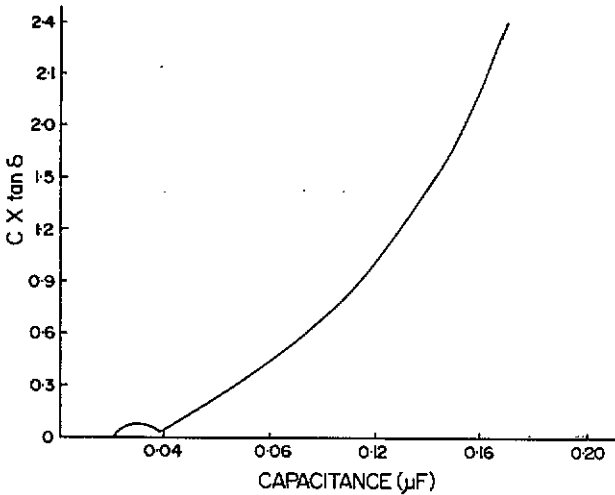


Figure 5. Cole-Cole plot for PPY at 290 K.

4.2 Effect of static bias

The effect of static bias (external field) on the dielectric properties of this system is seen from figures 6 and 7. The variations in differential capacitance and the dielectric loss with frequency at a static bias of 50, 100 and 200 mV were studied. The changes in the loss profiles and capacitance are clearly seen from the figures. This indicates that the observed charge density near the space-charge region is dependent upon the applied field and a charge-depleted region is created inside the polymer. The resonance is seen

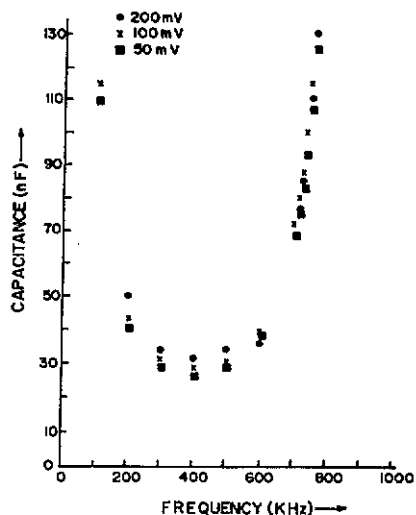


Figure 6. Variation in differential capacitance with frequency for doped PPY at static biases of 50, 100 and 200 mV. The thickness of the film is 10 μm .

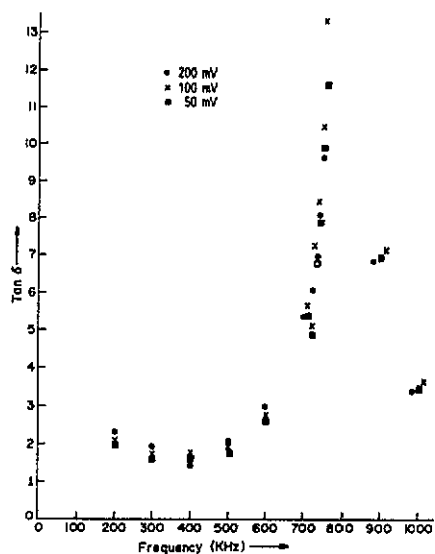


Figure 7. Variation in dielectric loss with frequency for doped PPY at static biases of 50, 100 and 200 mV.

Table 1. Variation in observed capacitance with frequency at frequencies greater than the resonating frequency.

Bias (mV)	Capacitance (nF) at the following frequencies		
	900 kHz	1000 kHz	5000 kHz
0	-46.52	-24.50	-0.48
50	-51.00	-26.00	-0.49
100	-56.80	-27.0	-0.50
200	-59.3	-27.3	-0.52

in all the cases. The values of capacitance in this region are listed in table 1. Similar dispersion patterns for PPY have been reported by Legros and Fourier-Lamer [21].

However, the behaviour of undoped PPY in the same frequency regime is different. Figure 8 depicts the variation in capacitance of Al-undoped PPY-Al capacitors with frequency. No resonance is observed in this case, indicating the absence of charge carriers. The dispersion is not as strong as in the case of doped PPY.

4.3 Effect of temperature

The effect of temperature on the above phenomena was also investigated. The measurements were carried out at several temperatures in the range 200–400 K. It was found that the variations in differential capacitance and dielectric loss with frequency were similar to those found at 290 K. Figure 9 shows the variation in dielectric loss with frequency for Al-PPY-Al capacitors at various temperatures. Although the shapes of

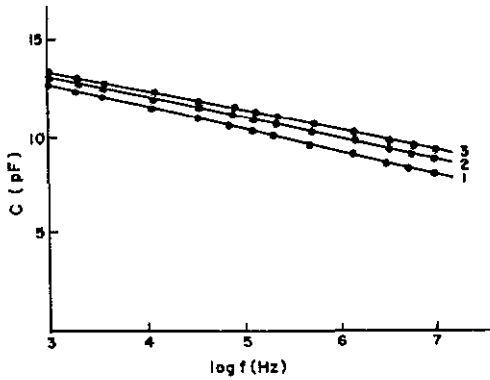


Figure 8. Variation in differential capacitance with frequency for undoped PPY.

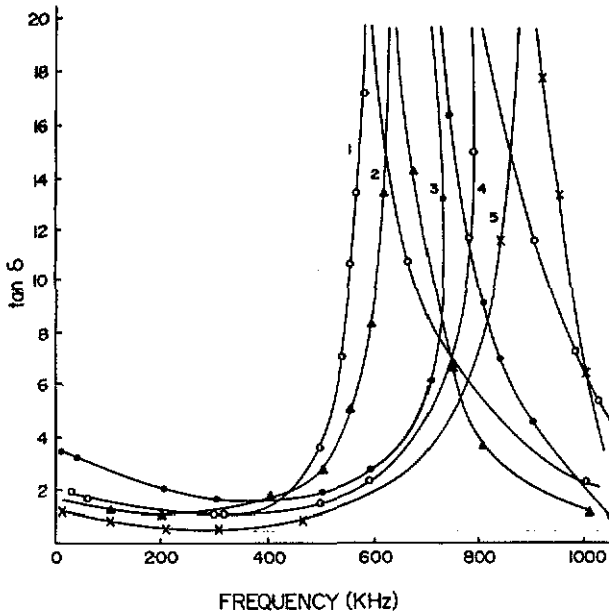


Figure 9. Variation in dielectric loss with frequency at different temperatures for doped PPY at 100 mV static bias: curve 1, 400 K; curve 2, 310 K; curve 3, 290 K; curve 4, 248 K; curve 5, 210 K.

the loss profiles are similar, the shift in the frequency at which the dielectric loss is a maximum is clear. This can be attributed to the change in the mobility of the charge carriers as all other parameters occurring in equation (9) do not vary significantly in this temperature range.

Now, returning to our formalism developed in section 2, the mobility of the charge carriers in PPY can be estimated using equation (9). The frequency at which the loss is maximum is obtained from the data (figure 9). Thus calculated mobilities are plotted against the corresponding temperatures in figure 10. We have taken $\epsilon = 100$ [21] and $n = 10^{20} \text{ cm}^{-3}$ [17]. It is seen that the mobility decreases with increasing temperature.

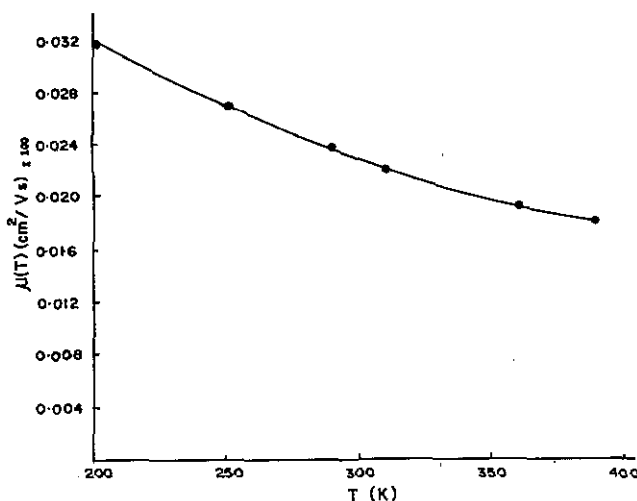


Figure 10. Variation in calculated mobility with temperature.

This needs further elucidation as the negative temperature coefficient can be understood only in the light of the structural properties of and conduction mechanisms proposed for the transport of charge carriers in PPY and other similar bond-conjugated materials.

It has been established that doped PPY is largely (90%) amorphous with poor crystallinity and the packing consists of planes of chains [22, 23]. The anions in PPY do not intercalate between the planes of the chains but instead appear to intercalate between the chains within the plane. The charge transport in these materials is believed to be due to polarons and bipolarons and is predominantly intrachain (along the chain) as opposed to interchain (between the chains). In practice, it is often difficult to separate the two since the degree of disorder (cross links, branching, etc) in the polymer is very high.

Interestingly, our investigations show multiple relaxation times. Although a distinction between the types of charge carrier or transport is not possible at this stage, the qualitative features of the charge transport are clearly seen. On the assumption that the charge carriers are polarons or bipolarons a comparison of our results with those obtained in [24], by solving the Boltzmann transport equation using the Hamiltonian of Su, Schrieffer and Heeger can be made. The temperature-dependent mobility found by us is consistent with their results. This suggests that scattering due to phonons is dominant in PPY and is the reason for the observed negative temperature coefficient. Much higher temperatures also inhibit the formation of kink states which results in diminished mobility. The negative temperature coefficient for the mobility is also observed in many organic conductors.

5. Conclusions

Dielectric relaxation studies on Al-PPY-Al capacitors have revealed many interesting structural and transport properties of charge carriers in PPY. Space-charge polarization has been observed in the above system and a simple analysis of this phenomenon on the basis of space-charge theories further helps us to understand the charge transport

mechanisms. The movement of charge carriers inside the PPY under the influence of an external field and the consequent creation of space charge gives rise to interfacial polarization. Approximations to space-charge theories are useful both in understanding the dielectric phenomenon and in estimating the mobility of charge carriers.

Our studies indicate that dielectric spectroscopy can be of great use in delineating the charge-transport phenomena in conducting polymers. Although, in principle, the effects of diffusion have to be taken into account for the best estimates of the values of mobility, the qualitative nature is apparent. However, it would be interesting to include the diffusion effects in the equations of motion of the space-charge boundary, and hence in the complex permittivity.

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