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Structural and electrical properties of soluble conducting poly(3-pentylthiophene)

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A solution of processible poly(3-pentylthiophene) (P3PT) was synthesized by chemical polymerization. The structure of the resulting polymer was investigated by gel permeation chromatography (GPC); infrared; ^{1}H and ^{13}C nuclear magnetic resonance; Ultraviolet visible spectroscopy (UV-Vis) and wide-angle X-ray scattering (WAXS) techniques. It was found that the microstructure of the chains has a low number of irregular couplings and thus has desirable electrical properties. In the small-angle region of X-ray scattering, a pronounced peak was observed with a d (coherence length) value of 1.51 nm for P3PT and 1.835 nm for poly (3-heptylthiophene (P3Hept). Electron spin resonance measurements showed that P3PT has 10^{18} spins g^{-1}, a g value 2.0039, and a ΔH_{pp} of about 6 Gauss. The Pauli-like susceptibility after doping P3PT with I_2 is of the same order as for poly paraphenylene (PPP) doped with AsF_5, and corresponds to a density of states at the Fermi level about 0.01 states eV^{-1} per carbon atom in the thiophene ring. The current-voltage (I–V) characteristics obtained for different temperatures were always linear. The dark room temperature conductivity was 10^{-8} S m^{-1} and distinctly increased after doping. The P3PT studied is a good candidate for potential commercial applications.

1. Introduction

Over the past few years there have been considerable efforts to obtain intrinsically conducting polymers which are both solution- and melt-processible. A large number of polymers of this type is now known, as a result of adding a short-chain alkyl or/and alkoxy side group to synthesized heteroaromatic monomers [1–4]. Substitution with longer-chain (more than three carbon atoms) substituents is effective because the products are soluble in a host of common laboratory solvents [3, 5, 6]. However, the presence of these side groups is responsible for profound changes in the structural properties of these polymers: the longer substituents can change the distance between the backbones of chains and may lead to changes in the morphology of the polymer. The weaker inter-chain interactions may also change the electronic behaviour. In particular, the separation of main chains is important for inter-chain transport of charge carriers in these systems. It has also been reported [7, 8] that the best electrical properties are found in poly(3-alkylthiophenes) and poly(3-alkylpyrroles) when the side chains in the heteroaromatica backbone are longer than four and shorter than 10 carbon atoms.

This type of polymer can be obtained by electrochemistry [8] and also by chemical procedures. One of the advantages of chemical synthesis is that poly(3-alkylthiophenes) of higher purity can be produced, compared to electrochemical method where *in situ* doping assists in incorporating impurities and obtaining a fully pristine material is difficult. On the other hand, the selectivity of coupling and configuration features appears to be better for polymers obtained by the chemical route [9].

2. Experimental procedure

Poly(3-pentylthiophene) (P3PT) was prepared chemically from 3-pentyl-thiophene and iron (III) chloride by adapting reported procedures [10, 11]. The 3-pentylthiophene was obtained by a cross-coupling reaction of 1-pentylbromide with 3-bromothiophene (prepared earlier from thiophene) in the presence of Ni-organic catalyst.

The crude product (85%) was purified by Soxhlet extraction with methanol and acetone to remove $FeCl_3$ (controlled by $AgNO_3$), and low-molecular fraction (oligomers) tested by the GPC method. The pure product (74%) was finally dried under reduced pressure at 328 K. GPC analyses were taken using a Spectra Physics GPC-instrument calibrated with polystyrene standards.

Nuclear magnetic resonance (NMR) spectra (^{1}H, ^{13}C) were recorded in deuterated chloroform solution on a Varian spectrometer. WAXS-experiments were performed at room temperature using a conventional powder diffractometer and Ni-filtered Cu-K_α radiation. The IR spectra were obtained with the KBr pressed method at room temperature. UV-Vis analyses were carried out in chloroform solution and as a thin film of P3PT.

I-V characteristics and conductivity measurements were performed by the two-point method on pressed pellets with vacuum evaporated Au contacts. Electron spin resonance (ESR) spectra were taken at two tem-

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peratures (liquid nitrogen and room temperature) using a Bruker spectrometer. Magnetic susceptibility was measured at temperature range 80–300 K by the Gouy method using the $Hg[Co(SCN)_4]$ as a calibrant.

3. Results and discussion

3.1. GPC

The chemical synthesis of the 3-pentylthiophene with the applied procedure gave a reddish-black powder with a yield of about 85%. After removing oligomers (11%) the pure polymeric product was analysed by GPC. The retention curve with a shoulder on the low-molecular weight side for P3PT is presented in Fig. 1a. The differential distribution of molecular weight is seen in Fig. 1b. The polydispersity index (M_w/M_n) was 4.8, and is typical for this class of materials [9]. The average chain length calculated from M_n corresponds to approximately 118 repeat units per average polymer chain. These results give a limited insight into the chain length for the resulting product, as they are based on a calibration curve of polystyrene standards.

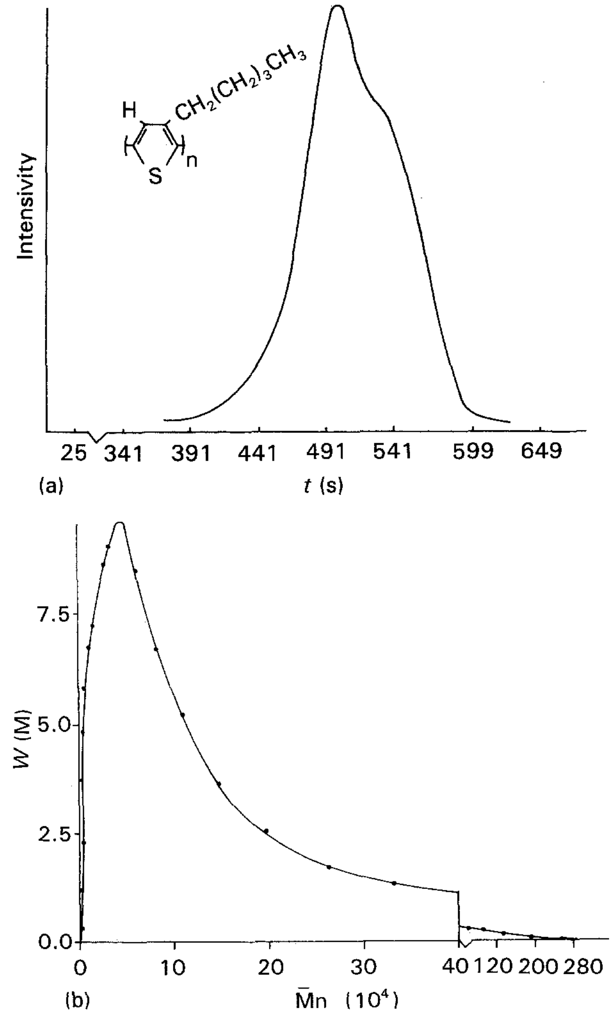

Figure 1 GPC of P3PT prepared in tetrahydrofuran (THF) solution. (a) Retention curve; (b) differential distribution of molecular weights. $\bar{M}_n = 1.8 \times 10^4$; $\bar{M}_w = 9.0 \times 10^4$; $\bar{M}_z = 4.9 \times 10^5$; $\bar{M}_w/\bar{M}_n = 4.8$.

3.2. IR

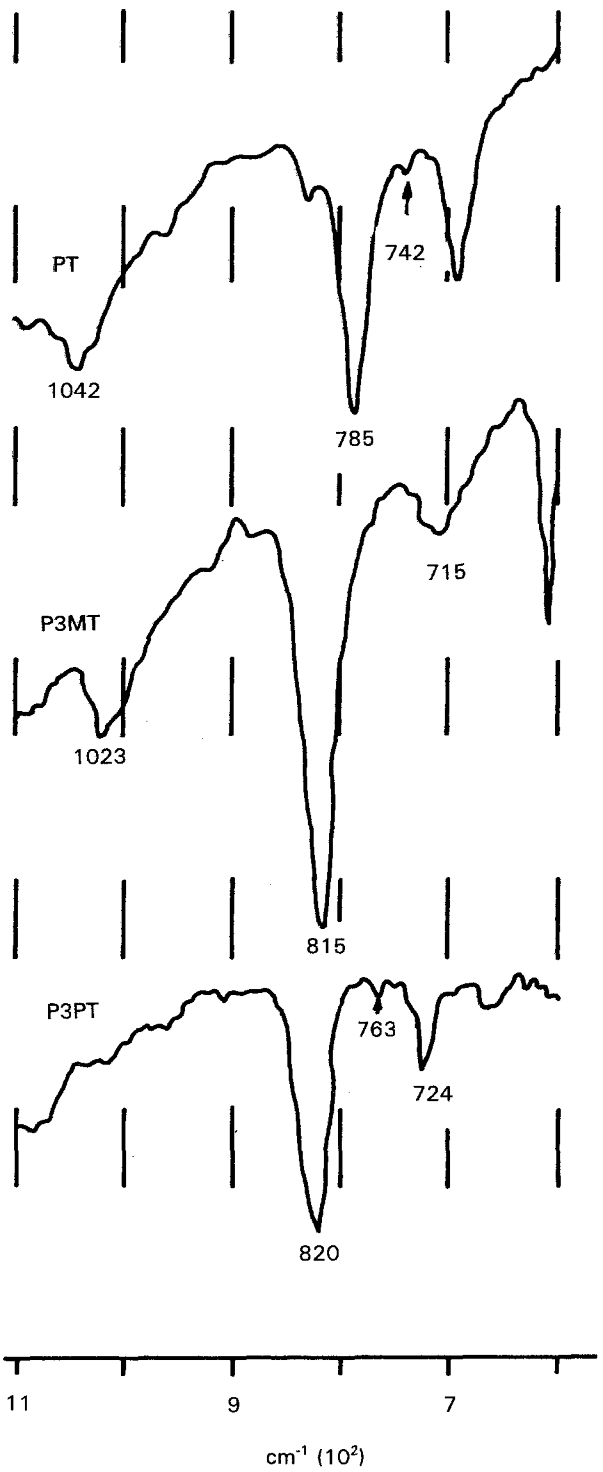

Figure 2 IR spectra of poly(thiophene) (PT); poly(3-methylthiophene) (PMT) and poly(3-pentylthiophene) (P3PT).

Fig. 2 shows the IR spectra of poly(thiophene) (PT); poly(3-methylthiophene) (PMT) and poly(3-pentylthiophene) (P3PT), and gives information about the influence on the polymer structure of the alkyl side groups. The absorption bands between 1050 and 650 cm^{-1} are characteristic of the substitution pattern. The absorption band at 785 cm^{-1} is characteristic of 2.5-disubstituted thienylene (out of plane δ(C–H)) [12], shifted to 815 cm^{-1} for 2.3.5-trisubstituted thienylene rings in poly(3-methylthiophene)-P3MT [13]; for P3PT this vibration is located at 820 cm^{-1}. The rocking vibration of methylene groups in the side chain of P3PT appears at 724 cm^{-1}. In all spectra shown in Fig. 2, the bands assignable to 2.4-coupled poly(thiphenes) were absent, the formation of the backbone of chains going through the 2.5-position only, which is favourable for good electrical properties [14]. The IR spectra of the polymers mentioned above, recorded at room temperature at full range (400–4000 cm^{-1}) were in good agreement with those known from literature [12–14].

3.3. NMR

The P3PT obtained via chemical procedure was studied by ^1H and ^{13}C NMR. The spectra were recorded at room temperature. As shown in Fig. 3, the spectrum in the high-field range shows signals at $\delta = 0.91$ p.p.m. assigned to methyl protons in the alkyl end group of the side chains; a peak at $\delta = 1.39$ p.p.m. assigned to $\lambda(4)$ methylene protons; a signal at $\delta = 1.59$ p.p.m. due to $\gamma(3)$ methylene protons; and a broad resonance line at $\delta = 1.69$ p.p.m. assigned to protons in $\beta(2)$ methylene groups. In this range there are also two pronounced peaks assigned to $\alpha(1)$ methylene protons, which give insight into the head-to-tail (HT) and head-to-head (HH) sequences (dyads) in the poly(3-alkylthiophenes) [15]. The nature of the signals $\delta = 2.81$ p.p.m. and higher-field at $\delta = 2.56$ p.p.m. were previously confirmed by analysis of the NMR spectra of only HH (about $\delta = 2.50$ p.p.m.) linked poly(3.4-dihexylthiophene) [9]. Following this attribution the calculation gave 81% content of HT configuration for chemically prepared P3PT. In the low-field region of aromatic protons, the ^1H NMR spectrum presented in Fig. 3 shows four peaks corresponding to the carbon-4 proton of thiophene rings, which arise from different configurations in triads of P3PT (four possible sequences of triads) [16]. The most intensive peak in this set is located at $\delta = 6.99$ p.p.m. and would be ascribed to the HT–HT configuration of triad sequences with a dominant value of integral intensity of 61.5%. The next, going to the lower-field resonance line at $\delta = 7.01$ p.p.m., was proposed to be attributed to HT–HH sequence. Two other peaks at $\delta = 7.03$ and $\delta = 7.06$ p.p.m. were assigned to the TT–HT and TT–HH configurations, respectively. Calculations taken as integral intensities of these three last peaks give a content of HT–HH = 14.0%, TT–HT = 11.5 and TT–HH = 13.0% in the chains of P3PT. The ^1H–^1H double-quantum filtered correlation spectra (DQF-COSY) given in Fig. 4 shows that in the region of

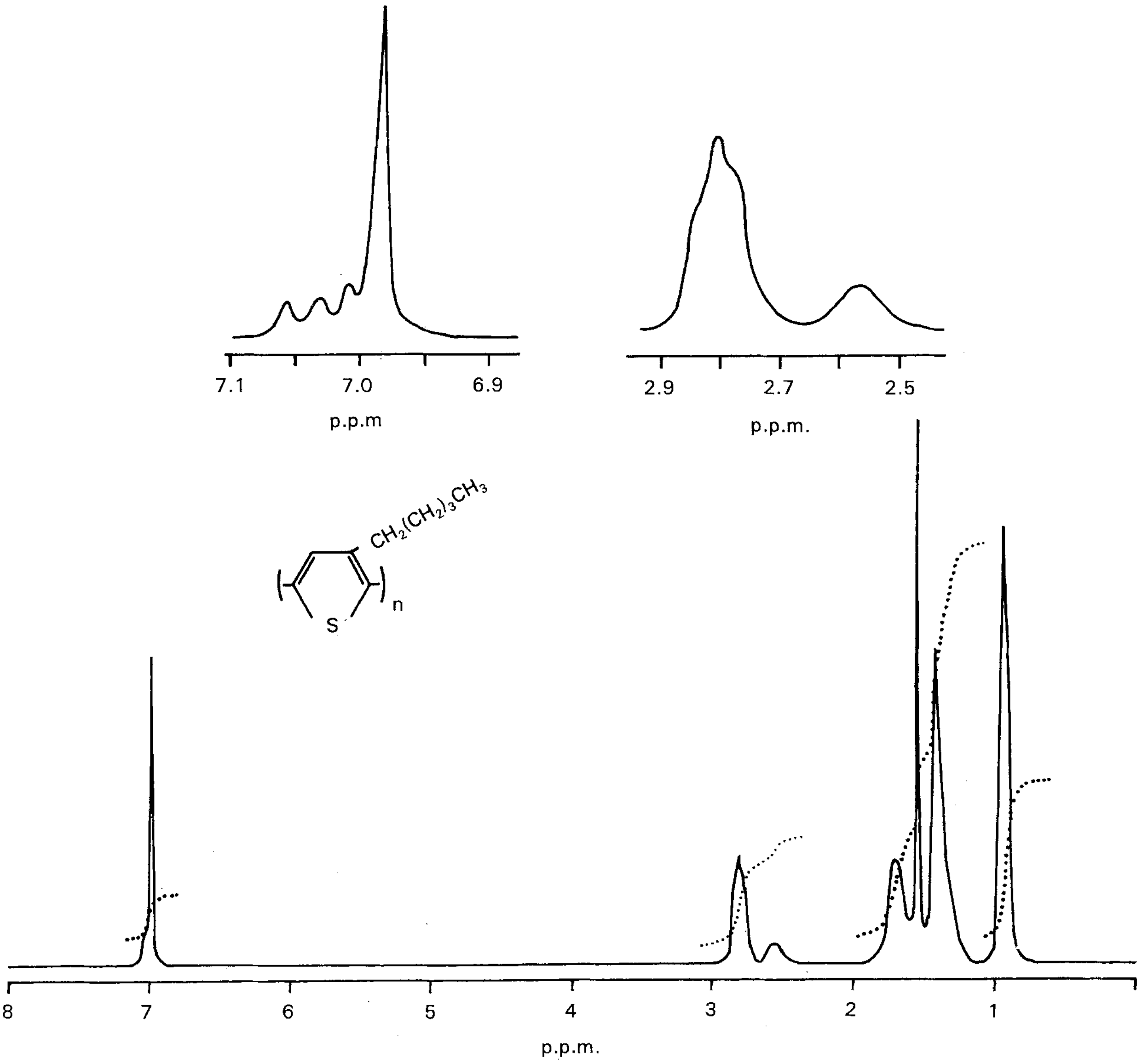

Figure 3 ^1H NMR spectrum of P3PT at 298 K in d-chloroform. The inset shows expanded ^1H NMR spectra in the range of aromatic resonances (left) and in the range of $\alpha(1)$ methylene signals (right).

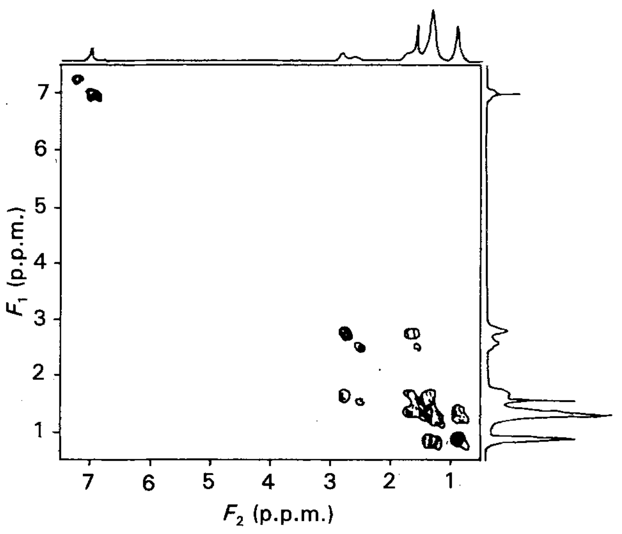

Figure 4 ^1H–^1H COSY spectrum of P3PT ($T = 298$ K).

chemical shifts of aromatic protons, no homonuclear correlation exists in this spectrum. In the range of methylene resonances, the COSY spectrum shows the strong correlation between the peak at $\delta = 2.81$ and (2)-methylene protons. On the other hand, the peak at $\delta = 2.56$ p.p.m. assigned to (1)-methylene (HH) is correlated with the peak at $\delta = 1.59$ p.p.m., which is due to (3)-methylene protons. The correlation of methyl protons at $\delta = 0.91$ p.p.m. with (4)-methylene protons at $\delta = 1.39$ p.p.m. is also clearly seen. The same type of spectra made for oligomer fraction (average degree of polymerization, DP = 10) of P3PT show the similar position of main resonance lines characterized above, but calculations taken from integral intensities of peaks assigned to HT and HH sequences of dyads gave lower HT configurations (75%) in the oligomer than in the polymer. The similar results were obtained from the resonance lines in the aromatic four-proton region. The HT–HT configuration also preferred in oligomers is about 53%, while in the polymer fraction the content of this configuration is 61.5%. With an increase in molecular weight, the content of the favourable configuration of HT–HT also increases; this is in line with the hypothesis that chemical polymerization follows the polymeric product with a smaller number of steric defects than electropolymerization [9]. These results also suggest that the product with a higher DP would have a better chain microstructure, in contrast to the results obtained by Waltman and Bargon [17].

3.4. WAXS

It has been reported [7, 9] that poly(3-alkylthiophenes) and poly(3-alkylpyrroles) obtained via the electrochemical route are rather non-crystalline materials with a broad amorphous halo an the wide-angle X-ray scattering region, and with a small angle peak corresponding to a periodic structure from a planar configuration of the polymer backbone. The value of *d*, the coherence length, of this small periodicity depends upon the length of side chains.

The chemically prepared poly(3-alkylthiophenes) were partially crystalline substances with pronounced peaks at the small scattering region [9]. Fig. 5 clearly shows that the poly(3-pentylthiophene) under study has a poorly crystalline structure with a *d* value of small-angle reflection corresponding to 1.51 nm. Comparison of this *d* value of P3PT with the result for poly(3-heptylthiophene) also given in Fig. 5, and with results in [18] for poly(3-hexylthiophene) and others [9], shows the influence of the length of the alkyl group on the crystalline structure in general (Fig. 5) and on the double-layered planar configuration of the polymer chains. The difference between P3PT and

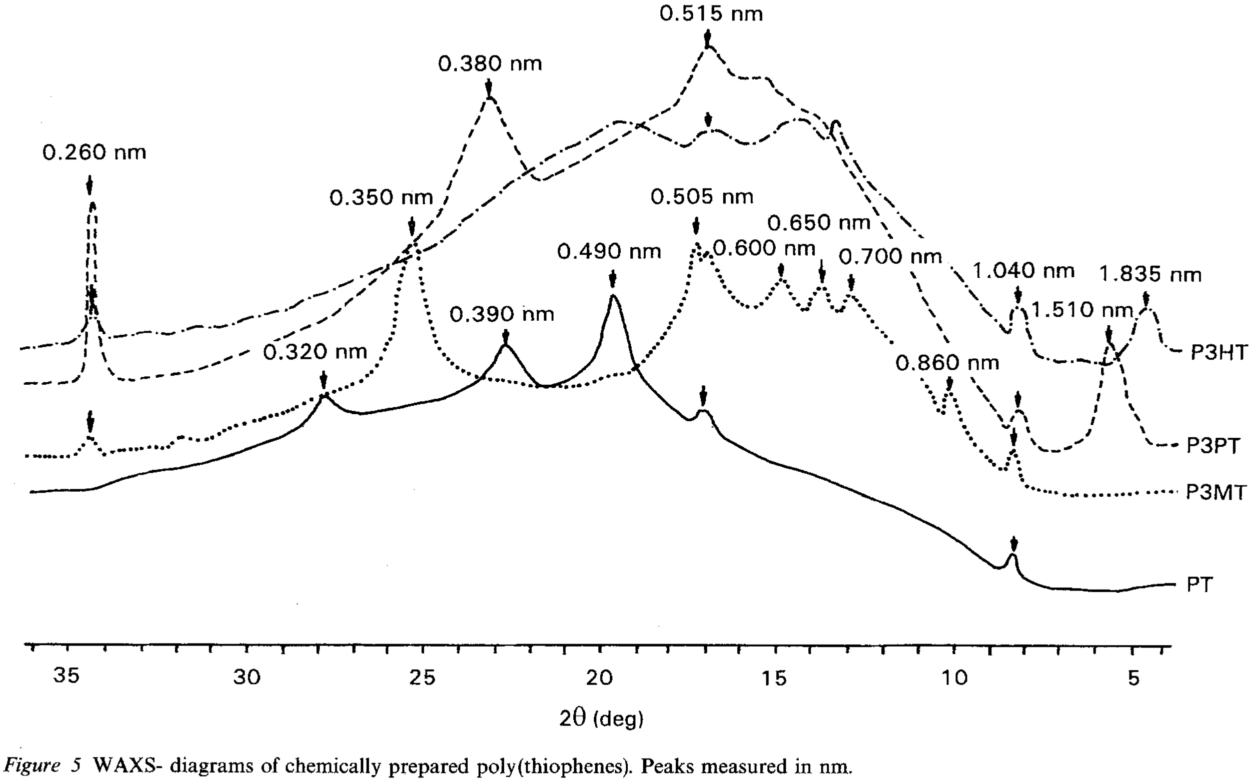

Figure 5 WAXS- diagrams of chemically prepared poly(thiophenes). Peaks measured in nm.

P3HeptT is 0325 nm, which gives about 0.16 nm on one methylene group added to the side chain. This is in excellent agreement with data for P3HT [18] and P3DT [9].

3.5. UV-Vis

The UV-Vis spectra reported previously [19] show that the lowest energy excitation due to interband transition (π–π*) recorded in tetrahydrofuran (THF) appears at about 2.80 eV, but when recorded as solution-cast thin film, shifts to a lower energy as a result of the increasing intermolecular interaction. However, the differences associated with the π–π* interband transition between polymer solution and the solid phase are small, demonstrating that the main role in this problem is played by the chemical structure of the polymer chains and not the phase state of the material.

3.6. ESR

The ESR spectra of pristine P3PT (Fig. 6) obtained at LN and at room temperature under vacuum (10^{-5} Torr) showed nearly the same character of lines. The concentration of spins at low temperatures was about twice that at room temperatures (1.4×10^{18} sg^{-1}). Taking into account the GPC results (DP = 118) it may be concluded that P3PT (very exactly purified) has one spin per 2.8×10^3 mers in the chains. The peak-to-peak distance (ΔH_{pp}) is slightly higher at liquid nitrogen temperature compared to the value at room temperature. ΔH_{pp} for P3PT is of the same order of magnitude as in unsubstituted poly(thiophene) [20] and 90% *cis* PA [21]. The ESR resonance lines show a small asymmetry between the A and B parts of the spectra, but in both cases each half is Lorentzian in shape. The g values for both temperatures are practically the same and are typical for poly(thiophenes).

3.7. Magnetic susceptibility

The static magnetic susceptibility was measured by a Gouy magnetic balance method. The absolute value of the magnetic susceptibility was determined by comparison with the standard. Fig. 7b shows the temperature dependence of the total static susceptibility of as-synthesized P3PT (with the oligomeric fraction and residual of catalyst) and pure polymer (after extraction) measured from LN to RT (298 K). The presence of $FeCl_3$ in the as-synthesized product showed

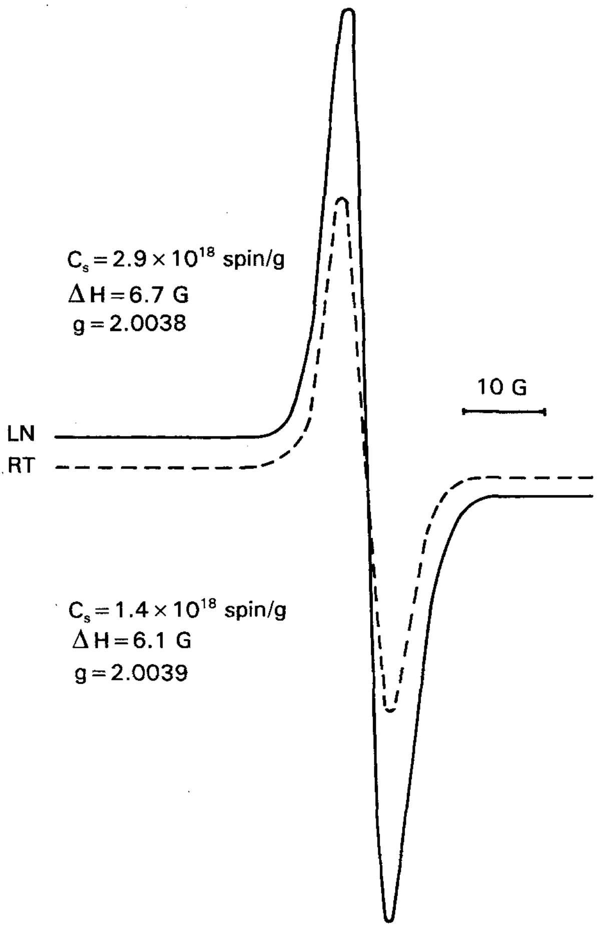

Figure 6 ESR spectra of P3PT recorded at liquid nitrogen temperature (LN) and at 298 K (RT). LN:$C_s = 2.9\times 10^{18}$ spin/g; $\Delta H = 6.7$ G; $g = 2.0038$; RT: $C_s = 1.4\times 10^{18}$ spin/g; $\Delta H = 6.1$ G; $g = 2.0039$.

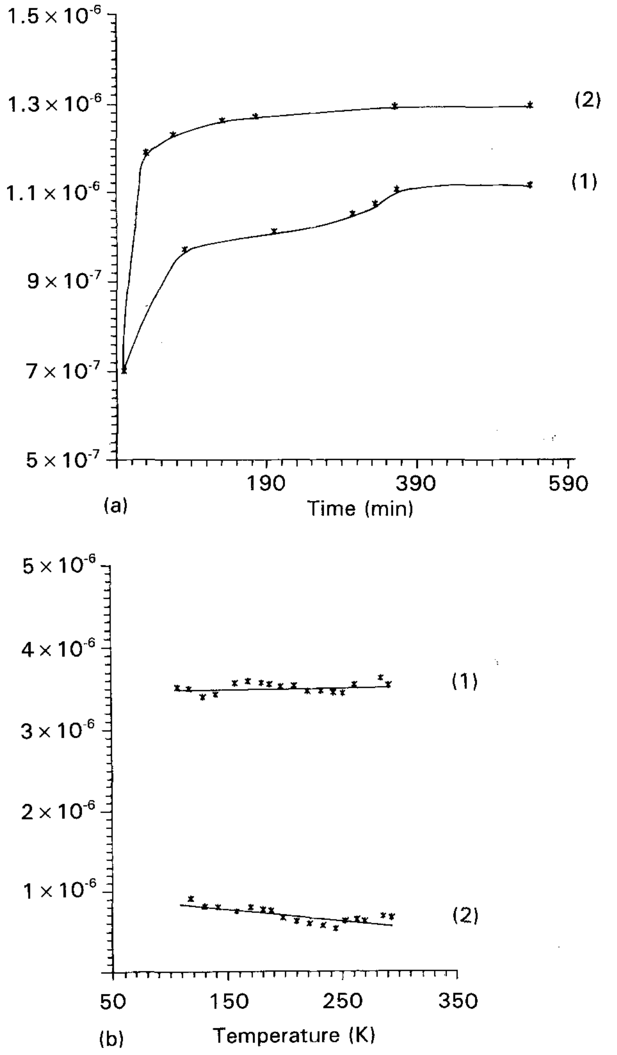

Figure 7 Total magnetic susceptibility of P3PT: (a) during the time of doping with I_2; (b) temperature dependence for undoped P3PT. (1) As-synthesized P3PT; (2) pure polymer.

that susceptibility is independent of temperature, and its value was distinctly higher than in the pure polymer. The total susceptibility may be expressed by the sum of a Curie (inverse-T) and a Pauli part (independent-T) [22]

$$\kappa_T = \kappa_C + \kappa_P$$

where

$$\kappa_C = C_s g \mu_B^2 / 3 k_B T \text{ and } \kappa_P = \mu_B^2 N(E_F)$$

C_s is the number of observed spins, g their mean Landé factor, and $N(E_F)$ is the density of states at the Fermi level. The calculation showed that Pauli-like susceptibility was about 7×10^{-7} e.m.u. $\text{cm}^{-3}\,\text{g}^{-1}$ for undoped P3PT.

Doping of poly(3-pentylthiophene) by I_2 (*in situ* experiments) at room temperature for degassed samples showed (Fig. 7a) that the magnetic susceptibility during this process increases distinctly and has a final value of 1.30×10^{-6} e.m.u. $\text{cm}^{-3}\,\text{g}^{-1}$ for 0.21 moles of I_3^- per 1 mole of mers (curve 2) (e.m.u. – electromagnetic unit) and $1.10\,10^{-6}$ e.m.u. $\text{cm}^{-3}\,\text{g}^{-1}$ for 0.09 mole of I_3^- (curve 1). Assuming that the doping process produce only the Pauli spins (ESR spectra showed that C_S increased by two orders of magnitude after doping), the final value of magnetic susceptibility is of the same order as that reported for poly(paraphenylene) doped by AsF_5 [23] and for *cis* PA doped by iodine [24], and higher than that reported by Peo *et al.* for PPP doped with SbF_5 [25]. The observed Pauli-like susceptibility of polymers doped with I_2 P3PT corresponds to a density of states at the Fermi level of about 0.039 states eV^{-1} per thiophene ring, or about 0.01 states eV^{-1} per carbon atom in thiophene.

3.8. Electrical properties

The dark-current voltage characteristics give information on the quality of ohmic contact, i.e. contact that is non-injecting and that has, in principle, linear current–voltage (I–V) relationship in both directions. In Fig. 8 the I–V characteristics measured in a sandwich-type configuration with the Au-contacts on the top and back of the polymer pellet are shown. The characteristics were obtained at a temperature near but below the glass transition of P3PT, above the glass temperature, T_g, of the polymer, and near the melting point of P3PT. In all cases the I–V relationships were linear, showing that the Au–P3PT–Au structures are ohmic (not rectifying behaviours) at measured temperatures and applied voltages.

The dark electrical conductivity of undoped P3PT at room temperature was $2 \times 10^{-8}\,\text{S}\,\text{m}^{-1}$, and after doping with iodine rose to about $10^{-4}\,\text{S}\,\text{m}^{-1}$ for 9% moles of I_3^- and $10^{-1}\,\text{S}\,\text{m}^{-1}$ for 21% moles of iodine taken as I_3^-. The temperature dependence of conductivity for pristine P3PT is shown in Fig. 9 as $\ln\sigma$ against $1/T$ (a) and $\ln\sigma$ against $1/T^{1/4}$ (b). The $T^{1/4}$ temperature dependence is well known in amorphous semiconductors, and is characteristic of Mott's model of variable range hopping [26]. The determination coefficient showed that the better fit of experimental points is for T^{-1} temperature dependence, but the

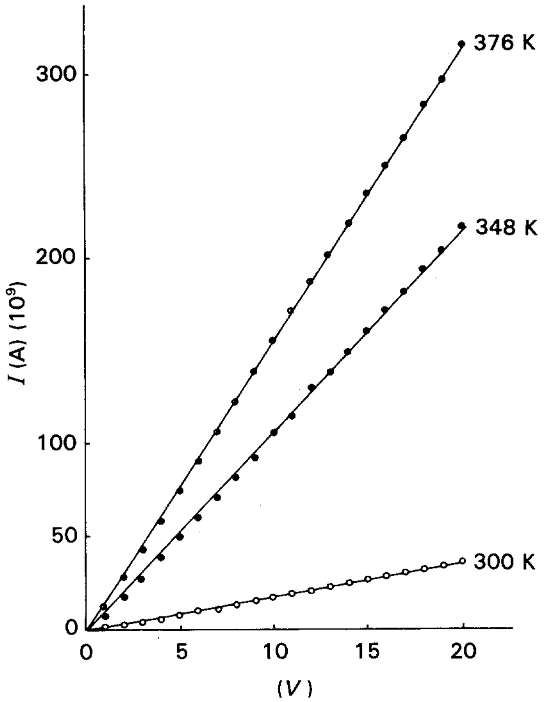

Figure 8 I–V characteristics of P3PT. $I = f(V)$.

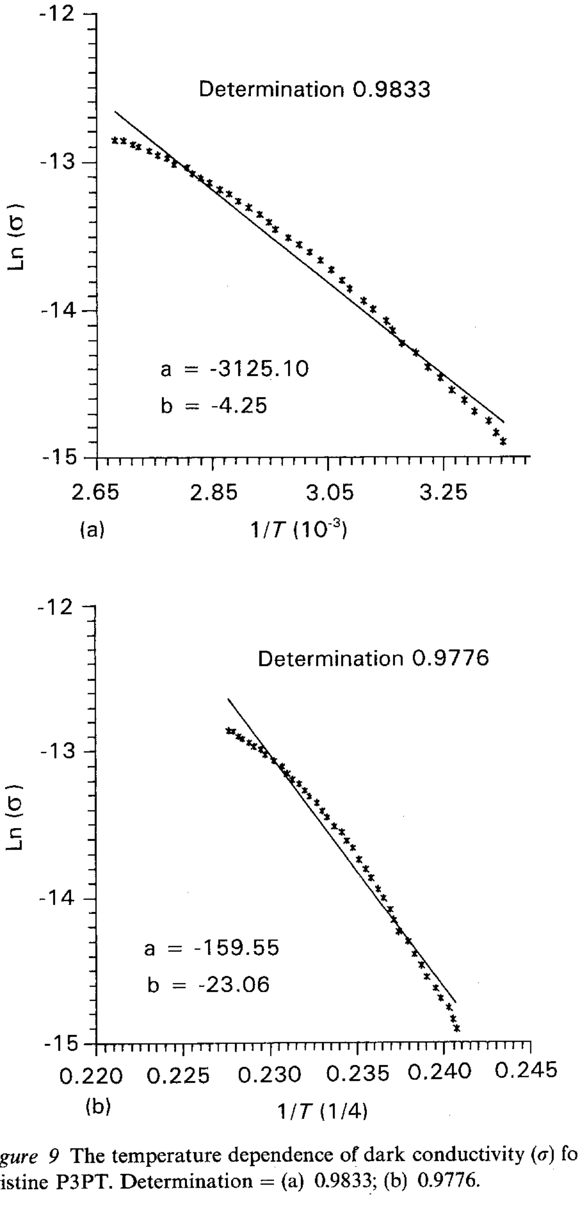

Figure 9 The temperature dependence of dark conductivity (σ) for pristine P3PT. Determination = (a) 0.9833; (b) 0.9776.

difference is too small to draw conclusions about the transport mechanism.

4. Conclusion

The results presented above demonstrate that solution-processible P3PT may have potential applications in the field of electronic devices.

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