Physical Sciences Section

STUDY OF PARAMAGNETISM IN PYRROLE BASED CONDUCTING POLYMERS USING ESR MEASUREMENTS AT LOW TEMPERATURES AND PRESSURES

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A series of ESR experiments were carried out at atmospheric as well as low pressures in order to find any relationship between paramagnetic species and the charge carriers in pyrrole based electrically conducting polymers. ESR spectra recorded for a range of polymer samples having electrical conductivities spread over four orders of magnitude suggest that apparently there is no link between the paramagnetic centres and bipolarons which serve as the major charge carriers in these materials. A series of ESR measurements at low temperatures for pyrrole based polymers show that most of the polymers obey Curie-Weiss law in terms of increase in spin populations. Difference in behaviour of various polymers in terms of changes in spin populations, line shape and line width is attributed to the difference in molecular structure and morphology.

Key words: Paramagnetic defects, Radical cation, Spin concentration, Deuterated and protonated polypyrrole, Polarons and bipolarons.

Introduction

Electrically conducting films based on pyrrole may be easily prepared by a one step oxidative polymerization and doping procedure (Diaz *et al* 1979; Kotheim 1986; Mitchell *et al* 1988, Mitchell *et al* 1990 and Kiani *et al* 1992). A number of analytical techniques such as x-ray diffraction (Mitchell *et al* 1988, Mitchell *et al* 1990 and Kiani *et al* 1992) IR, NMR, and ESR (Street *et al* 1992) have been extensively used to characterize these materials. The conduction mechanism in these conducting organic polymers have been under active study for the last two decades. It has been established that the charge carrying species in these conducting polymers are polarons and bipolarons (Bredas *et al* 1984, 1985 and 1986; Atkin 1990). Waller *et al* suggest that polaron is responsible for conduction at low doping levels. Kaufman *et al* have proposed that bipolarons are the major charge carriers in highly doped polymer films. The spin paramagnetism in these conducting polymers results from the existence of unpaired spins (polarons) along the carbon backbone. The polaron can be considered as a radical cation associated with a local distortion of the lattice. The bipolaron is the corresponding dicatonic species. Since bipolarons have no spin so ESR is blind to these species and is used to detect the polaron which has a spin $S=\pm1/2$. Thus, polarons (holes or electrons) are generally through to be the cause of paramagnetism in these conducting polymers. We report in this paper the results of the ESR measurements recorded for a variety of polymer samples, having electrical conductivities in the range of ~ 10^{-2} to 10^{2} s/cm. ESR measurements at atmospheric as well as low pressures for a range of polymer samples were made in order to study the effect of oxygen on these materials. In addition ESR spectra of a variety of polymer films including deuterated films of polypyrrole/toluene sulphonate (DPP/DPTS) , highly anisotropic films of polypyrrole/toluene sulphonate (PP/pTS) prepared by pulse mode, samples of polypyrrole with perchlorate (PP/C10$_4$) and sulphate as counter-ions (pp/SO$_4$), as well as films of N-methyl pyrrole, with toluene sulphate (PNMP/pTS) and perchlorate (PNMP/C10$_4$) as counter-ions were recorded at low temperatures. These low temperature measurements are intended to monitor any antiferromagnetic coupling between neighbouring spin sites. The data are intended to help in understanding the differing opinions, regarding the nature of the paramagnetic defects, and the type of charge carriers, present in pyrrole based polymers and thus to establish any relationship between charge carriers and these defects.

Experimental

Pyrrole, supplied by Aldrich, was purified before use by distillation under reduced pressure. Deuterated pyrrole was prepared by exchange of hydrogen by deuterium and d$_7$ sodium p-toluene was prepared by sulphonation of d$_8$ toluene. All other chemicals were commercially available and used without further purification.

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For open air measurements, polymer films were grown electrochemically, from a standard solution of 0.2M of monomer and 0.1 M of the appropriate salt. The procedures used for the preparation of these samples have been reported else where (Mitchell *et al* 1988 and 1990). The procedures for preparation of polypyrrole/toluene sulphonate (PP/pTS) films by a pulsed potential mode and co-polymers of pyrrole and N-methyl pyrrole by constant potential mode have been reported previously (Kiani *et al* 1992, Kiani and Mitchell 1992).

The ESR apparatus comprises of a Varian E-102 microwave bridge working in a frequency range of 8.85 to 9.65 GHz. The microwave power is provided by a klystron source. The klystron frequency is locked onto the sample cavity resonance by an automatic frequency control circuit. the spectrometer generates a modulation frequency which can be as high as 100 kHz, and whose amplitude is variable over four decades. The signal from the detector crystal is phase sensitively detected at the same frequency as the modulation, and this results in the normal first derivative ESR spectra.

For open air measurements, the sample was placed in a quartz tube so that it is at the centre of the microwave cavity (ESR-900). An electromagnet V-3601 with 12 inches diameter pole pieces connected with a 7 k.W power supply is responsible for producing a magnetic field. The spectrometer was interfaced with a computer (Hewlet Packard 236) in conjunction with a Varian data acquisition system. All spectra were recorded using an absorption mode. Data collection was controlled by a Basic program Varian, "E-936" providing graphical display, hard copy and disk data storage facility. Samples of known mass were prepared from films dried in a vacuum chamber at room temperature for several hours and then cut to about 2x3 to 2x4 mm in size. For low pressure measurements, the glass tube containing the sample was evacuated to a pressure of $5\pm3 \times 10^{-5}$ torr, before placing in esr spectrometer.

For low temperature measurements, an ESR 900 cryostat connected to a constant flow helium unit was used. The sample was fixed on a guartz tube and placed in the cavity. The helium is sucked through the system by a standard air compressor pump, and the flow rate controlled by two needle valves. The helium passes through a heater and a thermocouple, before pasing over the sample. the desired temperature is achieved by adjusting the values and by a temperature control unit VC-30.

ESR measurements for this study were made using magnetic field strengths of 3300 to 3400 gauss. Spectra were recorded using x-band microwave frequency. For all these measurements parameters such as microwave frequency, microwave power, and modulation amplitude etc. were kept constant for a particular experiment, while the magnetic field was swept. For measuring the spin concentration and the g-value, DPPH (diphenyl picryl hydrazyl) was used as a standard. The g-value of DPPH is known to be 2.0036 and spin concentration as 1 spin per molecule (Holden *et al* 1950). Relative intensities of the ESR spectral lines were obtained using the relation 1(John and wertz 1972):

$$I \propto Y_{max} (\Delta H)^2 \qquad (1)$$

where $2Y_{max}$ is the peak to peak derivative amplitude, and ΔH is peak to peak width. Line widths were measured as the distance between maxima and minima of the derivative ESR curve. Conductivity measurements were made using the conventional four probe method (Smits 1958 and Blythe 1980).

Results and Discussion

3.1. ESR Spectra of Pyrrole Based Polymers. Representative ESR spectra of free standing films of polypyrrole doped with p-toluene sulphonate (pp/pTS) and poly N-methyl pyrrole/toluene sulphonate (PNMP/pTS) recorded at room temperature are shown in Fig 1(a) and 1(b) respectively. Spectra obtained from fully deuterated analogue of PP/pTS (*i.e.* DDP/DpTS) and other pyrrole systems such as PP/SO$_4$ or PP/C10$_4$ were broadly similar. All the spectra observed were close to a Lorentzian shape but with some asymmetry. The line width and spin concentration showed marked variation for different films and indeed, for different parts of the same film. Table 1 summarizes the range of g-values, line widths and spin concentrations obtained for a variety of pyrrole and N-methyl pyrrole based polymer films prepared electrochemically in the presence of oxygen and Table 2 shows the variations observed in the parameters in different parts of a single film of PP/pTS. The width of the esr spectral line varies over a wide range, even for the films apparently prepared under the same conditions as shown in Tables 1 and 2. Other pyrrole based systems showed similar behaviour. Typical spin concentrations, as shown in Table 1, ESR ~ $(4\pm3)\times10^{19}$ spins/g although there are some significant variations from sample to sample. In general this corresponds to approximately 1 spin per ~ 160 pyrrole units. Clearly, this is a relatively low value as compared to the number of charge carriers (1 charge per 4-6 monomer units) and is consistent with the idea that paramagnetic impurities are not involved in the charge transport mechanism. The significance of the observed variations for different samples, however, remains unclear. To confirm this the spin concentration and the electrical conductivity for a range of electro-

Table 1
The range of g-values, linewidths and spin concentrations

Sample description	Number of samples studied	g-value (Range) (0.0005)	ΔH range (± 0.1)G	Range of spin concentration spins g⁻¹
PP/pTS	140	2.0023-2.0034	2.00-9.00g	$(1\pm.1) \times 10^{19} - (7 \pm 0.7)10^{19}$
DPP/DpTS	32	2.0022-2.0036	2.00-6.00g	$(1\pm.1) \times 10^{19} - (9 \pm 0.9)10^{19}$
PP/SO$_4$	32	2.0020-2.0036	2.00-4.00g	$(6\pm.1) \times 10^{19} - (4 \pm 0.4)10^{19}$
PP/C10$_4$	04	2.0032-2.0035	1.80-2.30g	$(3\pm.4) \times 10^{19}$
PNMP/pTS	12	2.0030-2.0036	1.30-2.00g	$(.6\pm.1) \times 10^{19} - (3 \pm 0.5)10^{19}$
PYL+NMP/PTS	08	2.0029-2.0032	1.40-4.00g	$(1\pm.1) \times 10^{19} - (7 \pm 0.7)10^{19}$
PP/pTS, P.M	10	2.0030-2.0034	1.80-4.50g	$(1\pm.1) \times 10^{19} - (5 \pm 0.5)10^{19}$

(P.M.shows pulse mode)

Table 2
ESR parameters obtained for samples cut from different parts

S.No.	ΔH (G)	Spins g⁻¹	Monomers spin⁻¹	g-value
1.	5.39 ± (0.1)g	$(2.27 \pm 0.2) \times 10^{19}$	240	2.0032 ± 0.0004
2.	4.39 ± (0.1)g	$(2.04 \pm 0.2) \times 10^{19}$	270	2.0029 ± 0.0004
3.	5.25 ± (0.1)g	$(1.4 \pm 0.14) \times 10^{19}$	410	2.0032 ± 0.0004
4.	5.45 ± (0.1)g	$(1.9 \pm 0.19) \times 10^{19}$	290	2.0030 ± 0.0004

chemically prepared PP/pTS samples are compared in Fig 2. As the figure shows there is no obvious relationship between these two parameters. This is consistent with the independent observations of both (Street *et al* 1992) and (Scott *et al* 1983 and 1986).
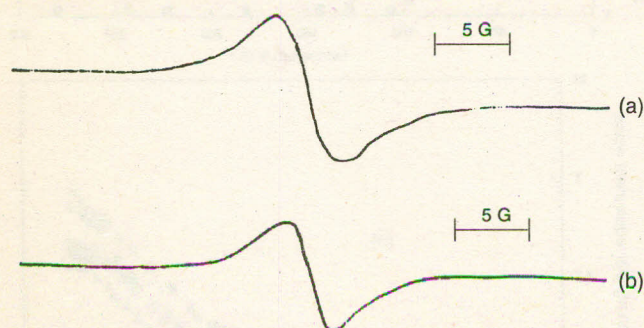

Fig 1. Representative ESR spectra of (a) 0.24 mg sample of free standing film of PP/pTS and (b) 0.3 mg sample of free standing film of PNMP/pTS obtained in the x-band over a scan range of 50 gauss.
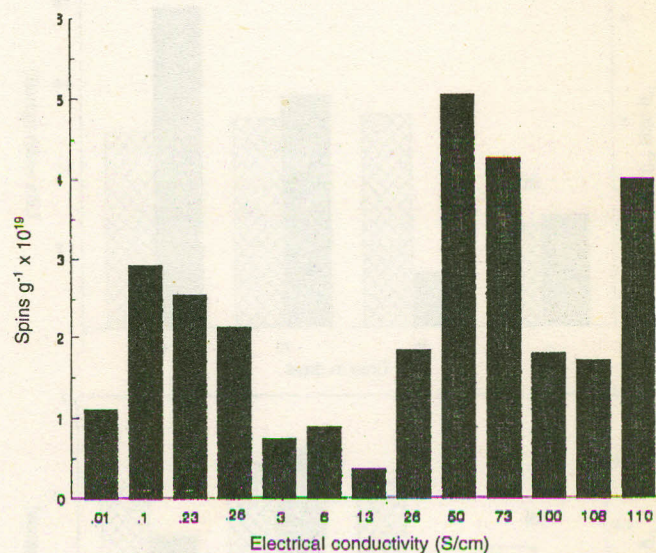

Fig 2. Spin concentration plotted against electrical conductivity for PP/pTS films having conductivities in the range of 10^{-2} -10^{2}S/cm.

Table 3
The effect of oxygen on various ESR parameters of PP/pTS

S.No.	Evacuated samples			Sample exposed to air		
	ΔH(G) ±(.01)G	g-value (±.0004)	Spin conc. spins g⁻¹	ΔH(G) ±(0.1)G	g-value (±.0004)	Spin conc. spins g⁻¹
1.	2.23	2.0035	$(1.5 \pm 0.15) \times 10^{19}$	3.21	2.0033	$(0.6 \pm 0.6) \times 10^{19}$
2.	2.28	2.0034	$(7 \pm 0.70) \times 10^{19}$	4.34	2.0032	$(2.5 \pm 0.25) \times 10^{19}$
3.	2.12	2.0036	$(3.8 \pm 0.4) \times 10^{19}$	4.45	2.0034	$(1.3 \pm 0.13) \times 10^{19}$
4.	2.19	2.0033	$(6.7 \pm 0.7) \times 10^{19}$	3.27	2.0030	$(3.0 \pm 0.30) \times 10^{19}$

3.2. Effect of Oxygen on Different Parameters. In order to monitor the influence of oxygen on the ESR parameters a number of polypyrrole samples prepared in the open atmosphere were placed in a sealed tube and evacuated. The ESR spectra from these samples were recorded and then re-recorded after exposure to oxygen. The changes observed are shown in Table 3. In general, it would appear that oxygen changes the number of spins in the sample and this is accompained by an increase in line width. Fig 3 (a and b) show the changes in spin concentration and line width (ΔH) of PP/pTS and PP/SO$_4$ films. As the Figure shows that spin concentration initially decreases and then increases with time. Prolonged exposure further increases the line width in some of the samples. The immediate increase on exposure to air ranged from 25% to 150% for different films. For most examples this increase in ΔH was found to be partially reversible on evacuating to a pressure of 10^{-5} torr. Similar trends in ΔH were noted for samples of DPP/DpTS.

3.3. Low temperature measurements. Low temperature measurements were made for a variety of polymer films including DPP/DpTS, PP/pTS, PP/ClO$_4$, PP/SO$_4$, PNMP/pTS, PNMP/ClO$_4$ and highly anisotropic films of PP/pTS prepared by pulse mode. It was hoped in this way to monitor any interactions (*e.g.* antiferromagnetic coupling) between neighbouring spin sites. In addition it was intended to probe any systematic changes between various pyrrole based polymer systems.

3.3.1. Changes in signal intensity. Samples of DPP/DpTS, PP/pTS, PP/C10$_4$ and PP/SO$_4$ give a very strong ESR signal at liquid helium temperatures as shown in Fig 4(a). This increase in signal intensity is entirely expected on the basis of the increase in population of the lower spin states due to lack of thermal excitation. Considering equation $N\beta/N\alpha = e$
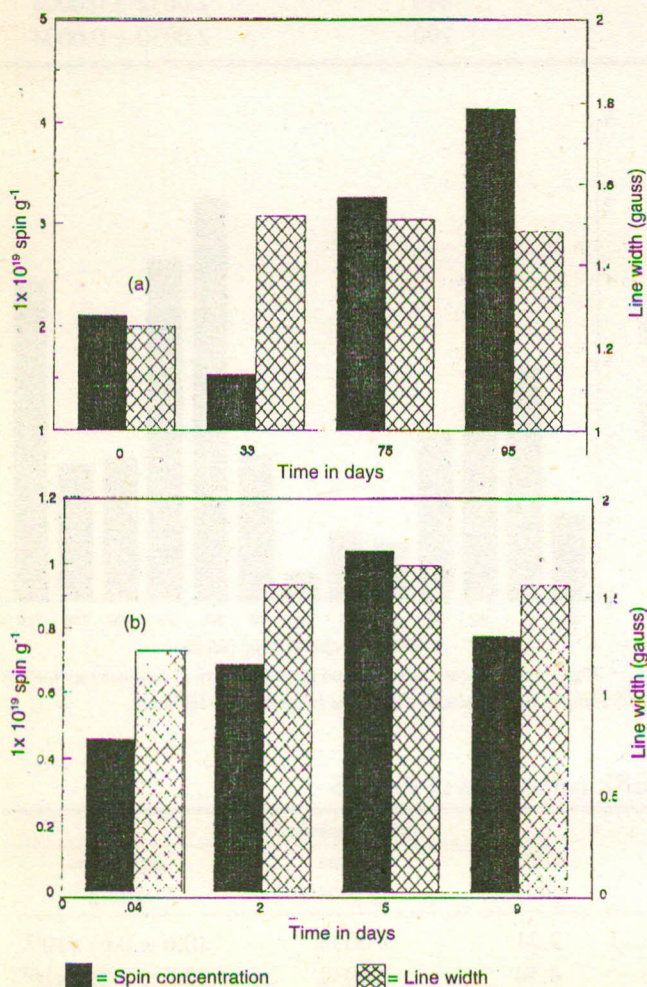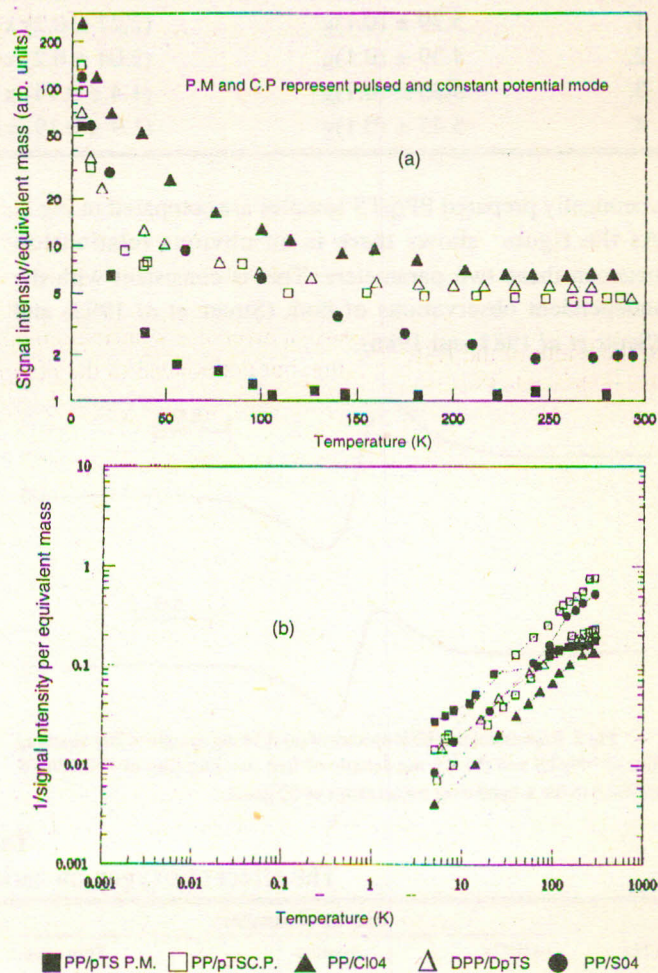

Fig 3. A plot showing the changes in spin concentration and line width of (a) PP/pTS and (b) PP/SO$_4$ films as a function of time.

Fig 4 (a). Showing the changes in signal intensity per equivalent mass as a function of temperature in DPP/DpTS, PP/SO$_4$, PP/C10$_4$ and PP/pTS. Reproducibility and experimental error bar ranges from 10 to 40%. (b) Plots showing 1/singal intensity per equivalent mass as a function of temperature on similar x&y scales for polymers shown in 4a. Most of the curves have a slope =1 except a few deviations.

$^{-h\upsilon/kT}$ where $N\alpha$ and $N\beta$ are the populations of the lower and the upper spin states. It can be seen that in these measurements where $h\upsilon \ll kT$ neglecting the higher order terms, this equation will reduce to the form $N\alpha\text{-}N\beta \propto h\upsilon/kT = I$. (when x is small $e^{-x} \sim 1\text{-}x$). Thus $I \propto 1/T$ or $1/I$ is proportional to T. Hence in order to observe the changes in signal intensity with temperature our plots should be linear. The data shown in Fig 4(a) can be seen in a different way in Fig 4(b) which shows a plot of measurement temperature and 1/signal intensity per equivalent mass on similar x and y scales. Most of the samples showed an approximately linear relationship (although for some samples some deviation from linearity was observed). In general such behaviour is typical of Curie paramagnetism (Solymar and Walsh 1988). Devia-

tions from Curie-Weiss law at higher temperatures were only observed for more conducting polymer films of PP/pTS prepared by pulse mode. For less conducting polymers this contribution is engligible even at room temperature. A comparison of changes in signal intensity per equivalent mass of PP/pTS and PP/C1O$_4$ with those of PNMP/pTS and PNMP/C1O$_4$ as a function of temperature is shown in Fig 5(a). These data are shown more clearly in Fig 5(b) which shows a plot of 1/signal intensity per equivalent mass plotted against temperature on similar x and y scales. This once again is consistent with Curie-Weiss law.

3.3.2. Changes in Line Width. Changes in line width of the ESR spectra in these polymers depend upon the type of
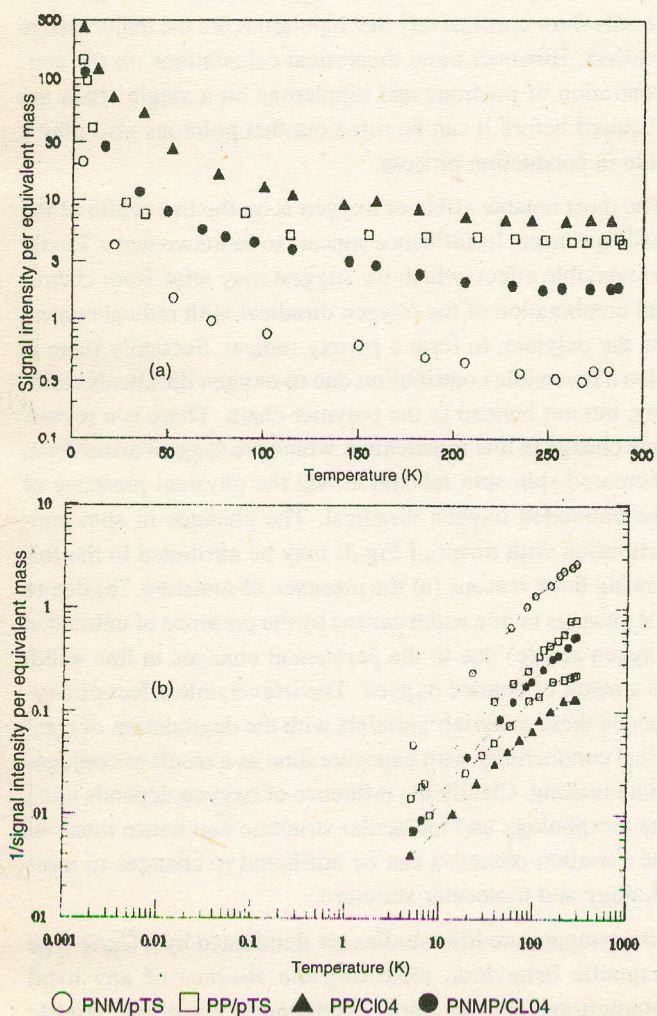

Fig 5 (a). Showing changes in signal intensity per equivalent mass with temperature in polymers of pyrrole and N-methyl pyrrole with PTS and C1O$_4$ as the counter-ions. Reproducibility and experimental error bar may range from 10 to 40%. (b) Plots of 1/signal intensity per equivalent mass as a function of temperature drawn on similar x &y scales for polymers as given in part a. Most of the curves have a slope equal to 1 except a few deviations.
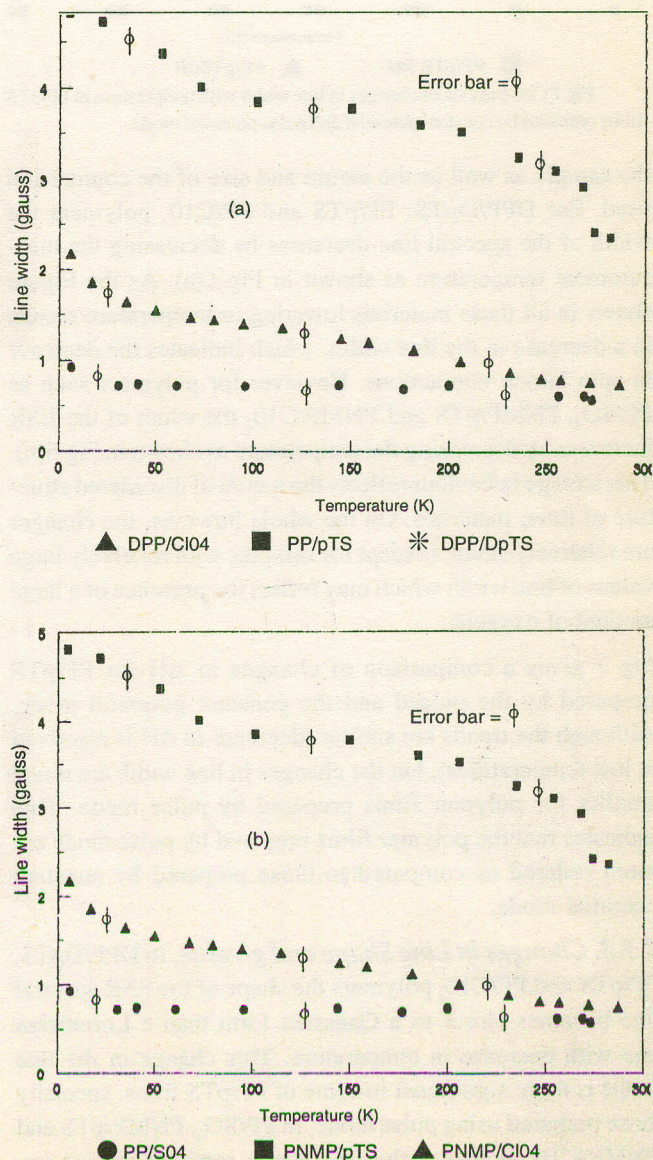
Fig 6. Showing the change in line width of (a) PP/pTS, DPP/DpTS and PP/C1O$_4$, (b)pp/SO$_4$, PNMP/pTS and PNMP/C1O$_4$ with temperatures.
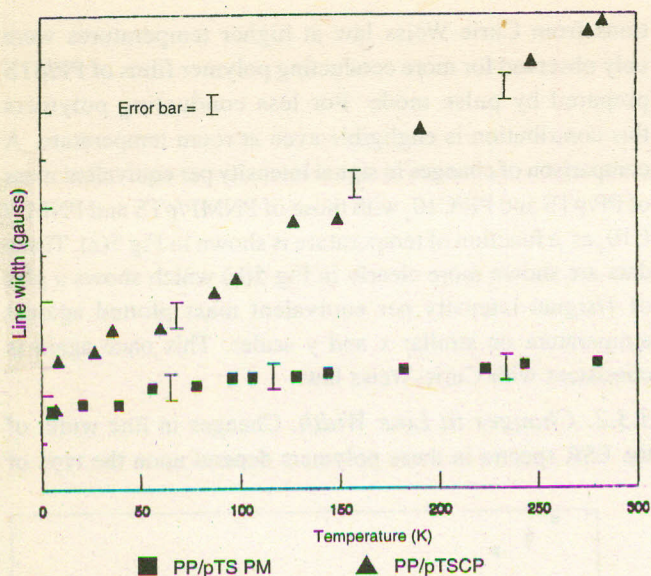
Fig 7. Comparison of changes in line width with temperature in PP/pTS films prepared by constant potential and pulse potential mode.

the sample as well as the nature and size of the counter-ion used. For DPP/DpTS, PP/pTS and PP/C10$_4$ polymers the width of the spectral line decreases by decreasing the measurement temperature as shown in Fig 6(a). As the Figure shows in all these materials lowering in temperature results in a decrease in the line width, which indicates the decrease in spin lattice interactions. However for polymers such as PP/SO$_4$, PNMP/pTS and PNMP/C10$_4$ the width of the ESR increases by decreasing the temperature as shown in Fig 6(b). This strange behaviour reflects the nature of disordered structure of these materials. On the whole however, the changes are relatively small, (except for samples with relatively large values of line width which may reflect the presence of a large amount of oxygen).

Fig 7 gives a comparison of changes in ΔH for PP/pTS prepared by the pulsed and the constant potential mode. Although the trends are similar (decrease in ΔH is observed at low temperatures), but the changes in line width are much smaller for polymer films prepared by pulse mode. This indicates that the polymer films prepared by pulse mode are more ordered as compared to those prepared by constant potential mode.

3.3.3. Changes in Line Shape and g-value. In DPP/DpTS, PP/pTS and PP/C10$_4$ polymers the shape of the ESR spectral line becomes closer to a Gaussian form than a Lorentzian one with decrease in temperature. This change in the line shape is more significant in some of PP/pTS films, specially those prepared using pulse mode. In PP/SO$_4$, PNMP/pTS and PNMP/C10$_4$ however the line shape remains almost unchanged *i.e.* closer to Lorentzian shape.

The results described in Fig 2 show that there is no correlation between spin concentration and conductivity in these conducting polymers. We suggest, in line with other workers in this area (Blythe 1980; Scott *et al* 1982 and 1983; Street *et al* 1983; Bredas *et al* 1984; Kaufman *et al* 1984; Bredas 1985; Genoud *et al* 1985; Nalwa 1989; Zotti and Schiavon 1989) that initial formation of paramagnetic sites (polarons) by oxidation cum doping process is followed by pairing to produce bipolarons. The difference in our results and findings of Waller *et al* (1989) who suggest that polaron may be responsible for the conduction process at low doping levels can be attributed to the large difference in the thickness of the polymer films and the level of doping. The thickness of the polymer films studied by these authors was only 1-5% of the polymer films investigated by us. Although these results show conclusively that bipolarons are the major charge carriers. However more theoretical calculations on the concentration of polarons and bipolarons on a single chain are required before it can be ruled out that polarons also play a role in conduction process.

The most notable effect of oxygen is on the line width of the ESR spectrum. Its influence appears to be in two ways. Firstly irreversible effect, which we suggest may arise from chemical combination of the oxygen diradical with radical centers on the polymer, to form a peroxy radical. Secondly there is also a reversible contribution due to oxygen diradicals residing, but not bonded to the polymer chain. There is a reversible change in line broadening, which we suggest arises from increased spin-spin relaxation, via the physical presence of the unbonded oxygen diradical. The changes in spin concentration with time (c.f Fig 3) may be attributed to the following three reasons (a) the presence of moisture, (b) due to the changes in line width caused by the presence of unbonded oxygen and (c) due to the permanent changes in line width as a result of bonded oxgyen. The irreversible effect of oxygen on these materials parallels with the degradation of electrical conductivity with exposure time as a result of conjugation breaking. Clearly the influence of oxgyen depends upon the morphology and molecular structure and hence much of the variation observed can be attributed to changes in morphology and molecular structure.

Low temperature ESR studies are dominated by a Curie type magnetic behaviour, reflecting the absence of any local interactions such as antiferromagnetic coupling. Highly conducting films, especially those prepared by pulse mode show large deviations from the Curie-Weis law at higher temperatures. These deviations from linearity may be associated with the change in line shape which is more prominent in these materials. The change in line shape

from Lorentzian to Gaussian at low temperatures affects the comparison of changes in ESR signal intensity of different pyrrole based polymers. Thus the deviations observed in samples prepared by pulse mode may be partly associated with change in line shape. This curie type behaviour with some deviations has also been reported by other (Kuzmany *et al* 1978; Genoud *et al* 1985) although its origin is unclear. In addition the spectra show a general reduction in both line width and g-value at low temperatures, although the effect is very small and not always obvious. Since Gaussian lines indicate the domination of spin-spin interactions over the spin lattice interactions (Raymond 1968; John and Wertz 1972) thus the changes in line shape and line width of more conducting polymer films at low temperatures may be attributed to a decrease in spin-lattice interactions. For less conducting polymer films such as PNMP/pTS, PP/SO4 and PNMP/ClO4 etc. the variations in line witdth may be attributed to the domination of spin-lattice interactions at low temperatures. The behaviour of deuterated and protonated materials was broadly similar and no evidence for hyperfine coupling to deuterium was observed. The reason for getting more spin concentration in deuterated samples remains unclear.

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