Available online at www.sciencedirect.com

ScienceDirect

polymer

Polymer 49 (2008) 481–487

www.elsevier.com/locate/polymer

Order–disorder transitions in poly(3,4-ethylenedioxythiophene)

Bjorn Winther-Jensen [a,*], Maria Forsyth [a], Keld West [b], Jens Wenzel Andreasen [b],
Paul Bayley [a], Steven Pas [a], Douglas R. MacFarlane [a]

[a] *Australian Centre for Electromaterials Science, Monash University, Clayton, Victoria 3800, Australia*
[b] *The Danish Polymer Centre, Risø National Laboratory, 4000 Roskilde, Denmark*

Received 26 September 2007; received in revised form 6 November 2007; accepted 30 November 2007
Available online 5 December 2007

Abstract

The commonly held perception that high conductivity in conducting polymers is linked to a high level of π-stacking order in the material is shown here to be of lesser importance in highly conducting poly(3,4-ethylenedioxythiophene) (PEDT), which has been prepared by chemical vapour phase polymerisation. Despite the fact that there is a highly energetic phase transition about 130 °C (110 J/g), and that this transition corresponds to a loss of the long-range π-stacking as observed in grazing angle XRD, the conductivity remains unchanged beyond the transition and only decreases by a factor of two when heating to above 200 °C. The XRD data suggest that order in two dimension remains above the phase transition measured by DSC and this order is sufficient to maintain a high level of electronic conductivity. Furthermore, as the ligand on the iron salt used in the synthesis is varied, the conductivity of the PEDT varies over two orders of magnitude. These phenomena cannot be explained by different degree of doping or crystallinity and it is proposed that the iron salt has an ordering effect during the vapour phase polymerisation.
© 2007 Elsevier Ltd. All rights reserved.

Keywords: PEDT; DSC; XRD

1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDT) is one of the most stable, highly conductive, inherently conjugated polymers (ICPs) known to date and as such finds numerous applications in devices including capacitors, LEDs, photovoltaics and antistatic coatings [1–6]. In recent times, novel synthetic routes involving base inhibited chemical polymerisation have allowed record conductivities of PEDT materials reaching greater than 1000 S/cm [7,8]. This method facilitates control of individual parameters including counter-ion (or dopant) in the ICP through the choice of the ligand in the Fe(III) salt, temperature and thickness. Vapour phase polymerisation (VPP), in which the pyrrole was condensed from the vapour phase onto a solid film of the oxidant has shown that the conductivity of the resulting polymer is dependant upon the ligand used, although it is not clear if this is due to the nature of the counter-ion or the structure imposed from the initial oxidant salt [9]. de Leeuw et al. have found that the conductivity of PEDT prepared via chemical polymerisation (cast from a solution) is also affected by the choice of ligand [6] and that the best conductivity is obtained by using *para*-toluenesulfonate (PTS). They concluded that this was possibly due to the smoother films resulting from this ligand.

Conductivity mechanisms in oxidized (doped) conjugated polymers such as poly(acetylene) [10,11], poly(aniline) [11,12], poly(pyrrole) and PEDT [12,13] are commonly reported as being limited by hopping or tunnelling with conductivity data being well fitted by Drude theory. It was assumed that this hopping existed between ordered 'metallic' domains [14]. Subsequently, Aasmundtveit et al. [15,16] and Luzny et al. [17] have shown, using grazing angle XRD, that regular three-dimensional order is present in both PEDT and PANI. The order in PEDT involved π-stacking in one dimension

---

* Corresponding author. Department of Materials Engineering, Monash University, Building 19, Clayton, Victoria 3800, Australia. Tel.: +61 3 99055343; fax: +61 3 99054940.
E-mail address: bjorn.winther-jensen@eng.monash.edu.au (B. Winther-Jensen).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.11.055

(d_{010}) and regular inter-chain spacing (d_{100}) and seemed independant of doping level in the case of the PEDT/PTS systems. Using alkyl-substituted monomers can change the structure of the ordered PEDT; a structure with order in two dimensions due to loss of long-range π-stacking was followed by decrease of conductivity [18]. Recently Epstein and Prigodin [14] have concluded that the order can explain the conductivity by invoking metallic ordered domains (π-stacking) in an amorphous surrounding whereby the charge carriers are tunnelling between these metallic regions. This mechanism would then suggests that a higher degree of order, as measured by XRD, should correlate with a higher conductivity and loss of this order within the metallic domain should therefore reduce the conductivity.

Another measure of order commonly used in determining the degree of crystallinity in polymer materials is thermal analysis. In oxidized conducting polymers it has been less commonly used and the few reports available suggest that the transitions measured are in fact irreversible decomposition of the material [19]. Oligomeric units of thiophenes have been successfully analysed using Differential Scanning Calorimetry (DSC) and have shown melting transitions around 306 °C and transition energies of 115 J/g [20]. It would be expected that a highly ordered polymer should also have phase transitions between a crystalline and amorphous state. Indeed the results reported here will show that significant thermal transitions are present in PEDT prepared by both chemical and electrochemical routes and the position and energy of these are variable.

This paper will investigate the effect of composition and temperature on the crystalline order in PEDT polymerised chemically by vapour phase polymerisation (VPP), using different Fe(III) salts. The correlations between structure and conductivity are discussed, including the role of long-range π-stacking as an important part of the conductivity mechanism.

2. Experimental

Preparation of various Fe(III) salts was carried out according to previous reports [9,21]. The ligands used in this study are camphor-sulfonate (CSA), chloride (Cl), 4-ethylbenzenesulfonate (EBS), tetradecylsulfonate ($C_{14}SO_3$) and *para*-toluenesulfonate (PTS). For the VPP process, PET, glass or silicon wafer substrates coated with an Fe(III) salt were exposed to a vapour of the monomer according to procedures earlier reported [7–9]. After the polymerisation the samples were washed twice in ethanol in order to remove iron(II) and excess counter-ion from the ICP films. Determination of Fe content by XPS typically shows the Fe content to be below the limit of detection (0.5 mol%) [22]. The thickness of the ICP films (all sub-micron) was determined using a DEKTAK profilometer. The resistance of the ICP films was measured by a four-point probe method (Jandel MR3), the high-temperature resistance measurement was preformed with a four-line setup "gold on Teflon" and the measurement were normalised to the measurement preformed with the Jandel equipment.

Grazing angle X-ray diffraction was made at The Danish Polymer Centre (Risø National Lab, Denmark) from PEDT obtained by VPP on spin-coated Fe(III) salt on silicon wafers. PEDT thicknesses for these samples were in the range from 120 to 160 nm.

Differential scanning calorimetry (DSC, Q100 from TA) was made on PEDT polymerised on glass-slides and dried at 60 °C for 1 h. The PEDT was removed from the glass substrate, grained and sealed in an aluminium cup.

Electro-polymerised PEDT was made on platinum foil using a standard three-electrode configuration under constant voltage (0.9 V) controlled by a Multichannel Potentiostat (VMP2 from Princeton Applied Research). The electrolyte solution (1 M NaPTS solution adjusted to pH 2 by adding *para*-toluenesulfonic acid) was saturated with the monomer (~0.3%).

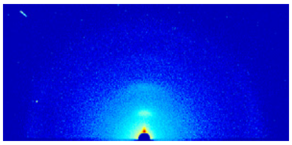
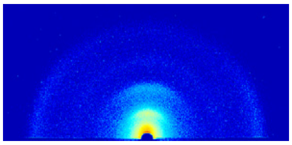
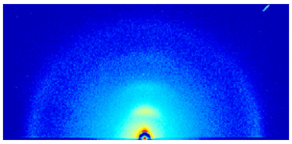
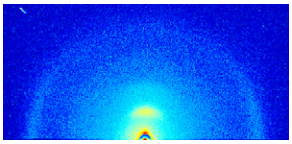
Ion-exchange of counter-ions in the PEDT films was done with the same electrode configuration and with the conducting polymer as the working electrode. Cyclic voltammetry (CV) was made with low scan-rates (1 mV/s) over 24 h (0.65 V to −1.0 V). The electrolyte was a one molar solution of the sodium salt of the introduced counter-ion and the solution was changed every 8 h. After CV the ion-exchanged PEDT films were resting at a potential of 0.3 V for 1 h to ensure a comparable doping level.

UV–vis–NIR spectra of PEDT thin films (on glass) were obtained using a Varian Cary 5G spectrophotometer.

3. Results and discussion

Table 1 presents conductivity and crystallographic data for PEDT polymerised using different Fe(III) salts. The ligand from the Fe(III) salt is incorporated in the PEDT as counter-ion. The conductivity for PEDT/PTS stands out from this series with more than a factor of ten higher values than that obtained with other ligands. In order to ascertain whether the difference in conductivity is due to the nature of the ligand itself or the structure imposed by the iron salt during polymerisation, some materials were ion-exchanged post-chemical polymerisation as discussed above. The resultant conductivity was reproducibly the same for the ion-exchanged material as for the parent material; i.e., the conductivity of the film prepared using $FeCl_3$ did not improve upon ion-exchange with PTS anions and conversely, the PTS prepared films did not lose conductivity when exchanged with Cl^- (Table 1). This conclusively demonstrates that the structure imprinted in the PEDT during polymerisation is the determining factor. This is consistent with observations made by West [23]. The use of the VPP technique avoids the presence of a solvent during the polymerisation and thus only interaction between iron(III) salt and the monomer determines the structure of the resulting polymer. The crystallographic parameters extracted from the grazing angle XRD experiments indicate that there is little and random apparent difference in the normalised intensity (I_{100}) and also in the π-stacking distance (d_{010}) as a function of ligand and thus this cannot explain the differences in conductivity, as discussed previously [24]. On the other hand the inter-chain distance (d_{100}, understood as the distance between layers of pi-stacked (d_{010}) chains [15,16]) reflects the differences in conductivity. Qualitatively the 2D-XRD images also suggest differences between the materials prepared with

Table 1
X-ray diffraction and conductivity data for PEDT with different counter-ions

	Counter-ion	d_{100} (Å)	Normalised I_{100}	d_{010} (Å)	σ (S/cm)
	Cl, ion-exchanged from PTS				921
	PTS	13.94	0.7e−3	3.46	933
	$C_{14}SO_3$	13.71	1.2e−3	3.51	79
	EBS	13.32	0.5e−3	3.48	74
	CSA	12.87	1.7e−3	3.46	15
	Cl				19
	PTS, ion-exchanged from Cl				15

different ligands. In particular the lowest conductivity material indicates significantly more diffuse scattering compared to the other materials. The data shown here is also consistent with previous reports by Inganas et al. for similar systems [15,16].

3.1. Thermal behaviour

The thermal analysis traces shown in Fig. 1 also supports extensive ordering in all materials investigated, although the transition temperatures, size and appearance are different. The transitions all appear to begin around 100 °C and peak around 140 °C except in the case of CSA where two distinct peaks are observed. In fact there is some indication of this second peak even in the other PEDT materials (in particular Cl^-). The energies of these transitions are all above 110 J/g, which is large compared to the melting transition in sexithiophene [20]. The transition energies for PEDT were calculated for an entity of four repeat units plus a counter-ion (presuming a degree of doping of 0.25 as suggested by Aasmundtveit et al. [15]), which gives energies in a range from 0.9 to 1.5 eV (this energy unit is necessary in order to compare with literature values for similar size units). Compared to the calculated and measured binding energies for crystalline quarto-thiophene (0.4 eV for the same entity [20]) – the data here suggest a very high degree of order in VPP PEDT which is lost during the phase transition observed by DSC and XRD. To determine whether these events are truly representing a thermodynamic phase transition or simply a decomposition reaction, as previously reported for polypyrrole [19], the reversibility of the transitions was examined. Fig. 2 shows that, for the PEDT/PTS material, the second thermal trace obtained immediately after the first run is completely featureless suggesting that in fact the transition is not reversible. However,

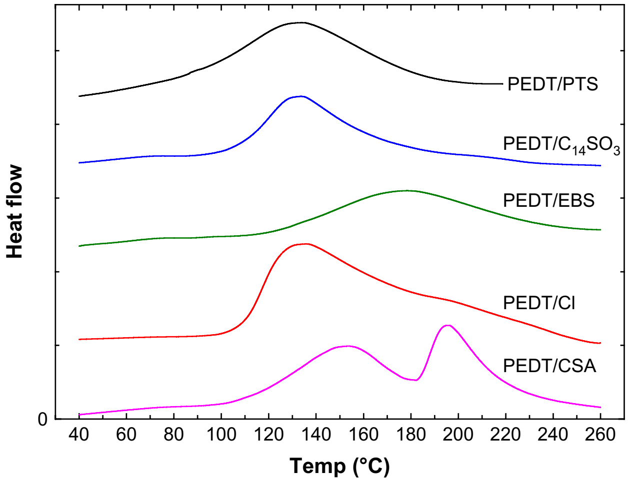


Fig. 1. DSC of VPP PEDT, 10 °C/min for VPP PEDT from different iron(III) salts.

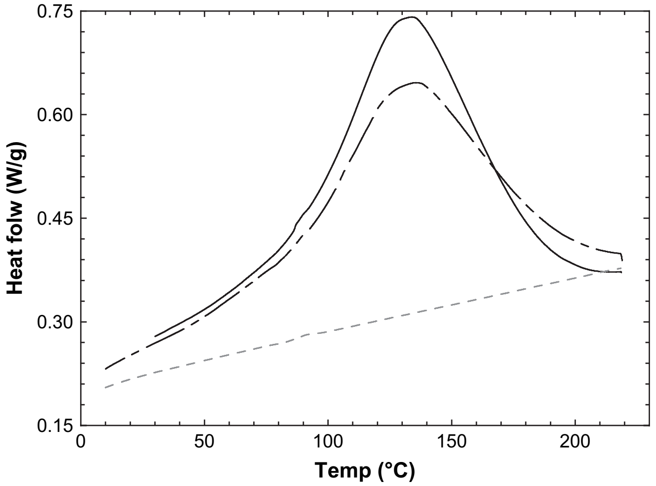


Fig. 2. DSC of PEDT/PTS, 10 °C/min. 1st run: full line, 2nd run (10 min after 1st run): grey dotted line, 3rd run (4 weeks after 1st run): black dotted line.

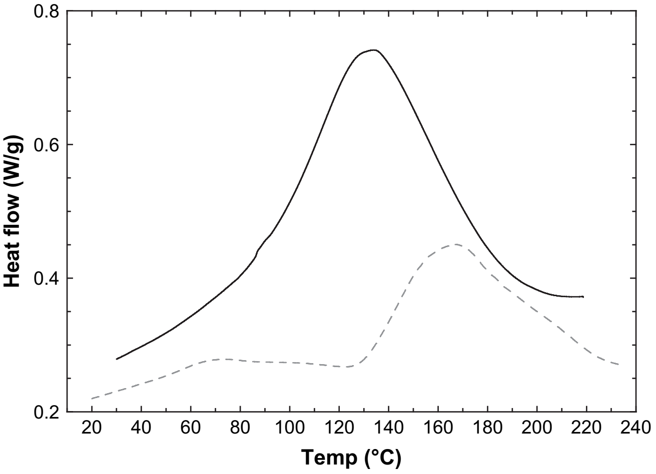


Fig. 3. DSC of PEDT/PTS, 10 °C/min. Vapour phase polymerisation (full line) and electro-polymerised (dashed line).

after standing at room temperature for 28 days, the third trace shown in Fig. 2 has almost reproduced the initial run. This confirms reversibility and strongly supports that this thermal event represents a thermodynamic structural change. To investigate the apparently slow re-ordering of PEDT, samples of PEDT/PTS were heated to 150 °C for 1 h in a vacuum oven in a dry-box and DSC traces were obtained after increasing annealing time at 25 °C. In Table 2 the transition energies are presented. After 12 h the transition energy has recovered to about 2/3 of the original value and after five days the DSC trace was practically identical to the initial one and no further change were observed.

In Fig. 3 we compare the thermal behaviour of PEDT/PTS prepared using traditional electrochemical polymerisation with the chemical polymerisation discussed in this work. The thermal features and conductivity for the electrochemically prepared material are comparable to those observed in the case of the lowest conductivity PEDT/Cl sample. The energy of the thermal transition in the electrochemically prepared PEDT/PTS material is almost half of that measured for the chemically prepared films which also suggests that the conditions of polymerisation – and the structure thereby imprinted – are more important than the counter-ion (or dopant) present in the final material.

3.2. Temperature dependent XRD for PEDT/PTS films

To investigate the nature of the phase transition the XRD patterns for the PEDT/PTS films were obtained at 140 °C and compared to room temperature patterns before and after this temperature excursion (Fig. 4). The dramatic loss in intensity at higher angles (Fig. 4a compared with 4b) strongly suggests a disruption of the long-range π-stacking at elevated temperatures beyond the DSC transition. Surprisingly, the lower angle reflections attributed to the inter-chain (d_{100}) distances are still very prevalent. After cooling back to room temperature and collecting the XRD patterns of the same sample once again, the higher angle peaks reappear, although less intensely. The time elapsed between the data in Fig. 4b and c is approximately 3 h, significantly more than the time between the thermal traces in Fig. 2a and b. The return of the π-stacking order again confirms the reversibility of this high-temperature transition, as observed from the annealing experiment discussed above.

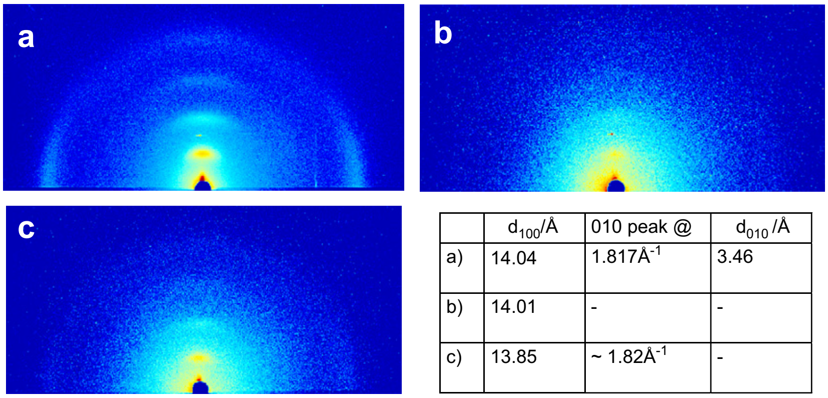
Table 2
Phase transition energies from DSC data for PEDT/PTS after heating to 150 °C and annealing in N_2 dry-box

Days annealed at 25 °C	Transition energy (J/g)
1/2	87
1	83
2	100
3	112
5	117

The residual two-dimensional order observed at 140 °C is illustrated schematically in Fig. 5. In this case, the π-stacking dimension has been disrupted, possibly just by a small tilt away from the 180° plane, whilst the other two dimensions (along the chain and between the chain stacks) remain little changed. Such a structure may be expected to show liquid crystalline properties such as birefringence. Polarised light microscope experiments have only indicated completely isotropic properties in this temperature region, however, if the domains involved are smaller than the wavelength of visible light, as in fact suggested by Epstein and Prigodin [14], no birefringence would be observed. This would then provide some understanding for maintenance of the conductivity through this transition as seen in Fig. 6 discussed below.

3.3. Resistance behaviour through the phase transitions

Fig. 6 presents the resistance data for the PEDT/PTS film cycled from room temperature to 260 °C in a dry nitrogen environment and back again. The resistance curve obtained upon heating shows a gradual increase in resistance with increasing temperature which may be interpreted either as being ‘metallic’ behaviour or simply a loss of order leading to lower



	d_{100}/Å	010 peak @	d_{010} /Å
a)	14.04	1.817$Å^{-1}$	3.46
b)	14.01	-	-
c)	13.85	~ 1.82$Å^{-1}$	-

Fig. 4. X-ray diffraction of PEDT/PTS. (a) Pristine film at room temperature (dried overnight at 10^{-1} millibar), (b) at 140 °C (10^{-1} millibar N_2), (c) at room temperature ~3 h after heating (10^{-1} millibar N_2).

conductivity. It is interesting to note that there is no *sudden* transition in resistance at the phase transition (presumably an order–disorder transition) measured via DSC and XRD. One might expect that a sudden loss in long-range π-stacking order, suggested in the XRD pattern at 140 °C, should lead to a dramatic increase in the measured resistance of the material if the conduction mechanism is strongly reliant on metallic domains represented by regions of π-stacked units.

The resistance during the cooling experiment presents a change in slope around the phase transition temperature; changing from a metallic-like or temperature independent behaviour above the transition temperature to a semi-conductor behaviour below ~100 °C. Throughout the entire heating/cooling temperature scan, the resistance increase only by a factor of two which is insignificant in contrast to the major changes observed in the XRD and thermal behaviour. The subsequent resistance measurements of PEDT/PTS upon heating, which were taken immediately after the first heating/cooling cycle, closely followed the data from the first cooling. However, when stored over a longer period (5 days) the sample returned almost to its original resistance (Fig. 6). This time frame is in very good agreement with the time for re-ordering seen by DSC as discussed above. Fig. 7a and b demonstrates that this conductivity/temperature behaviour is not restricted to the PEDT/PTS system but is also present in the PEDT/EBS and PEDT/CSA materials although these have higher overall initial resistance. The reversible behaviour was also observed in these materials.

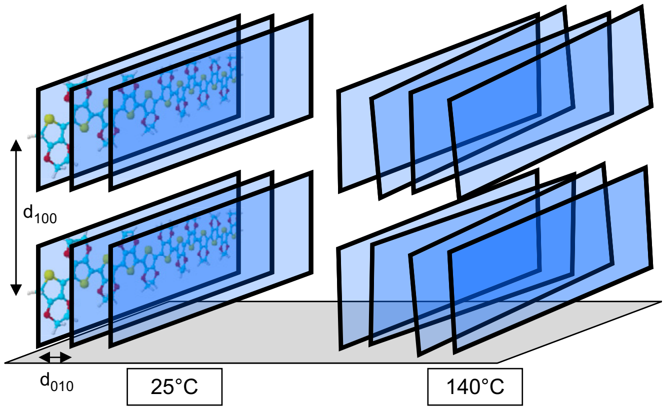


Fig. 5. Schematic illustration of the change to two-dimensional order in PEDT at high temperature. The grey plane illustrates the plane of the substrate.

3.4. UV–vis and Raman characterisation

It has been reported that electro-polymerised PEDT films have a maximum absorption in the UV–vis–NIR spectrum around 1250 nm, which has been interpreted as a measurement of the band-gap in the material [25]. However, in contrast, for chemically polymerised PEDT/PTS films [26,27] an increasing free carrier tail has been seen. In the materials prepared here, using VPP methods and different Fe(III) salts (Fig. 8), a range of behaviours are observed for this free carrier tail region. For the materials with lower conductivity (e.g., PEDT/$C_{14}SO_3$) a maximum absorbance around 1550 nm is seen whilst the most conducting PEDT/PTS material presents a continuously increasing absorbance, which is more indicative of metallic behaviour. The measurements were also taken at temperatures above the transition temperature (150 °C) to determine whether there was a correlation between the order–disorder transition and the observation of such a free carrier tail, however, the

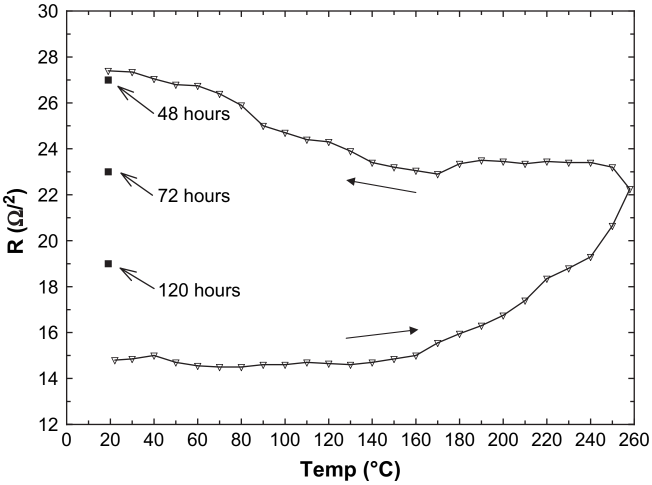


Fig. 6. Resistance of PEDT/PTS film under N_2 by heating, cooling (triangles/black line) and re-ordering at room temperature (black squares).

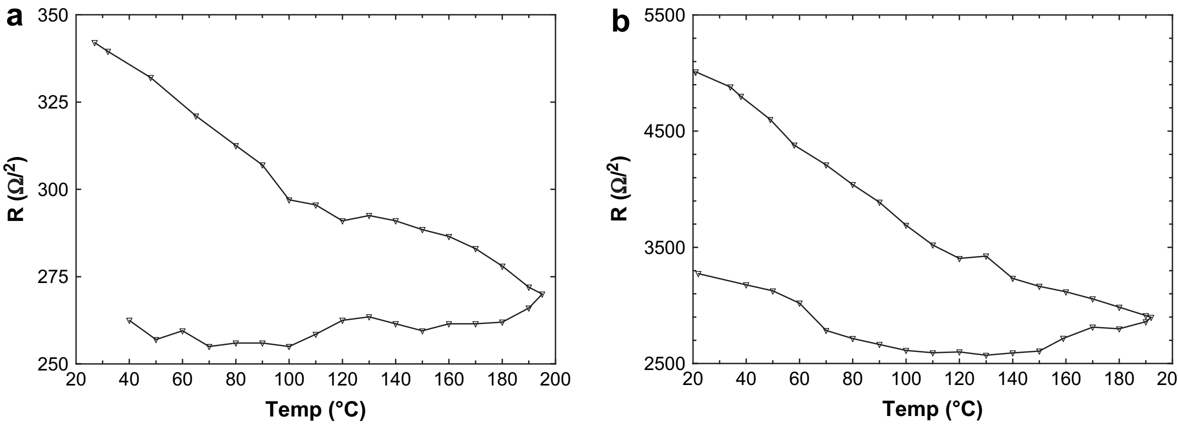


Fig. 7. Resistance versus temperature under N_2 for (a) PEDT/EBS and (b) PEDT/CSA.

spectra did not change. If we hold with the assumption that an increasing absorbance (rather than a distinct peak) suggests metallic behaviour, then the results here strongly suggest that, at least in this system, the metallic behaviour – and thereby the conductivity – of the material is disconnected from the presence of a long-range three-dimensional order (π-stacking).

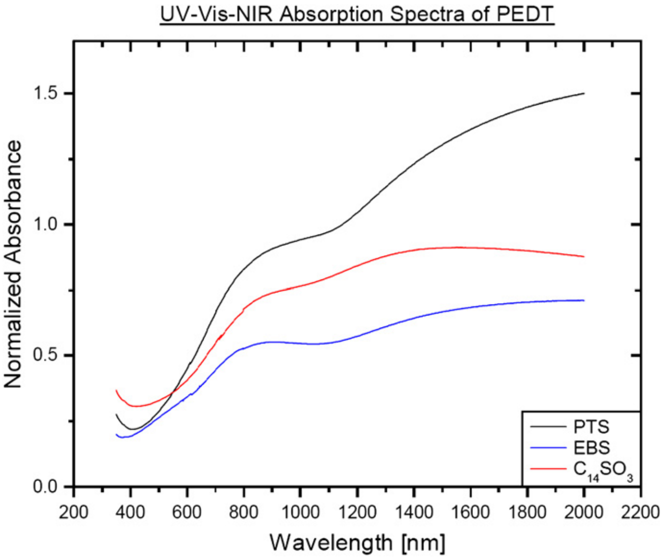


Fig. 8. UV–vis–NIR spectra of VPP PEDT using different Fe(III) salts.

4. Conclusion

Reversible solid–solid phase transition in vapour phase polymerised PEDT have been observed with DSC and XRD at around 140 °C for the materials vapour phase polymerised using a range of iron(III) salts. During the phase transition the long-range π-stacking order disappears, whereas the intra-chain distance remains relatively unchanged. The phase transition energy as calculated from the thermograms is of the order of 110 J/g, sufficient for the energy required to destroy the π-stacking – assuming that the material is highly ordered in the first place (i.e., at temperatures below the measured thermal transition).

The common understanding of the conductivity in inherently conducting polymers (ICPs) is based on hopping or tunnelling between highly ordered 'metallic' domains. The understanding of these domains is that the order is dominated by π-stacking of the ICP conjugated units and thus we should expect to see a dramatic decrease in conductivity beyond the order–disorder transition temperature. However, this is not the case, even for the most conducting PEDT samples (~1000 S/cm) no significant change in conductivity is measured around the transition temperature (determined from DSC and also observed in XRD measurements). This indicates that long-range π-stacking – and thereby 'metallic' domains – are not the key structural property promoting high conductivity, or that the conductivity is significantly affected by some other limiting factor. The latter statement is also supported by a lack of correlation between the degree of crystallinity (i.e., amount of 'metallic' domains) and the conductivity. Surprisingly there seems to be a correlation between conductivity and inter-chain distance, resulting from a ordering effect when polymerising PEDT using various iron(III) salts, where larger inter-chain distances give a higher conductivity.

References

[1] Groenendaal L, Jonas F, Freitag D, Pielartzik H, Reynolds JR. Adv Mater 2000;7:481–94.
[2] Skotheim TA, Elsenbaumer RL, Reynolds JR. Handbook of conducting polymers. Taylor & Francis Group, LLC; 2007.
[3] Gadisa A, Tvingstedt K, Admassie S, Lindell L, Crispin X, Andersson MR, et al. Synth Met 2006;156(16–17):1102–7.
[4] Winther-Jensen B, Krebs FC. Sol Energy Mater Sol Cells 2006;90: 123–32.
[5] Sun SS, Sariciftci NS. Organic photovoltaics. Taylor & Francis Group, LLC; 2007.
[6] de Leeuw DM, Kraakman PA, Bongaerts PFG, Mutsaers CMJ, Klaassen DBM. Synth Met 1994;66:263–73.
[7] Winther-Jensen B, West K. Macromolecules 2004;37:4538–43.
[8] Winther-Jensen B, Breiby DW, West K. Synth Met 2005;152:1–4.

[9] Winther-Jensen B, Chen J, West K, Wallace GG. Macromolecules 2004;37:5930–5.

[10] Ishiguro T, Kaneko H, Nogami Y, Ishimoto H, Nishiyama H, Tsukamoto A, et al. Phys Rev Lett 1992;69:660.

[11] Kohlman RS, Zibold A, Tanner DB, Ihas GG, Ishuguro T, Min YG, et al. Phys Rev Lett 1997;78:3915.

[12] Kohlman RS, Epstein AJ. In: Skotheim T, Elsenbaumer R, Reynolds J, editors. Handbook of conducting polymers. 2nd ed. New York, NY: Marcel Dekker; 1998. p. 85–121.

[13] Martens HCF, Reedijk JA, Brom HB, de Leeuw DM, Menon R. Phys Rev B 2001;63:073203.

[14] Prigodin VN, Epstein AJ. Physica B 2003;338:310–7.

[15] Aasmundtveit KE, Samuelsen EJ, Pettersson LAA, Inganas O, Johansson T, Feidenhans R. Synth Met 1999;101:561–4.

[16] Aasmundtveit KE, Samuelsen EJ, Inganas O, Pettersson LAA, Johansson T, Ferrer S. Synth Met 2000;113:93–7.

[17] Luzny W, Samuelsen EJ, Djurado D, Nicolau YF. Synth Met 1997;90:19–23.

[18] Breiby BW, Samuelsen EM, Groenendaal L, Struth B. Polym Phys 2003;41:945–52.

[19] Thiéblemont JC, Brun A, Marty J, Planche MF, Calo P. Polymer 1995;36:1605–10.

[20] Scandola M, Finelli L, Bongini A, Barbarella G, Sotgiu G, Zambianchi M. Macromol Chem Phys 2001;202:1878–82.

[21] U.S. Patent 4,697,001, 29.09.1987.

[22] Winther-Jensen B, West K. Synth Met 2005;148:105–9.

[23] West, K. Unpublished work.

[24] Winther-Jensen B, Forsyth M, West K, Andreasen JW, Wallace GG, MacFarlane DR. Org Electron 2007;8:796–800.

[25] Lapkowski M, Pron A. Synth Met 2000;110:79–83.

[26] Pettersson LAA, Ghosh S, Inganas O. Org Electron 2002;3:143–8.

[27] Pettersson LAA, Johansson T, Carlsson F, Arwin H, Inganas O. Synth Met 1999;101:198–9.