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Bis(ethynyl)-polymers

Part III *Physico-chemical characterization of poly(2,5-thiophenediyl)ethynylene and poly[ethynylene(2,5-thiophenediyl)ethynylene]*

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Poly(2,5-thiophenediyl)ethynylene and poly[ethynylene(2,5-thiophenediyl)ethynylene], synthesized in our laboratory, have been investigated in order to characterize their physicochemical properties. The optical and infrared spectra of the two polymers were studied as well as their thermal properties by means of differential scanning calorimetry and thermogravimetric analysis. The electrical conductivity of the two polymers in the pristine state and in the I_2-doped one has been measured and the effects due to the doping on the spectroscopic and thermal properties have been studied.

1. Introduction

The interest in conjugated polyhydrocarbon chains [1] is not surprising if one considers the large field of possible applications: as electrical conductors, photoconductors and as materials suitable for electroluminescence and non-linear optics. It has already been shown that the introduction in the main chain of para-linked arylene and heteroaromatic rings enlarges the category of such interesting materials. The inherent electronic conductivity of all these polymers is typically due to the π conjugation of the chain backbone, although doped 1,4-*cis*-polyisoprene [2] also exhibits significant electrical conductivity. However, if double and single bond alternation within the polyhydrocarbon chain leads to very high electrical conductivity upon doping, the same does not happen when single, double and triple bonds alternate. These chains are nevertheless promising for their marked non-linear optical properties [3]. The theoretical *ab initio* calculations carried out to investigate the electronic structure of conjugated organic polymers has been extensively reviewed by Bredas (see [1]).

After having devised in our laboratory a new convenient procedure [4] for the introduction of ethynyl groups into an aromatic moiety and prepared 1,4- and 1,3-diethynyl benzenes and 2-bromo-1,4-diethynyl benzene, we polymerized these substrates as well as 2,6-diethynylpyridine by oxidative coupling of two ethynyl groups [5]. Within the same research project we have also prepared poly(2,5-thiophenediyl)ethynylene [6, 7] (PETh) and poly[ethynylene(2,5-thiophenediyl)ethynylene] (PDETh) [6, 8].

The synthesis of these two polymers was accomplished according to the oxidative coupling procedure described by Hay [9]. The parent monomer (2,5-thiophenediyl) was synthesized by the $Pd(PPh_3)_4$-catalysed coupling of (trimethylsilyl)acetylene and 2,5-diiodothiophene. The protecting trimethylsilyl groups were removed by hydrolysis according to the method of Takahashi *et al.* [10]. PDETh was obtained by oxidative coupling of the parent monomer with oxygen and catalytic amounts of CuCl. Fig. 1 illustrates the scheme of the reaction.

Besides our interest in studying the conductivity properties of this kind of very π-electron-rich macromolecular systems, it is worth noticing that such a high density of double and triple bonds enables these polymers to generate hypercross-linked organic solids [11–13], thermally very stable materials with particularly good mechanical properties after cross-linking.

The physico-chemical characterization of the two above-mentioned polymers was the aim of the present work.

2. Materials and methods

The reddish-brown powder of PETh and the dark brown powder of PDETh obtained after synthesis were first extracted in Soxhlet under a nitrogen atmosphere with petroleum ether and then with acetone. All the solvents used were RPE grade.

The UV–VIS measurements were accomplished by means of a U-2000 Hitachi spectrophotometer.

The optical spectra of the solid samples were obtained by means of a Cary 2300 Varian spectrophotometer, equipped for diffused reflectance measurements.

The IR spectra were collected on samples diluted on KBr discs by accumulating, on a Hitachi 270–30 dispersive spectrophotometer, at least 5 spectra to increase the signal-to-noise ratio. The spectra were studied making use of the software installed on the instrument's computer, which allowed the second derivative analysis.

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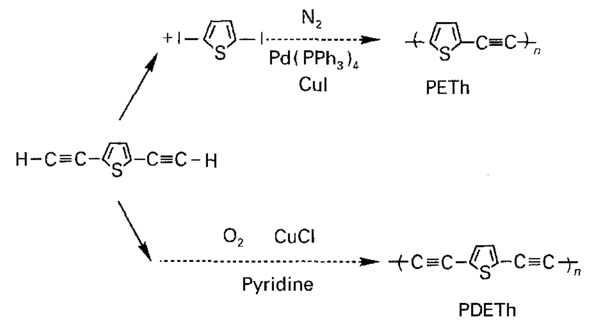

Figure 1 Schematic representation of the polymerization reaction of PETh and PDETh.

Fourier transform–infrared–attenuated total reflectance (FT–IR–ATR) spectra were obtained by means of a Philips PU 2800, by using of ZnSe crystal mounted on a SPECAC ATR device (the number of internal reflections was 25 and the incidence angle was 60°).

Differential scanning calorimetry (DSC) measurements were obtained by means of a Mettler TA 3000 apparatus under nitrogen flow. The heating rate was $10\ \mathrm{K\,min^{-1}}$. The sample weight was in the range 2.50–6.00 ± 0.05 mg.

Thermogravimetric analysis (TGA) was accomplished by a Perkin–Elmer System 7/4 thermobalance in the temperature range 20–800°C. The heating rate was $10\ \mathrm{K\,min^{-1}}$. All measurements were carried out under a nitrogen flow on samples whose weight was in the range 1.50–4.00 ± 0.05 mg.

Electrical-conductivity measurements were accomplished using a 4329A Hewlett-Packard High Resistance Meter under a test voltage of 100 V. The sample powders were compressed under an applied load of $5\ \mathrm{ton\ cm^{-2}}$ as discs with a diameter of 13 mm and an average thickness of 0.6 mm. The discs were placed in contact with two flat-plate electrodes (guarded geometry). All the measurements were taken after 1 min.

The doping experiments on powder samples, previously dried in vacuum, were carried out with iodine in saturated gas phase at various temperatures. The contact time of the doping agent with the samples was always 20 h.

3. Results and discussion

The synthesized polymers were first extracted in a soxhlet apparatus under a dinitrogen atmosphere in order to remove any low molecular weight products. The extraction was carried out first with petroleum ether and then with acetone, the last treatment being the most effective. The extraction time was 48 h during which the absorbance variation at 405 nm of the extraction solvent was followed, in order to evaluate the progress of purification. Acetone was found to be the most effective in removing low molecular weight compounds. The absorbance markedly decreased during the first 24 h, then a plateau was reached indicating that a slow but continuous release of oligomers was still going on. The extraction yield for PETh was nearly 50%, while for PDETh it was 94%. The extraction kinetics was, however, similar for the two polymers, and is shown in Fig. 2 for PETh. In this case the extracted products were identified as consisting mainly of catalyst and diethylammonium salt deriving from the polymerization solvent, which could explain the low yield of the extraction. The coloured compounds absorbing at 405 nm were shown to be monomers and oligomers slowly diffusing from the solid. These could be either species entrapped during the polymerization process or arising from a depolymerization process activated by the acetone.

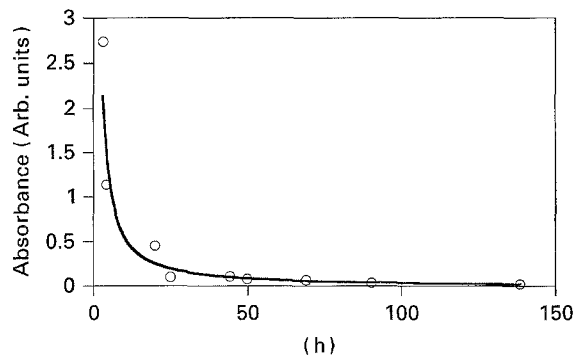

Figure 2 Variation of the 405 nm UV absorbance during soxhlet extraction of PETh in acetone.

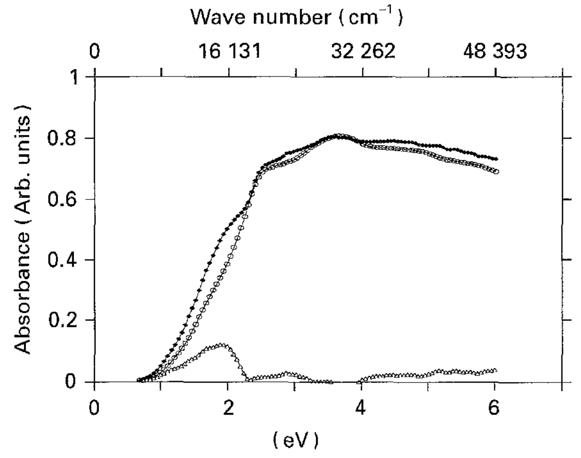

Figure 3 Optical spectra of (○) PETh and (▲) PDETh and (△) the difference spectrum PDETh-PETh.

3.1. Electronic absorption properties

Fig. 3 shows the electronic absorption spectra of PETh and PDETh. As can be seen, the two polymers have similar characteristics, showing a maximum of absorbance at about 3.6 eV and structures at 2.5 eV; in the case of PETh, a sharp shoulder appears at 1.9 eV while, in the case of PDETh, the shoulder at the same wavelength is broader. In the spectrum of PETh it is also possible to recognize a broad maximum centered around 4.8 eV. The band edge in both cases is found at about 1 eV.

Fig. 3 also shows the difference spectrum of PDETh–PETh. As can be seen, a new peak appears near 1.9 eV. A spectra deconvolution was then carried out in order to fit the experimental data with gaussian functions. The results are shown in Figs 4 and 5. In

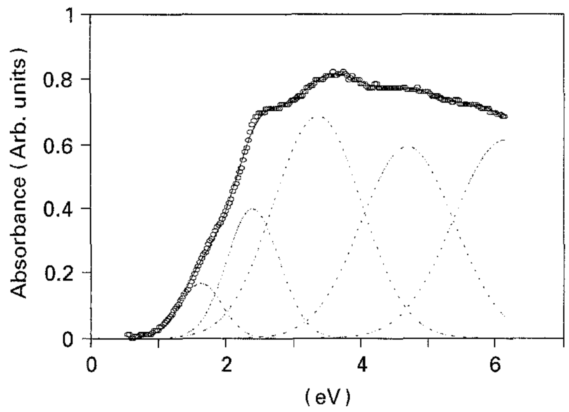

Figure 4 PETh optical spectra deconvolution: (○) experimental points (—) convolution curve, (···) deconvoluted gaussians.

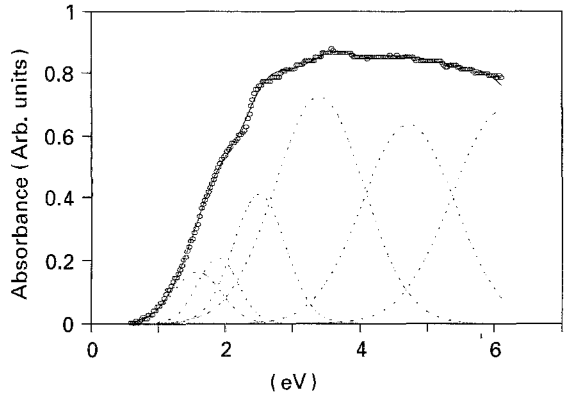

Figure 5 PDETh optical spectra deconvolution. For key, see Fig. 4.

both cases the coefficient of determination, r^2, was better than 0.999 with no evidence of significant systematic variation from the residuals analysis. It is clear that the spectrum of PDETh is indeed obtained by convoluting the five principal gaussians of the PETh spectrum and a sixth gaussian function centred at 1.9 eV, as is also evident from the difference spectrum shown in Fig. 3.

3.2. IR spectroscopical properties

The spectroscopical characteristics of PETh and PDETh in the 4000–400 cm^{-1} region, obtained by using the FT–IR–ATR technique, are shown in Fig. 6. One of the most relevant features is the absorption at 800 cm^{-1}, which can be assigned to the out-of-plane bending of the aromatic C–H. The triple bond stretching is found at 2180 cm^{-1} and, in the case of PDETh, also at 2140 cm^{-1}. This peak could be due to a larger π electron delocalization in the latter polymer, caused by the presence of the two adjacent acetylenic units in the repeating unit. Another important absorption is found at 3290 cm^{-1}, which can be attributed to the C–H stretching of the terminal–C≡C–H group. From its intensity, it is possible to obtain an approximate value of the number average molecular weight of the two polymers: PDETh = 4800 u.m.a.; PETh = 3400 u.m.a. These figures were obtained by the ratio Abs$_{799}$/Abs$_{3294}$, the two bands being due to γCH of the thiophene ring and to the νCH, respectively. It is worth mentioning that, because of the insolubility of these polymers, the determination of their molecular weights cannot be made easily; an estimate of these parameters can be extracted from the optical density of these two IR bands, but the method is not very accurate.

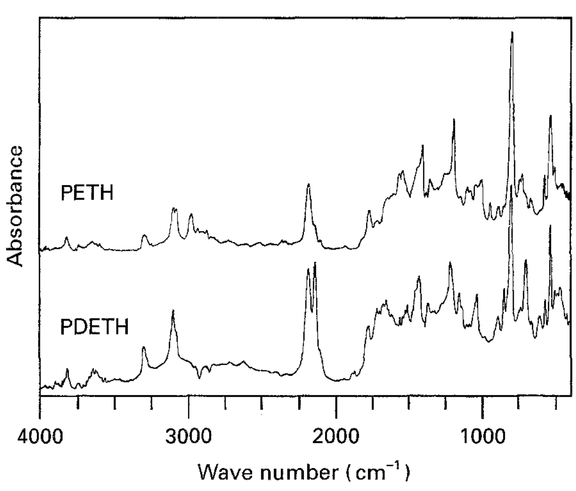

Figure 6 FT–IR–ATR spectra of PETh and PDETh powders.

The influence of the temperature on the IR characteristics of PETh and PDETh has already been discussed [7, 8]. Here we want to deepen the discussion on these effects. Fig. 7 shows the IR transmittance spectra of PETh obtained as a function of the temperature, after heating under a dinitrogen atmosphere, by means of a dispersive spectrophotometer. As may be seen, all the peaks are affected by intensity variations and broadening. In particular, the ring stretching bands in the region 1100–1600 cm^{-1} reduce to only three broad bands after heating to 350 °C. At such a temperature the triple bond absorbance at 2180 cm^{-1} also disappears (Fig. 7D). At 400 °C, all the transformations in the sample proceed further, mainly involving the thiophene hydrogens, whose band at 800 cm^{-1} is drastically reduced. From the above information it could be possible to make the hypothesis that the pheonomena occurring are cross-linking processes involving hydrogen abstraction from the thiophene rings by the triple bonds of the acetylenic units. In this way fused rings or macrocycles would be formed, making more difficult the in-plane bending of the non-reacted aromatic rings. This could explain the disappearance of the related bands at 537 and 570 cm^{-1}. The new peaks at 925, 850 and 800 cm^{-1} could be attributed to a formal disproportion reaction at high temperature. Such a reaction is well known in the case of heteroaromatic ring derivatives, the above-mentioned peaks being typical of 2-substituted thiophenes. The cross-linking processes were also indicated by the large increase in the free, delocalized spin number revealed by the EPR experiments previously reported [7].

The PDETh FT–IR–ATR spectrum, obtained after heating the powder at 250 °C, was very similar to that of PETh, only differing by the 3290 cm^{-1} band of the terminal –C≡C–H groups, which still persisted after

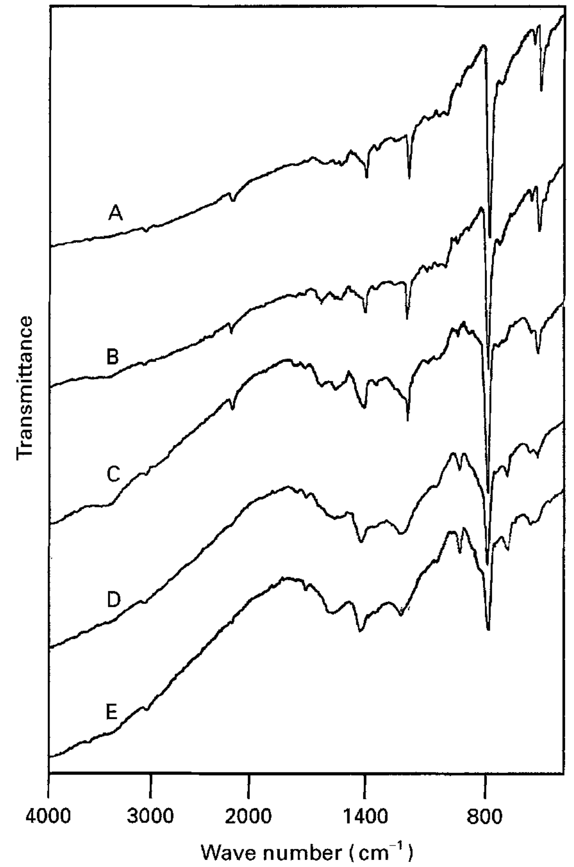

Figure 7 IR transmittance spectra of PETh obtained as a function of the temperature by means of a dispersive spectrophotometer.

the high-temperature treatment, and by the coalescence of the two peaks at 2180 and 2140 cm^{-1}, both attributable to the triple-bond stretching.

The strong similarity between the spectra of heated PETh and PDETh supports the hypothesis that the cross-linking processes are of the same nature in the two polymers. Such interpretation was also given for similar materials on the basis of ^{13}C-NMR experiments [11]. For PETh, the EPR measurements indicated an increase of the decoupled spin density for the thermally cross-linked material [8]. The higher $\Delta H_{1/2}/\Delta H_{pp}$ ratio measured for the pristine PDETh compared to that of PETh confirmed the higher conjugation present in the former polymer.

3.3. Thermal properties

The thermal properties of the two polymers have been investigated by means of TGA and DSC techniques. Fig. 8 shows the TGA results for PETh and PDETh, respectively. In both cases a good thermal resistance of the materials is revealed, mainly under a dinitrogen atmosphere. In the presence of oxygen, both polymers show a weight increase, more pronounced for PDETh. In this case the oxygen uptake reaches 12% at 245 °C. After this temperature the degradation processes start to cause a weight decrease which ends around 500 °C in oxygen, while it is much slower in nitrogen. In the case of PETh, the weight increase in oxygen does not exceed 2%. It is worth noticing that in oxygen, while at a plateau, i.e. at temperatures higher than 500 °C, PDETh retains just 2% of its initial weight, PETh retains 33%, but its weight continues to decrease in a nitrogen atmosphere.

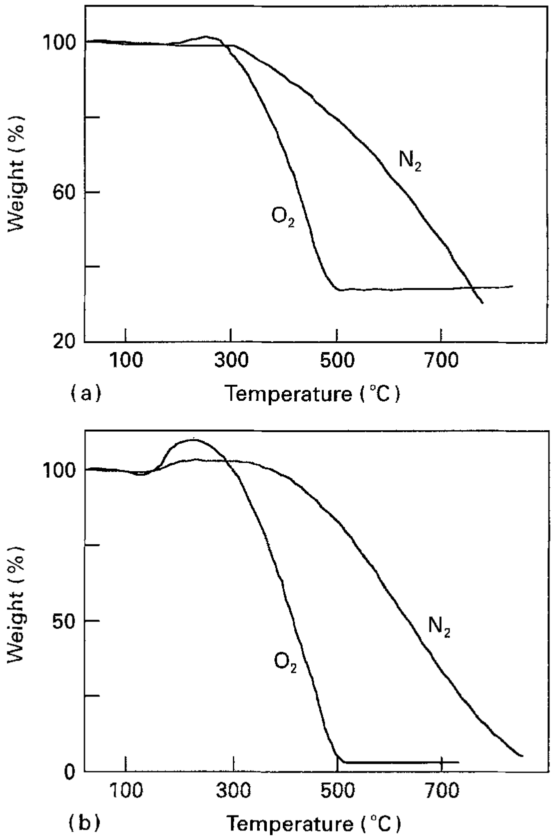

Figure 8 TGA curves of (a) PETh and (b) PDETh.

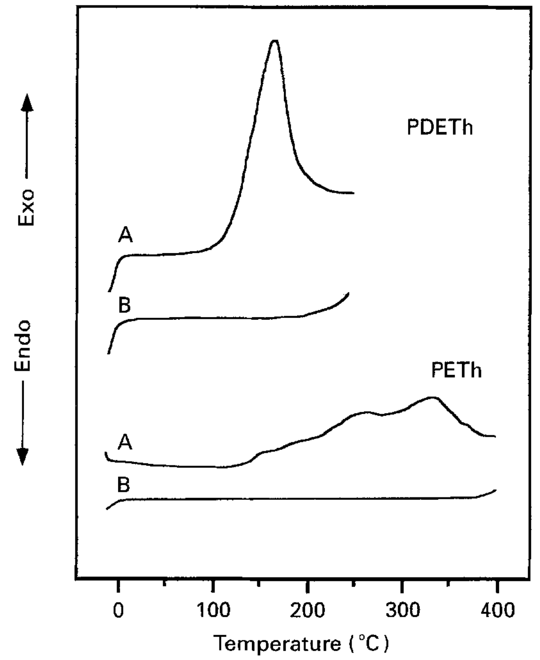

Figure 9 DSC thermogram of PETh and PDETh.

Fig. 9 shows the DSC thermograms of PETh and PDETh, respectively. In both thermograms, the A traces refer to the first run in the DSC cell, while the B traces are relative to the reheating of the materials. For both polymers, the B traces appear to be flat over all the temperature range explored. On the contrary, while for PDETh a single peak at nearly 160 °C is seen over the temperature range scanned during the first heat treatment, in the case of PETh the convolution of at least three curves appears, the first peak being found at nearly 150 °C (in this case the temperature range explored was wider). The first endothermic process revealed by the two polymers could be attributed to fusion, in agreement with the crystalline nature of these materials indicated by their X-ray diffraction spectra [7, 8]. The melting of the materials would be accompanied by cross-linking and degradation reactions, as indicated by the subsequent endothermic peaks in the PETh thermograms, as well as by the flatness of the DSC B traces and by the IR analysis results of the two polymers already discussed.

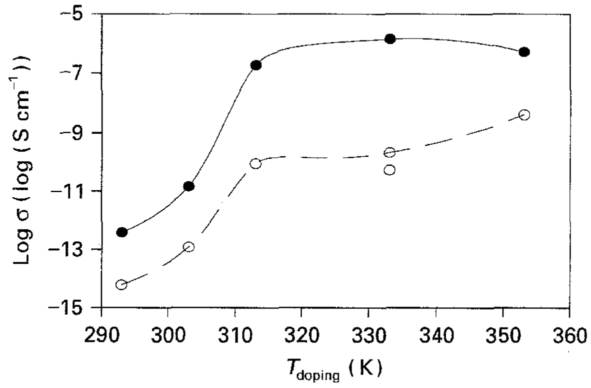

Figure 10 (○) PETh and (●) PDETh electrical conductivity variation as a function of the doping temperature.

3.4. Electrical conductivity

The larger quantity of PETh available for the electrical transport properties characterization, compared to PDETh, has conditioned the number of experiments and measurements that will be discussed here. Table I shows the electrical conductivity variation of the two pristine polymers as a function of the treatments to which they were subjected.

As may be seen, both polymers, after washing, are good insulators. In the case of PETh the removal of the reaction impurities causes a drastic reduction of the electric conductivity of nearly seven orders of magnitude. The efficiency of acetone in washing such a polymer, which has been demonstrated by the UV–VIS spectroscopical measurements already discussed (See Fig. 1), is also demonstrated by this relevant drop of electrical conductivity. The data also show that the compressed powder kept at room temperature for 1 month retained its conductivity, while heating the sample caused a σ increase of four orders of magnitude. We think that such a variation could be due to the formation of free radicals, which was pointed out by the EPR experiments.

The value of the electrical conductivity observed for PDETh after extensive washing with petroleum ether and acetone was found to be 2.5×10^{-15}S cm^{-1}. This value is very near to that measured for PETh, the difference being negligible.

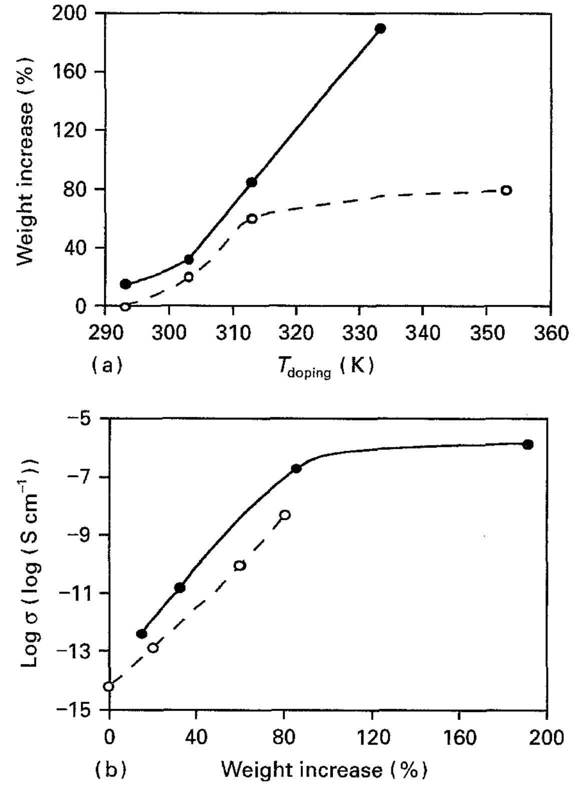

Figure 11 (a) Weight-increment of (○) PETh and (●) PDETh versus doping temperature, and (b) electrical conductivity variation of (○) PETh and (●) PDETh versus iodine uptake.

Doping our powders with iodine in the gas phase gave rise to a large variation of the transport properties of the two materials. Fig. 10 shows how σ varied as a function of the doping temperature, the conductivity, being reached by PDETh at the highest T nearly three orders of magnitude over than that of PETh.

TABLE I Electrical conductivity of pristine PETh and PDETh as a function of the treatments to which they were subjected.

Material	σ (S cm^{-1})
PETh	
Raw material after reaction	6×10^{-8}
After washing with petroleum ether	1×10^{-8}
After washing with acetone for 130 h	6×10^{-15}
Compressed powder after one month at RT	6×10^{-15}
Compressed powder heated at $T = 400$ °C	3×10^{-11}
PDETh	
After washing with petroleum ether and acetone	2.5×10^{-15}

In both cases the temperature favours the doping of the polymers either by a mass effect of the dopant (its vapour pressure increases with T) or by its easier diffusion within the materials (or by both).

A noticeable difference is found between the two polymers if the iodine uptake is followed as a function of the doping temperature, i.e. of the vapour pressure of iodine, as may be seen in Fig. 11a. While the weight of PDETh continues to increase markedly in the temperature range considered, the uptake of iodine by PETh appears to be much slower, with a tendency to level off. In contrast with the above-mentioned behaviour is the conductivity trend as a function of the weight increase. Fig. 11b illustrates that while PDETh continues to increase in weight upon doping, σ levels

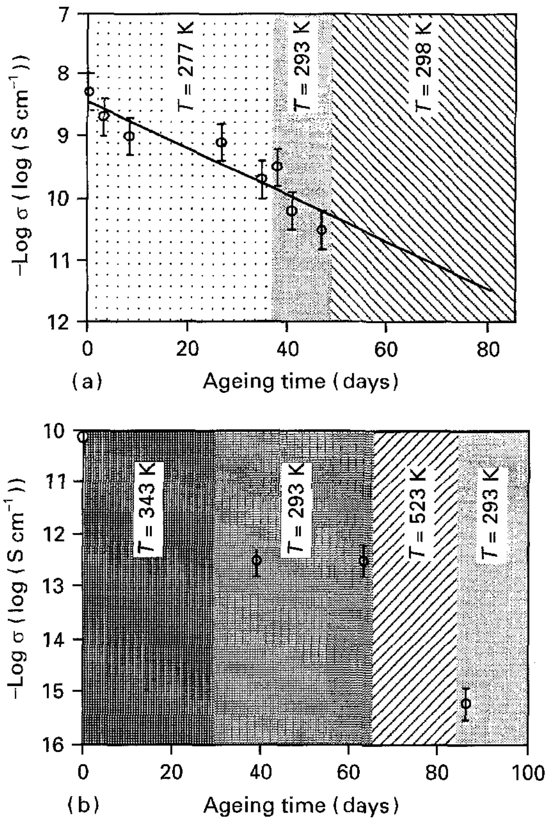

Figure 12 Electrical conductivity variation with ageing for PETh (a) doped at 353 K and kept under nitrogen, and (b) doped at 333 K and kept in air.

up to a value of 10^{-6} S cm^{-1}. The PETh polymer, on the contrary, does not show such a σ levelling, reaching the maximum of conductivity at nearly 80% of its weight increment. IR evidence obtained in our laboratory on the doped materials permits confirmation that iodine favours cross-linking and degradation reactions, similar to those thermally induced, which were previously discussed.

Finally we have investigated the ageing behaviour of the doped PETh. Fig. 12a shows how the polymer, doped at 353 K, continuously loses its conductivity over a period of 80 days. During such a time the doped polymer was kept under a nitrogen atmosphere while the temperature was varied in the range 277–298 K, as is illustrated by the sectorization of Fig. 12. In such a narrow temperature range, no variation was found in the rate of decrease of the electrical conductivity of the material, which varied by nearly three orders of magnitude over 80 days.

The change was much faster when the polymer, doped at 333 K (i.e. in a milder environment), was kept under more severe temperature conditions, as appears from Fig. 12b. In this case air was substituted to dinitrogen. The sample was first kept for 30 h at 343 K, so losing nearly two orders of magnitude of σ. It was then maintained for 35 h at 293 K, retaining its electrical conductivity over this period, and then for 20 h at 525 K. After that the temperature was lowered again at 293 K, the dedoping process resulting at this point being practically complete.

4. Conclusion

The electronic absorption spectra of PETh and PDETh have been obtained and it was shown that the PDETh spectrum is obtained by convoluting the five principal gaussians of the PETh spectrum and a sixth gaussian function centred at 1.9 eV. Also the IR characteristics of the two polymers have been investigated and a strong similarity between the spectra of the heated PETh and PDETh was found. The DSC and TGA data showed that at temperature higher than nearly 150–160 °C, which could be related to the melting of the material, cross-linking and degradation processes intervene, in agreement with the IR finding. Doping of the PETh and PDETh powders with iodine in the gas phase gave rise to a large variation of the transport properties of the two materials, PDETh reaching conductivity values higher than PETh. However, ageing experiments carried out on PETh samples showed the instability of such a modification of the electrical properties of this polymer.

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