

Defects in conducting polymers

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Abstract. New types of defects such as solitons, polarons and bipolarons in conducting polymers have been discussed in this article. In the light of recent experimental results, the bipolaronic model of conduction has been re-examined. It is shown that more elaborate experiments are essential to confirm the hypothesis of charge transport via bipolarons in these newer synthetic metals.

Keywords. Defects; solitons; polarons; bipolarons; conducting polymers.

1. Introduction

Conducting polymers are relatively recent entrants in literature (Scott *et al* 1983; Bloor 1983; Baughman 1984; Chance *et al* 1984; Heeger 1985; Hayes 1985; Bott 1985; Streitwolf 1985; Kumar *et al* 1985; Malhotra *et al* 1986 a,b) pertaining to polymer science and have been so named because these newer synthetic metals have been experimentally shown to exhibit values of electrical conductivity ranging from $10^{-3}\Omega^{-1}\text{cm}^{-1}$ to $10^3\Omega^{-1}\text{cm}^{-1}$. The principal reason for such a widespread interest in this fascinating field of research has been the potential applications of these conducting organic materials in batteries, displays, molecular electronics etc (Baughman 1984). As a result, a large number of conducting polymers such as polyacetylene (Streitwolf 1985), polypyrrole (Scott *et al* 1983), polythiophene (Tourillon and Garnier 1982) and polyparaphenylene (Yakushi *et al* 1983) (figure 1) have been generated using chemical and electrochemical methods. The latter technique has the additional advantage of producing conducting polymers in their respective doped states. A pre-requisite of a conducting polymer to exhibit electrically conducting behaviour is the conjugation i.e. alternation of single and double bonds resulting into the overlap of π -electrons. Bond conjugation in a typical degenerate (figure 2a) system such as trans-polyacetylene can be disrupted giving rise to solitonic excitations which are not only believed to carry electricity but have been shown to be responsible for the spin-charge reversal observed in this well-studied material. In another series of conducting polymers such as polypyrrole, polythiophene, polyfuran and polyindole etc, whose ground states are energetically inequivalent, it is the polaronic excitations which transport electrical charge (Malhotra *et al* 1986a). With increased doping concentration in the non-degenerate (figure 2b) conducting polymers, the concentration of polarons may increase resulting in the formation of bipolarons which occupy distinct energy levels in the band-gap. Bipolarons are doubly charged compared to polarons but are spinless. Recently, there have been some controversies relating to the existence of bipolarons as fundamental charged species. In this paper some of the current hypotheses concerning bipolarons are discussed.

It has been ascertained that conducting polymers are largely amorphous with a small degree of crystallinity or polycrystallinity. Like solid polymers, conducting polymeric materials contain different kinds of structural irregularities or defects such as branch-points, cross-links and conformational defects etc. Such defects can arise

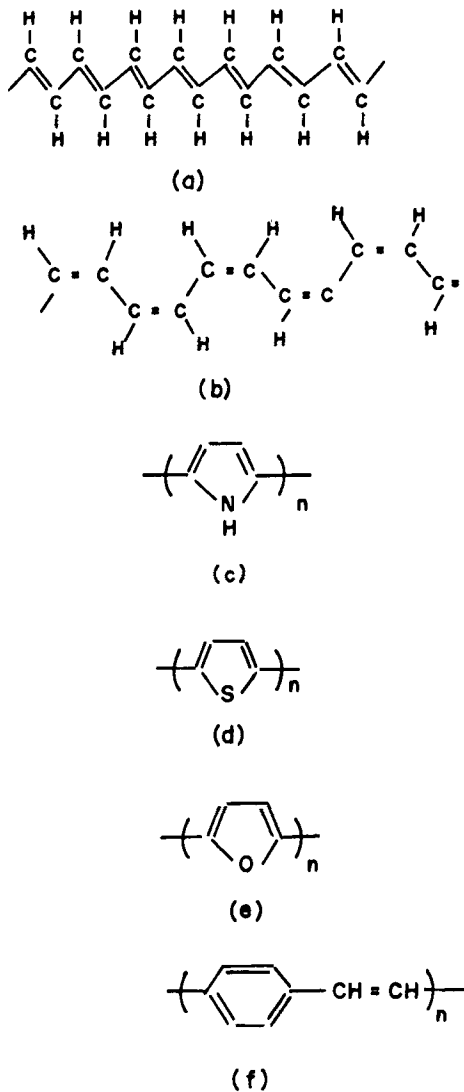


Figure 1. Structures of (a) trans-polyacetylene (b) cis-polyacetylene (c) polypyrrole (d) polythiophene (e) polyfuran (f) polyparaphenylene.

as single errors during polymer formation or these may be clustered together because of a failure of the physical conditions which determine a given structural property. Besides these, the crystalline regions of the conducting polymers may be detected as a result of existence of a host of classical defects such as vacancies, dislocations and clusters etc which are usually caused by packing of atoms or molecules.

This article will briefly outline the experimental techniques to characterize conjugational defects in conducting polymers, properties of such defects and motivation behind the proposal of these defects. The paper concludes with a discussion on current thinking in relation to the bipolaronic model of conduction in conducting polymers.

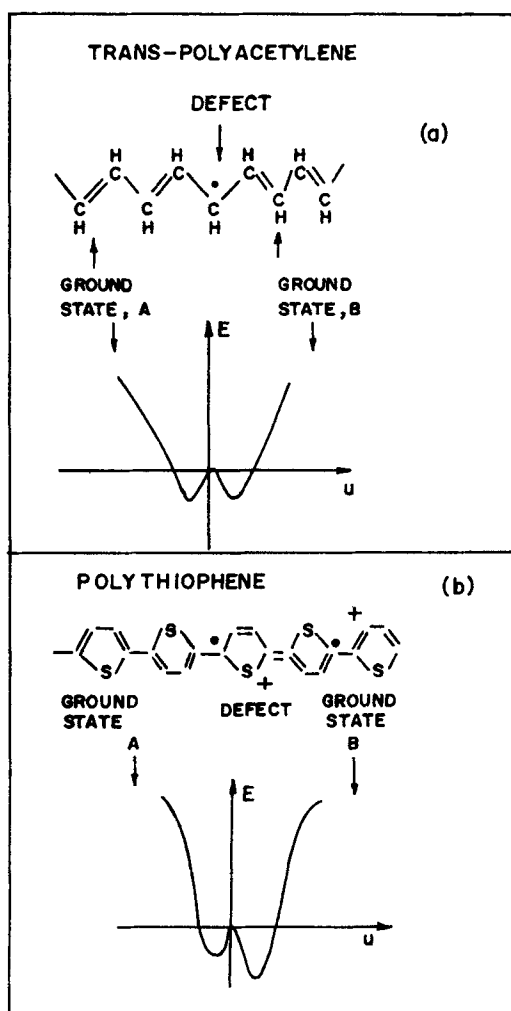


Figure 2. Schematic representations of ground states of (a) trans-polyacetylene — degenerate case (b) polythiophene — non-degenerate case. E, energy; u , distortion parameter.

2. Experimental techniques

Defects in conducting polymers have been investigated using a variety of experimental techniques such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and image analyzer (Malhotra *et al* 1986). With electron microscopic techniques, it has been possible to determine the grain-size, voids and also the free-volume in polymeric materials. X-ray diffraction measurements have been helpful in imaging vacancies, clusters and also dislocations in the crystalline regions of polymeric materials. The diffuse scattering of X-rays has been related to the existence of disorder of the atoms within the material. Positron annihilation measurements and particularly the lifetime of ortho-positronium in molecular materials, have been shown to be a very sensitive probe for the detection of free-volume in condensed materials (Malhotra and Petrick 1983; Malhotra and

Ramanathan 1985). In fact, it has been possible to determine the distribution of free-volume, vacancy clusters, bubble size and also void size using positron annihilation lifetime measurements (Malhotra and Pethrick 1983). Optical microscopy has also been used to map the large defects such as voids and also bubbles, provided conducting polymers are tailored in thin film form (Malhotra *et al* 1986b). Solid state ^{13}C NMR has been shown to be a very promising technique (Devreux *et al* 1985) to investigate the structure of conducting polymers whose characterization has so far been prevented by the insoluble nature of these organic materials. Specific volume measurements as also the calorimetric methods can throw light on the degree of non-crystallinity in the polymeric conductors. The temperature dependence of density, electrical conductivity and also the dielectric constant coupled with the frequency dependence of each of these parameters can reveal information relating to the dynamic nature of the defects in question. Electron spin resonance (ESR) is a complimentary technique to investigate the magnetic properties of the polymers. The spectrum parameters such as multiplicity, position, shape, linewidth, intensity and symmetry can be analyzed in terms of the static and dynamic characteristics of the paramagnetic species (Bernier 1986). ESR measurements on conducting polymers have been extremely helpful in understanding the mechanism of electrical conduction in conducting polymers. It will not be out of place to mention that the present knowledge relating to conjugational defects in conducting polymers can be singly attributed to the difficulties arising out of the interpretation of the results of ESR measurements on systems such as polyacetylene (Weinberger *et al* 1979) and polypyrrole (Scott *et al* 1983). We shall discuss these re-results in § 3.1.

As in conventional materials, optical spectroscopy is a powerful tool available to an experimentalist to ascertain the existence of a variety of defects but such measurements have been found to be very helpful to validate the different theoretical concepts existing in the literature (Chance *et al* 1984). Optical spectroscopy measurements in visible, infra-red and ultraviolet regions have been performed in the case of a few conducting polymers and we shall present some of these results from literature in § 3.1 to bring out the strengths and weaknesses of the bipolaronic model of conduction.

3. Defect structures in conducting polymers

Most conducting polymers known until today in literature are organic in nature and can be made electrically conducting if suitably doped. Prior to doping most of these conducting polymers are by and large insulating (electrical conductivity, $\sigma \sim 10^{-8} - 10^{-10} \Omega^{-1} \text{cm}^{-1}$) in nature. During polymerization of such conducting materials e.g. trans-polyacetylene, it is possible that the bond-alternation of atoms constituting a molecular chain may be disturbed leading to the creation of domain walls or the so-called solitons in such a system (Chance *et al* 1984; Heeger 1985). Existence of such a solitonic defect has been shown to be theoretically viable principally because the structures (Chance *et al* 1984) of trans-polyacetylene separated by domain walls are energetically equivalent and hence stable (figure 2). Solitons can either exist in neutral or charged states (figure 3). Neutral soliton is electrically neutral but possesses a spin- $\frac{1}{2}$ because the nuclear charge of the CH unit balances the negative charge of the dangling electron existing at such a defect. Charged soliton is spinless but is electrically charged. The concentration of charged solitons can be increased by doping trans-polyacetylene with a suitable dopant. The ground states of other

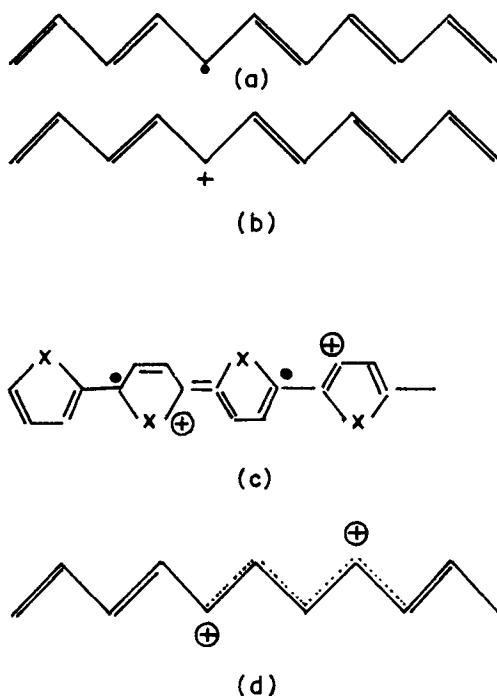


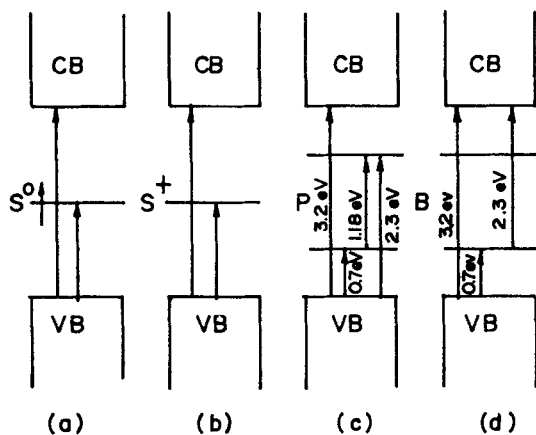
Figure 3. Schematic representations of conjugational defects in conducting polymers (a) neutral soliton (b) charged soliton (c) polaron (d) bipolaron.

conducting polymers such as polyaniline, polythiophene and cis-polyacetylene etc become energetically inequivalent when separated by a typical defect hitherto named as polaron (figure 2). Polaron is also visualized as an electron in a polarized lattice of a given material. It is electrically charged and contains as well a spin (figure 3). Population of polarons in a conducting polymer can be varied by changing both the temperature and the extent of doping. With increased concentration of polarons, it is possible that two polarons may approach near enough and result in the formation of a bipolaron (figure 3). Compared to polaron, bipolaron is doubly charged but spinless (Scott *et al* 1983; Baughman 1984; Chance *et al* 1984; Hayes 1985). The properties of these typical defects, solitons, polarons and bipolarons are shown in table 1. It is interesting that these defects occupy distinct energy levels (figure 4) in the band gap of a given polymer. Proposition of such a hypothesis has been particularly helpful in the interpretation of optical spectra (Kaufman *et al* 1984) experimentally observed in the case of trans-polyacetylene, polypyrrole and polythiophene etc which have also been theoretically explained. In the next section we shall see how these peculiar defects such as solitons including polarons and bipolarons have contributed to explain the spin-charge reversal observed in conducting polymers.

Besides these special defects (Wunderlich 1976), conducting polymers are likely to contain a variety of other defects such as cross-links, branch-points and conformational defects (figure 5). Such defects may arise as a result of faulty chemical process of linking of monomer units yielding an undesired linkage and breakage of chemical regularity. Another kind of chemical defects is based on branching i.e. linear polymer chain branches off into two independent chains that may grow at different rates. Further, cross-links create special mechanical properties e.g. the elasticity of rubber

Table 1. Typical properties of solitons, polarons and bipolarons.

Defect		Spin	Charge
Soliton	*Neutral	$\frac{1}{2}$	0
	*Charged	0	$+ e $ or $- e $
Polaron		$\frac{1}{2}$	$+ e $ or $- e $
Bipolaron		0	$+2 e $ or $-2 e $

**Figure 4.** Schematics of energy levels of (a) neutral soliton, S^0 (b) charged soliton, S^+ (c) polaron, P (d) bipolaron, B . CB, conduction band; VB, valence band.

is due to cross-linking (Zerbi 1982). The clustering of tacticity defects can create different kinds of structures. If tacticity defects cluster closely in certain regions of the polymer, stereo-blocks are found with a random length and distribution. However, if single-tacticity defects occur at random, a region of atactic polymers is formed. Defects can also occur in the conformational coiling of polymer chains. Conformational defects occur during crystallization of an otherwise chemically and stereo-chemically regular chain because of kinetic and energetic factors; these defects have been termed primary conformational defects. Conformational defects can also be forcefully induced because of the existence of chemical or stereo-chemical defects; such defects have been called induced conformational defects. It may be mentioned that such irregularities including classical defects will not be further discussed.

It may be remarked here that the formation of such defects including conjugational defects such as solitons, polarons and bipolarons is not always undesired. Since defects affect the chemical and physical properties of the material, introduction of particular defects such as solitons, polarons and bipolarons may be the only means to attain reasonable magnitudes of electrical conductivity of conducting polymers.

3.1 Spin-charge reversal in conducting polymers

Weinberger *et al* (1979) measured Pauli susceptibility, χ_p and electrical conductivity, σ , in trans-polyacetylene-(CH) $_x$ as a function of doping. Their results are shown in figure 6a. At low doping (<1%), trans-polyacetylene is non-conducting but the

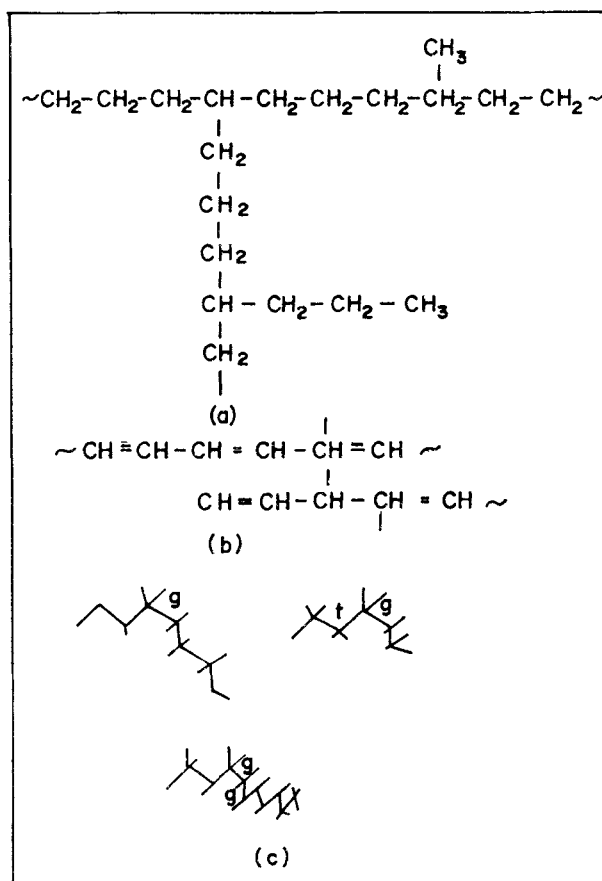


Figure 5. Structural defects in polymers (a) branch points in polyethylene (b) cross-links in polyacetylene (c) conformational defects in polydimethylene. g, gauche, t, trans.

corresponding χ_p value, though low, is finite. With increased doping concentration, χ_p decreases sharply and becomes nearly zero whereas σ shows a steady increase up to about 3% of doping after which it increases slowly. With further increase in doping beyond 6%, χ_p suddenly shows a sharp increase up to 7% after which it increases slightly. It is apparent that the larger increases in χ_p are not reflected in the corresponding variations of electrical conductivity indicating that the charge carriers do not probably carry spin. This anomalous relationship between spin and charge can be explained if it is assumed that the pristine trans-polyacetylene contains a certain concentration of neutral solitons formed during polymerization. However, with increased doping concentration, neutral solitons are transformed into charged solitons which may be either positively or negatively charged depending upon whether the dopant is p-type or n-type. It appears that at about 3% of doping, most of the neutral solitons become charged and are available for transport of electrical charge. It has been further suggested that at about 7% of doping, double bonds constituting the trans-polyacetylene are broken resulting in a spurious increase in the concentration of neutral solitons and consequent increase in χ_p .

Polypyrrole is another conducting polymer which exhibits similar spin-charge reversal (figure 6b). Since polypyrrole is energetically non-degenerate and hence

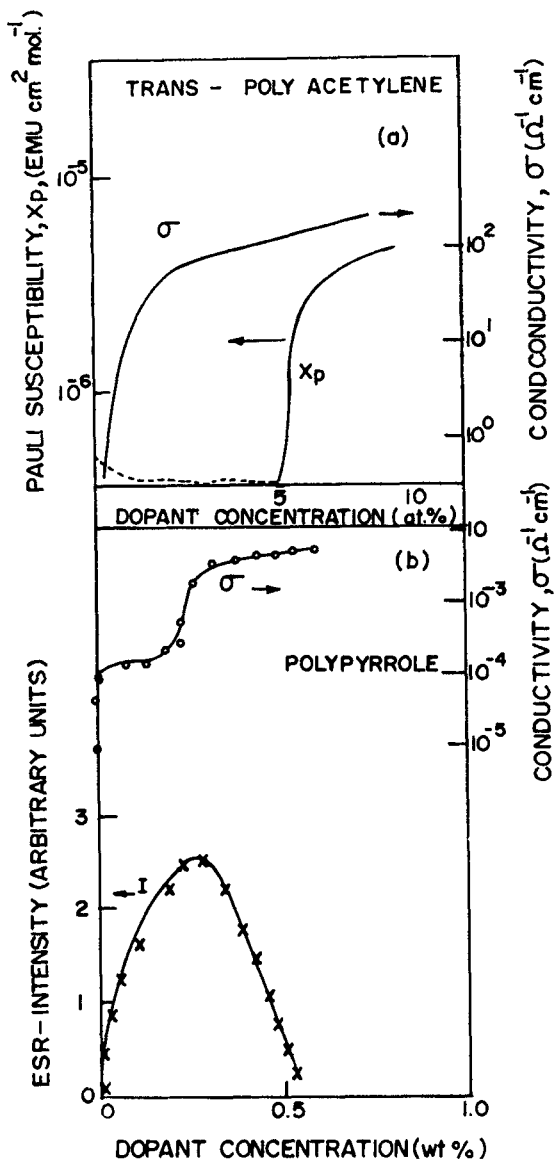


Figure 6. (a) Variation of electrical conductivity, σ and Pauli susceptibility, χ_p as a function of dopant concentration in the case of trans-polyacetylene (b) variation of electrical conductivity, σ and intensity, I of ESR signal as a function of dopant concentration in case of polypyrrole (Weinberger *et al* 1979; Scott *et al* 1983).

cannot support solitons, it is thought that this particular conducting polymer contains polarons generated during polymerization. With increased doping, concentration of polarons increases. A bipolaron results in the case of persistent attractive interaction between polarons. Thus at sufficiently high concentration of dopant, it is the spinless bipolarons which transport the electrical charge (Scott *et al* 1983).

Further results in support of the above tentative conclusion relating to formation of bipolarons have come from optical spectroscopy carried out in the case of

polypyrrole doped with perchlorate ions (figure 7). Four absorption peaks are observed at 0.7, 1.18, 2.3 and 3.2 eV. With increased dopant concentration, the intra-band transition (1.18 eV) weakens and eventually disappears. This important observation coupled with the fact that these optical absorption peaks shift to higher energies with increased dopant concentration are strong evidences in favour of evolution of polarons into bipolarons. Similar results have been observed in the case of polydimethylpyrrole (Yakushi *et al* 1984). Even in trans-polyacetylene, it is thought that bipolaron formation thus occurs initially but it subsequently disintegrates into charge solitons which are stable.

At this stage, it appears that the bipolaronic model of transport of electrical charge in conducting polymers is perhaps the logical end of the investigations discussed so far. Recent measurements of ESR by Genoud *et al* (1985) conducted in situ in thin films of polypyrrole perchlorate indicate that bipolaron formation is principally governed by the persistent interaction between polarons existing in a conducting polymer. In the case of repulsive interaction between two polarons, bipolarons

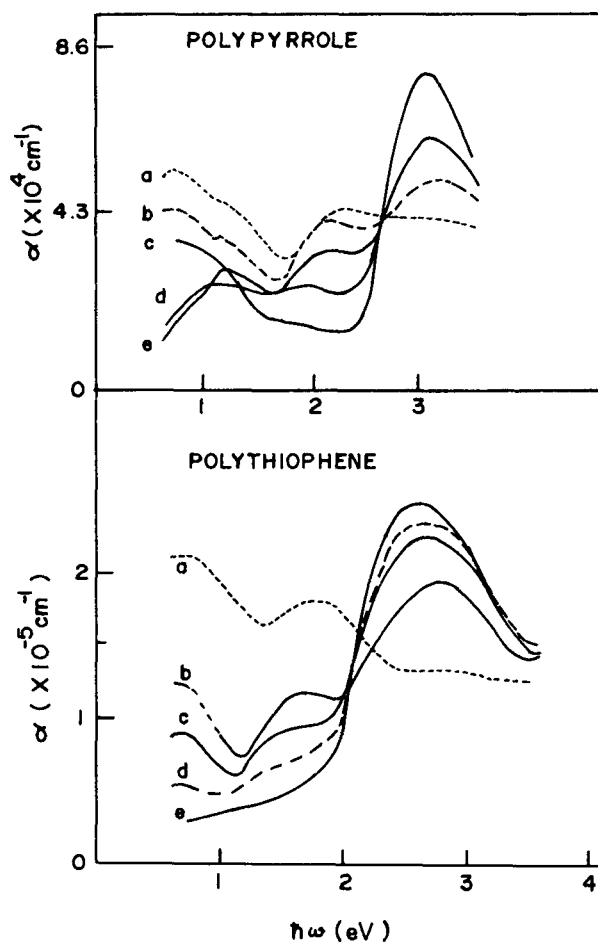


Figure 7. Optical spectra as a function of wavelength (eV) in polypyrrole (a, 20%, b, 11%, c, 9%, d, 5% and e, 0.5%), (Kaufman *et al* 1984); and in polythiophene (a, 20%, b, 11%, c, 9%, d, 5% and e, 0%), (Chung *et al* 1984).

cannot be formed. It has also been suggested that a bipolaron may combine with a neutral site to give two polarons in polypyrrole perchlorate.

Polythiophene (figure 1)—a non-degenerate conducting polymer—has also been investigated in greater detail. Three optical absorption peaks have been observed at 0.6, 1.4 and 2.1 eV (figure 7b) respectively in conducting polythiophene (Malhotra *et al* 1986b; Vardney *et al* 1986). Disappearance of intra-band transition indicates that only bipolarons are present in this typical conducting polymer. This result has been attributed to a large number of crystalline regions in polythiophene resulting in higher probability of recombination of polarons into bipolarons (Vardney *et al* 1986). There have been some discrepancies in this particular conducting polymer. Lower energy peak (0.6 eV) shows no shift with increased dopant concentration whereas higher energy peak (1.4 eV) shifts towards higher energies with increased doping (Chung *et al* 1984). Moreover, the ratio of intensities $I(w_1)/I(w_2)$ corresponding to lower energy and higher energy peaks respectively has been taken to be 2 as against its predicted theoretical value of 6. Also, the intensity of the inter-band transition not only decreases but shifts towards higher energy.

ESR measurements conducted on polyaniline (Huang *et al* 1986) indicate that only polarons are perhaps formed in this typical conducting polymer. Absence of any spin-charge reversal relationship has profoundly baffled the investigators.

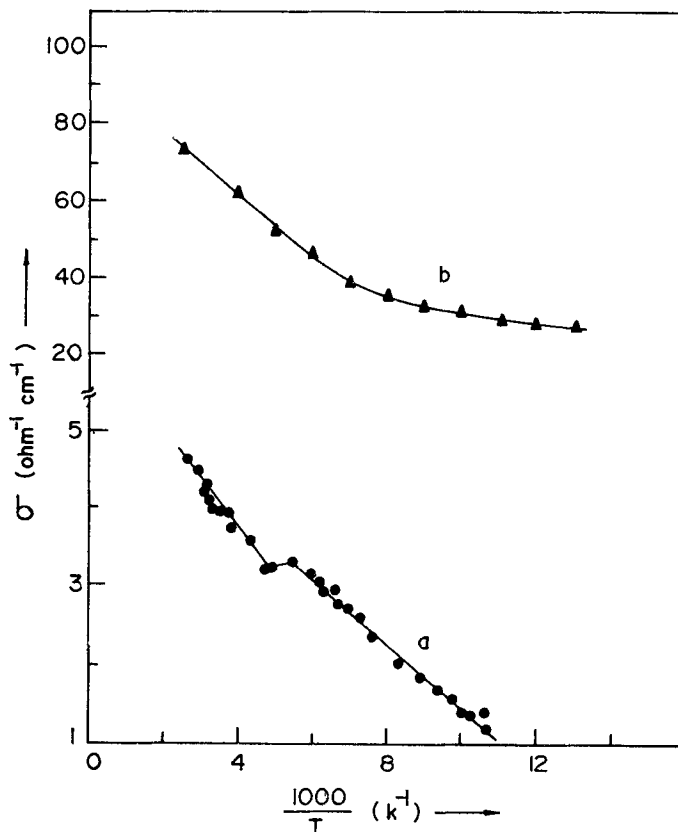


Figure 8. Variation of electrical conductivity, σ as a function of $1000/T$ observed in polyphenylene oxide—pyrrole (Kumar *et al* 1985).

4. Experiments currently in progress

It is abundantly clear that there has been considerable re-thinking on the validity of the bipolaron model applicable to conducting polymers. Experiments carried out on different conducting polymers bring out dissimilar results and hence the apparent lack of unanimity relating to bipolaron as fundamental charged species. In view of this fact, we have undertaken an extensive programme of research on conducting polymers particularly with a view to unravel the role of bipolarons. A number of conducting polymers such as polypyrrole, polythiophene (Malhotra *et al* 1986b), polyphenylene oxide-pyrrole (Kumar *et al* 1985) and polyaniline have been prepared and characterized. The results of electrical conductivity measurements on co-polymer of pyrrole and phenylene oxide are reproduced in figure 8. ESR measurements on some of the systems mentioned above are currently in progress and will be reported in a separate publication. It should be interesting to study the resulting increase in the polaronic interaction by increasing the population of polarons by irradiating (Vardney *et al* 1986) a given conducting polymer.

5. Concluding remarks

In view of the large number of applications such as in batteries, conducting adhesives, electromagnetic interference shielding devices, displays, solar cells and Schottky diodes, the volume of research inputs to investigations on conducting polymers is likely to grow manifolds in the near future. As a result many more research problems of pressing nature in addition to spin-charge reversal, temperature dependence of electrical conductivity, solubility and processibility etc of conducting polymers will be posed to researchers who in turn will take this promising field of research to greater heights similar to the one witnessed in the case of microelectronics today.

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