Thermochimica Acta, 149 (1989) 101–109
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

PHYSICO-CHEMICAL CHARACTERIZATION OF POLY(*p*-PHENYLENE SULPHIDE) SINGLE CRYSTALS

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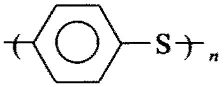
(Received 11 November 1988)

ABSTRACT

Poly(*p*-phenylene sulphide) has been crystallized from dilute solutions of diphenyl ether in the temperature range 151–212 °C. The effect of the crystallization conditions has been investigated by IR spectroscopy, showing the importance of air in inducing dibenzothiophenic structures in the polymer. The melting behaviour of the crystals has been studied as well as the density characteristics as a function of the crystallization temperature. Substantially high values of the density of the crystallized samples have been found ($\rho = 1.42–1.44$ g cm^{-1}) which may with difficulty fit the theoretical expectations based on the crystal structure of this polymer that is commonly accepted in the literature.

INTRODUCTION

Recently scientific interest in poly(*p*-phenylene sulphide) (PPS) has



grown remarkably owing to its electrical properties upon doping with strong electron acceptors, which allow it to become highly conducting [1–5]. This macromolecule, however, has found success basically as a high-performance polymer [6,7], stable at high temperatures and with high strength properties. In addition it is fusible, soluble and melt processable. All these properties make PPS very attractive for technological applications in new materials such as thermoplastic composites.

Beside such a remarkable interest from the technological point of view, the scientific attention payed to PPS is also determined by the fact that, being soluble and fusible, its physico-chemical properties can be well characterized, thus allowing precise correlations between structure and properties.

The crystal structure of the material, worked out in 1971 by Tabor et al. [8] on melt-crystallized, stretched films of PPS, has recently been the subject

0040-6031/89/$03.50

of some debate in the scientific community since a new proposal was put forward by Garbarczyk [9]. On the other hand all the physical investigations of this polymer have been done on melt crystallized specimens. Although in a note [10], Padden and Lovinger reported that they precipitated single crystals and embryonic spherulites of PPS from dilute solutions in α-chloronaphthalene, no more details of such experiments have appeared in the literature during subsequent years.

For this reason, having in mind the object of establishing detailed correlations between structure/morphology characteristics and electrical conduction properties, we began to study the crystallization of PPS from dilute solutions in diphenyl ether [11–13]. In the mean time, confuting the Garbarczyk paper [9], Lovinger et al. [14] have very recently published the results of their crystallization experiments from dilute solutions of α-chloronaphthalene [10], regarding the crystallographic characteristics of PPS.

EXPERIMENTAL

Ryton-V1 powder from Phillips Petroleum Co. was used for our crystallization experiments. The number average molecular weight of the polymer was $\langle M_n \rangle = 11\,000–12\,000$. PPS powder was first treated in a Soxhlet apparatus with tetrahydrofuran to remove oligomeric fractions and then dissolved, under nitrogen atmosphere, in diphenyl ether ($c = 0.1\%$ w/w) near to the boiling temperature of the solvent ($T_b = 257.9\,°C$). The polymer was then crystallized in a laboratory-designed dry thermostat made of an electrically heated aluminium cylindrical block giving a constant crystallization temperature (T_c) within $\pm\,0.5\,°C$. The crystallization experiments, in the temperature range 151°C–212°C, were also carried out avoiding contact with air and keeping the solutions under a nitrogen atmosphere. The duration of these trials varied from 24 to 168 h, proportionally to the T_c. The precipitated materials, filtered at T_c, were then washed with ethyl alcohol in order to replace the solvent used for crystallizing with a more volatile one to make in vacuo drying of the crystals easier.

The IR analysis was accomplished by means of an Hitachi 270-30 spectrophotometer on samples dispersed in KBr disks.

A Mettler TA-3000 differential scanning calorimeter (DSC) was used for the thermal analysis on PPS specimens which were sealed in aluminum pans. The weight of the specimens ranged between 2.50 and 6.00 ± 0.05 mg. The heating rate was 10 K min^{-1} in all the measurements.

Density measurements were carried out by means of the flotation method and by means of the density gradient column method by using the CCl_4–EtOH solvent pair.

Determination of the apparent dissolution temperature (T_d) was carried out by observing the clearing point of the polymer suspension during heating in a Buchi 512 apparatus.

RESULTS AND DISCUSSION

As has already been shown [12], PPS crystallized from dilute solutions of diphenyl ether shows the morphology of small, needle-shaped, lamellar crystals, with one axis, parallel to the basal plane of the lamella, much more developed than the others. The same morphological features are in evidence when the crystals are grown from α-chloronaphthalene solutions [14] (the results of the morphological study carried out on our crystals by means of a transmission electron microscopy technique will be discussed extensively in a forthcoming paper).

The critical temperature conditions in which the crystallization experiments must be carried out led us to verify whether any chemical alteration of the polymer backbone could occur, depending on the presence of air in the crystallization vessel. Figure 1 shows the IR spectra recorded from PPS both in its untreated state and crystallized from diphenyl ether solutions in air and in nitrogen atmosphere ($T_c = 211.8\,^\circ$C). As may easily be recognized, the main differences concern the three lines at 750, 875 and 1240 cm^{-1} which appear when the polymer is crystallized in the presence of air. The absorbances could be attributed to the formation of dibenzothiophene sulphide structures, by comparison with the IR spectrum of poly(dibenzothiophene sulphide) [15]. Such evidence clearly indicates that much care has to be taken in controlling the crystallization conditions as far as air is concerned, owing to the high T_c and the fairly long time required to complete the experiment. Analysis of the IR spectra also reveals the high crystallinity of the precipitated materials, as shown [16] by the pronounced intensity ratios A_{1392}/A_{1580} and A_{970}/A_{952} and by the sharpness of the band centred at 820 cm^{-1}.

Such evidence was confirmed by the density measurements, as shown in Fig. 2. The density values obtained were nearly constant over the entire range of the T_c explored and particularly high ($\rho = 1.42$–1.44 g cm^{-1}) if compared with that predicted crystallographically on the basis of the Tabor structure [8] which gives nearly the same figure. For the virgin resin, unannealed, Brady [16] reports a value of $\rho = 1.32$–1.36 g cm^{-1}, and for the annealed one $\rho = 1.36$–1.40 g cm^{-1}. The high density measured would imply a very reduced amorphous region on the top of the lamellar crystals, which would be in agreement with the finding that the PPS chains are folded just once [13], and would have particular relevance in determining the electrical properties of the material (which will be reported elsewhere [17]). In any case our density data indicate the need for a deeper investigation of the crystal structure of PPS. The results of such a study, which is being carried out in our laboratory, will be discussed in a forthcoming paper [18].

The thermal properties of PPS crystallized from the glassy state and from the melt have been studied extensively by Cheng et al. [19], while the kinetics of crystallization from the same physical states were investigated by Lovinger

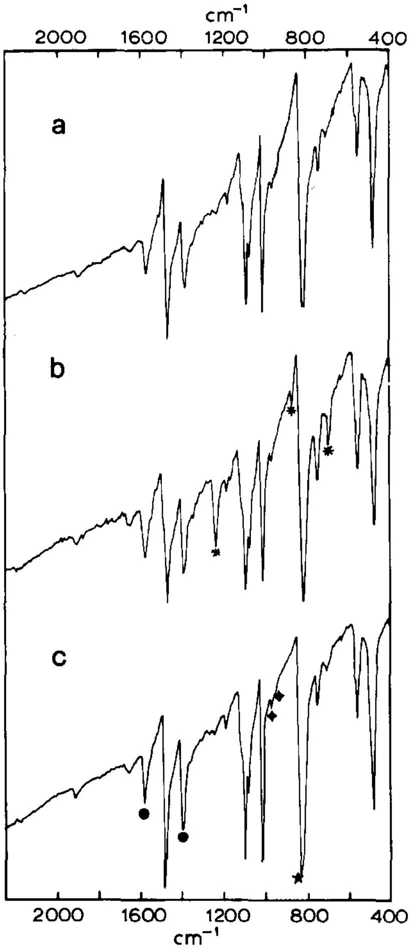


Fig. 1. IR spectra of (a) virgin PPS, (b) PPS crystallized from solution in presence of air and (c) PPS crystallised from solution under a nitrogen atmosphere.

et al. [20] and Lopez and Wilkes [21]. Although the small crystal size of our precipitated materials does not allow an easy analysis of their thermal properties, the DSC measurements carried out as a function of T_c showed that the melting traces are characterized by the two melting peaks already found by Cheng [19]. Figure 3 shows the DSC thermograms of two samples crystallized at 151.0 °C and 211.8 °C. As may be seen, the low temperature melting peak, observable in the melting trace of the sample crystallized at 151.0 °C, is present just as a shoulder in the sample precipitated at 211.8 °C. Figure 4 shows the dependence of the melting temperature of PPS upon T_c and Fig. 5 the relationship between T_c and the total enthalpy of fusion, due to both the melting peaks. It can be seen that in the higher supercooling region T_m does not vary for either of the melting peaks, whereas in the lower supercooling region an increase is observed in T_m with the above-mentioned

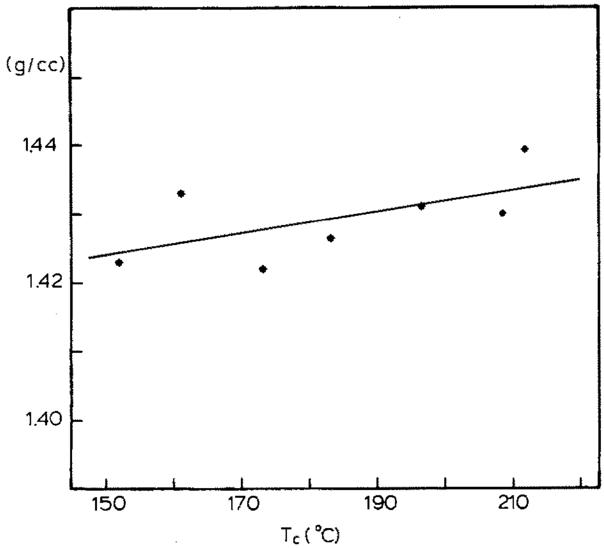


Fig. 2. Dependence of density of PPS crystallized from solution upon the crystallization temperature.

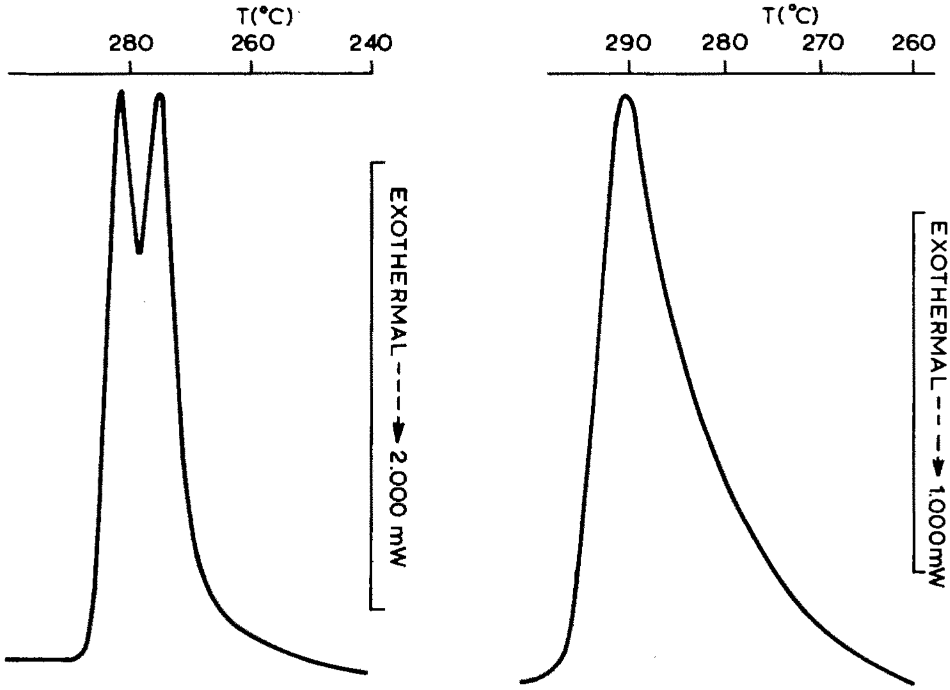


Fig. 3. DSC melting traces of PPS crystallized from solution at $T_c = 151.0\,°C$ (left) and at $T_c = 211.8\,°C$ (right).

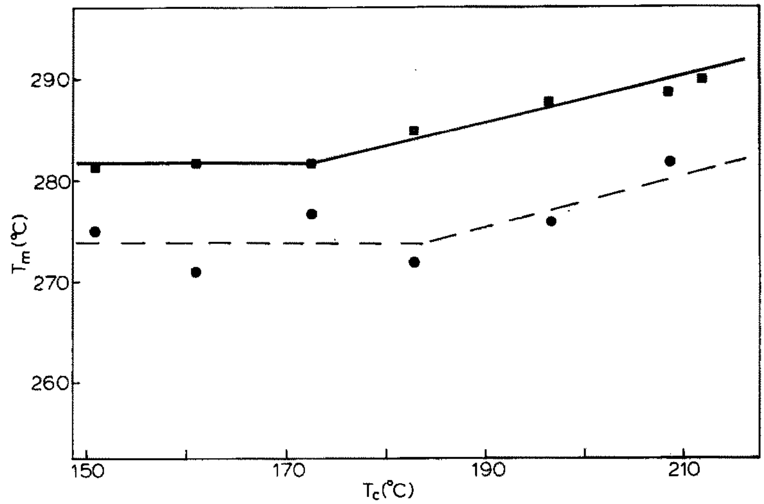


Fig. 4. Dependence of the melting temperature of PPS single crystals upon T_c. The trend of the two peaks is recorded.

gradual disappearance of the lower melting peak. Also, the total enthalpy of fusion, i.e. the sum of the contributions corresponding to the higher melting peak and the lower melting peak, seems to exhibit a slightly increasing trend with T_c, despite the notable uncertainty in the experimental data. The heat of fusion, measured at $T_c = 211.8\,°C$, is 61.5 J g^{-1}, which would indicate a

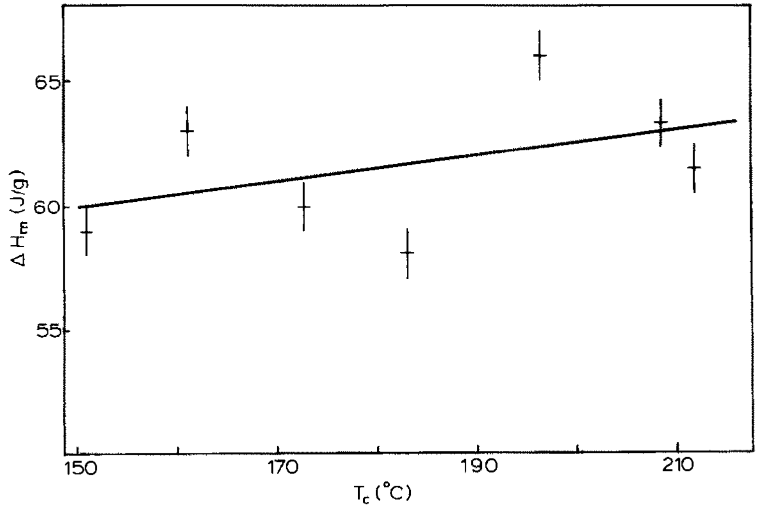


Fig. 5. Dependence of the heat of fusion of PPS single crystals upon T_c. The enthalpy values recorded represent the integral heat of the two melting peaks.

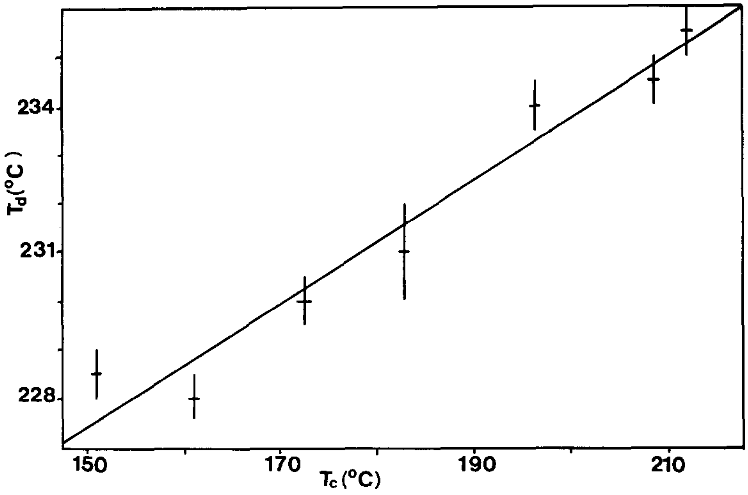


Fig. 6. Dependence of the dissolution temperature of PPS single crystals obtained from solution upon the crystallization temperature.

77% crystallinity for such a sample, assuming the correctness of the heat of fusion of the 100% crystalline PPS given by Brady [16]. Such a result would be in contrast to our density measurements, which yield figures very close to the theoretical crystallographic value given by Tabor et al. [8]. Moreover, the DSC traces obtained from PPS samples which had been crystallized at $T_c = 211.8\,°\mathrm{C}$ gave evidence of a glass transition at $T_g = 58.9\,°\mathrm{C}$, although this was quite difficult to detect, with a $\Delta C_p = 0.044$ J $(\mathrm{gK})^{-1}$. This value, too small to be considered completely reliable and far from the experimental errors would, according to Cheng et al. [19], suggest a very reduced "rigid amorphous fraction" $[f_r - W^c(T)]$, where $f_r = 1 - [\Delta C_p(\mathrm{m})/\Delta C_p(\mathrm{a})]$ and $W^c = \Delta H_f(\mathrm{m})/\Delta H_f$, $\Delta C_p(\mathrm{m})$ being the increase in the heat capacity of semicrystalline PPS at $T = T_g$; $\Delta C_p(\mathrm{a})$ is the heat capacity increase of 100% amorphous PPS; ΔH_f is the heat of fusion of 100% crystalline PPS; and $\Delta H_f(\mathrm{m})$ is the heat of fusion of semicrystalline PPS. In our case $[f_r - W^c(T)] = 7\%$, a value which, in any case, would indicate a high degree of perfection of the crystals obtained. A more detailed study on the thermal properties of our solution-grown crystals of PPS will be reported elsewhere [22].

The crystallized material was also analysed for the dependence of dissolution temperature (T_d) of the crystals upon T_c. Figure 6 shows the results of such an experiment, which indicates an increase of T_d with T_c, as expected if the packing stability of the crystals increases. However, in this case a contribution to such a rise of T_d could also be due to cross-linking processes which could to some extent have occurred through the high T_c explored, even though the crystallization experiments were accomplished in an inert atmosphere.

CONCLUSIONS

Some of the physico-chemical characteristics of PPS crystallized from dilute solutions of diphenyl ether have been assessed as a function of the crystallization temperature. The IR analysis has shown the effect of air on the variation of the chemical characteristics of PPS during crystallization, by induction of thiophenic structures. Crystal density measurements and calorimetric properties have also been investigated and discussed in relation to the crystallographic data present in the literature, which may only with difficulty be fitted based on our findings. In fact, the experimental values obtained for the density of our solution-grown crystals were in the range $\rho = 1.42\text{–}1.44$ g cm^{-1}, figures too high in comparison with the theoretical ones predicted by Tabor [8].

ACKNOWLEDGEMENTS

We are grateful to Prof. V. Crescenzi for many helpful discussions. This research was supported by CNR, "Progetto Finalizzato Chimica Fine e Secondaria I".

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