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THERMAL PROPERTIES OF POLY(*p*-PHENYLENE SULPHIDE) SINGLE CRYSTALS

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ABSTRACT

The thermal properties of poly(*p*-phenylene sulphide) crystallized from dilute solutions have been investigated by means of differential scanning calorimetry. The effect of the heating rate on the melting temperature was analysed as well as the dependence of the thermal properties after fusion of the crystals obtained at different crystallization temperatures. A variation of the crystallization temperature after fusion was also observed for the different crystals. Doping the polymer with Lewis acids substantially modified the thermal traces, with the disappearance of the low temperature melting peak.

INTRODUCTION

Poly(*p*-phenylene sulphide) (PPS) is a macromolecule with very attractive technological properties [1–4]: high strength, high thermal stability, solubility, fusibility, i.e. being easily processed, as well as having the interesting property of becoming electrically conductive when doped with electron-acceptor molecules. All of these characteristics render PPS suitable for an attempted correlation of its structural and physical properties with the electrical conductivity. Thus, single crystals of PPS were obtained from dilute solutions [5–7], the most precise correlations being possible for the crystalline state. PPS showed a lamellar, needle-shaped morphology [6–8] with the macromolecular chain axis perpendicular to the basal plane of the lamellae. The physico-chemical characteristics of these materials were studied as a function of the crystallization temperature (T_c) [6,7]. The temperature of melting and the heat of fusion of the crystals were also investigated [7]. The thermal properties of PPS crystallized from the glassy and molten states have already been studied in depth by Cheng, Wu and Wunderlich [9], who identified the two melting peaks which are characteristic of the material obtained by crystallization from solution [7]. These authors demonstrated the presence of a "rigid amorphous fraction" above the glass transition which, in contrast, was barely detectable in our solution-grown crystals. The

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present paper concentrates on the characterization of the thermal properties of single crystals of PPS, in particular their melting behaviour.

EXPERIMENTAL

The pure PPS polymer used was a Ryton-V1 powder from Philips Petroleum Co., with an average molecular weight $\langle M_n \rangle$ of 11 000–12 000. The details of the crystallization experiments have been described previously [6,7]. The single crystals used for the differential scanning calorimetry (DSC) investigation were sealed in aluminium pans. The sample weights were in the range 2.50–6.00 mg ± 0.05 mg. The thermal measurements were all accomplished by using a Mettler TA-3000 DSC apparatus. The instrument was calibrated for heat flow and temperature according to the standard procedures suggested by Mettler. The temperature range explored was from -40 to 320 °C. The heating rate normally used was 10 K min^{-1} and was varied from 5 to 30 K min^{-1} in order to study the melting behaviour of our samples. Non-isothermal crystallization experiments were accomplished at the constant cooling rate of 10 K min^{-1} by direct cooling from the melt of samples previously held for 2 min at 320 °C. All the measurements were made under nitrogen flow. Evaluation of the DSC traces for melting and glass transition behaviour was achieved using the built-in algorithms of the apparatus.

RESULTS AND DISCUSSION

As has already been shown in a previous paper [7], the melting traces of PPS single crystals grown from dilute solutions are characterized by two melting peaks. The dependence of the melting temperature and of the heat of fusion on the crystallization temperature (T_c) have been discussed in the above-mentioned references. The relative height of the two peaks, i.e. the enthalpy of melting due to the low temperature peak (ΔH_m^L) compared with that due to the high temperature one (ΔH_m^H), is a function of the crystallization temperature. Figure 1 shows such a dependence. As can be seen, the enthalpy fraction relative to the low temperature melting peak ΔH_m^L decreases with increasing T_c. It must be emphasized that the small size of the crystals represents an obstacle to the accuracy of the calorimetric measurements. However, the temperature differences between the two peaks are such that they may be attributed to physical causes. In order to study the melting behaviour, different heating rates have also been used and the results are given in Fig. 2, which shows the melting traces of samples crystallized at $T_c = 172.6$ °C, obtained at heating rates in the range 5–30 K min^{-1}. As can be seen, the melting traces are strongly influenced by the heating rate with

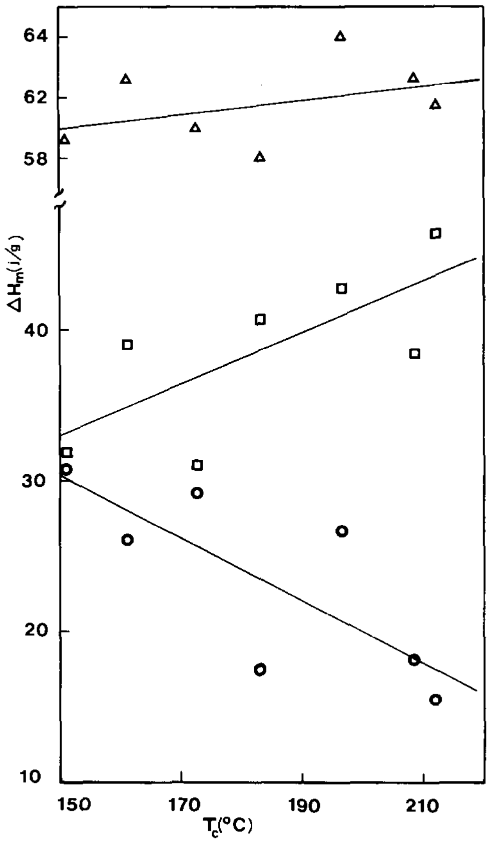

Fig. 1. Dependence of the enthalpy of melting due to the low temperature peak (○ = ΔH_m^L), of that due to the high temperature peak (□ = ΔH_m^H) and of the total enthalpy of melting of PPS crystallized from dilute solutions of diphenyl ether upon the temperature of crystallization.

the low temperature melting peak decreasing as the higher temperature one increases.

Figure 3 shows that the T_m of the two melting peaks decreases with increasing heating rate. In Fig. 4 it can be seen that, although the total enthalpy of fusion ΔH_m^T stays constant as the heating rate is varied, ΔH_m^L decreases and ΔH_m^H complementarily increases. This is in contrast with the data of Cheng and co-workers [9] obtained from PPS crystallized from the melt, in which the lower melting crystallinity increased with increasing heating rate, while the total crystallinity remained constant. Such a difference could be interpreted in terms of a prevailing reorganization process which takes place when the crystals are grown near the melting point, even from the more entropic molten state; when the crystals are formed in solution, recrystallization would occur on heating. However, Cheng and

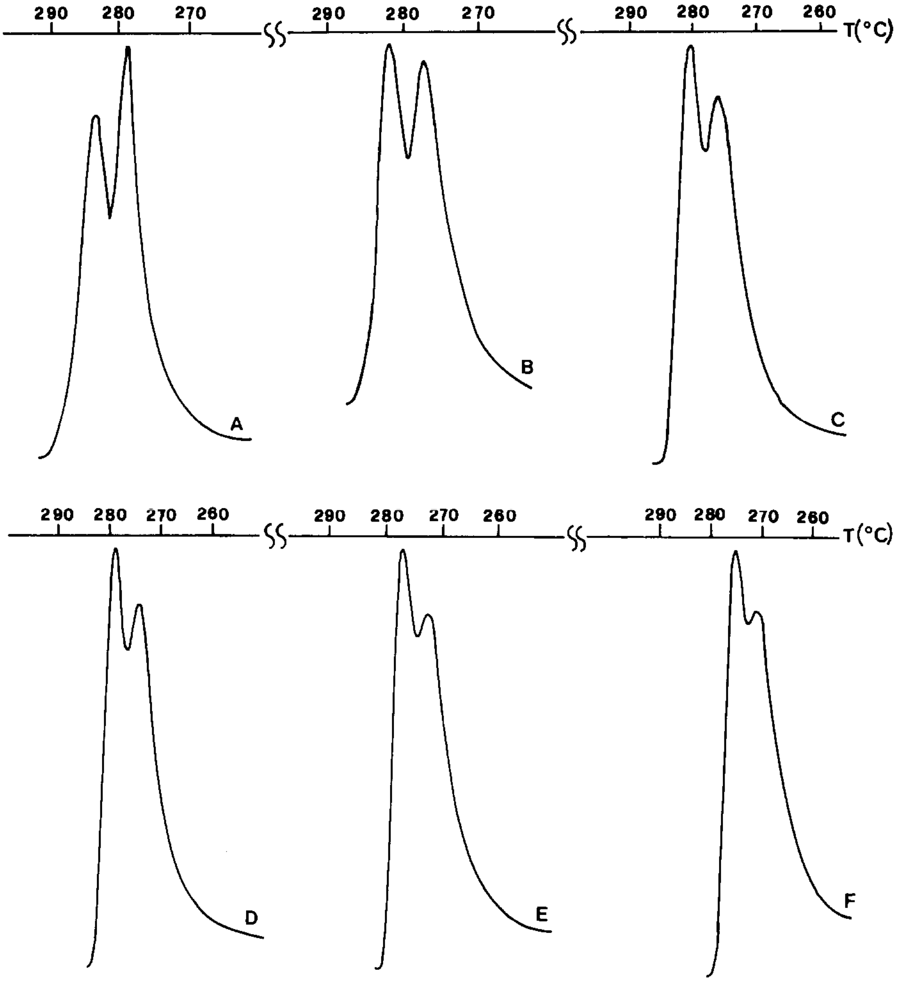

Fig. 2. DSC melting traces of PPS samples crystallized from solution at $T_c = 172.6\,°C$, obtained at different heating rates: A = 5 K min^{-1}; B = 10 K min^{-1}; C = 15 K min^{-1}; D = 20 K min^{-1}; E = 25 K min^{-1}; and F = 30 K min^{-1}.

co-workers [9] interpreted their results in terms of recrystallization for crystals grown below 503.2 K, and reorganization when $T_c > 503.2$ K.

We have also attempted to determine the equilibrium melting temperature of PPS by means of the Hoffman and Weeks method [10]. Figure 5 shows the Hoffman–Weeks plot obtained by extrapolating to the line $T_m = T_c$ the data for PPS crystallized from solution and from the melt, although the difficulty in obtaining crystals at low ΔT of supercooling may give uncertain results [9]. The resulting $T_m^{\ominus}$ of 303 °C is in good agreement with the results of Lovinger et al. [11] and of Lòpez and Wilkes [12]. By using the data of the

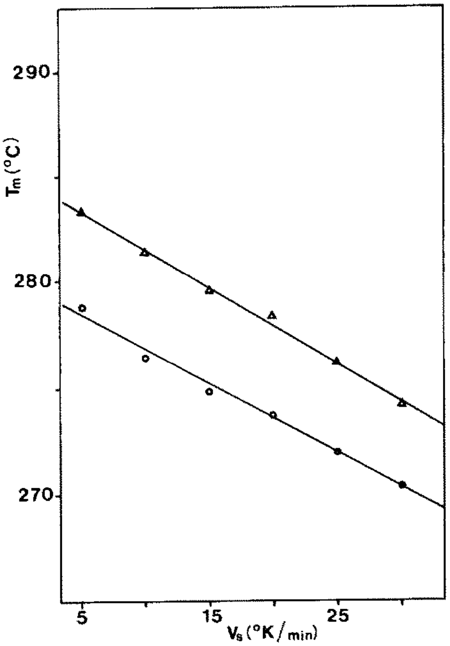

Fig. 3. Dependence upon the heating rate of the T_m corresponding to the two peaks in the melting traces of PPS crystallized from solution at $T_c = 172.6\,°C$ (○ low temperature peak; △ high temperature peak).

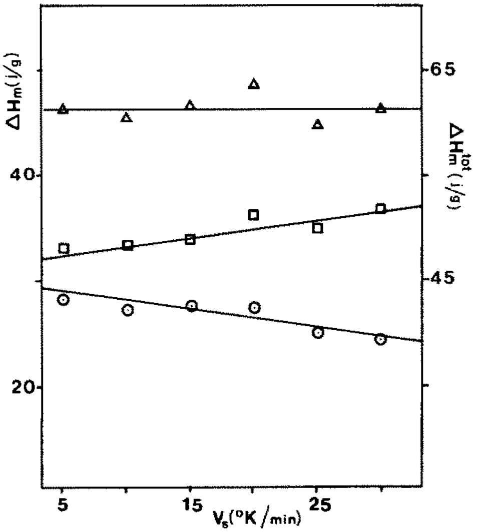

Fig. 4. Relationship between heat of fusion ΔH_m and heating rate for PPS samples crystallized from solution at $T_c = 172.6\,°C$. (⊙, ΔH_m^L; □, ΔH_m^H; and △, ΔH_m due to both the low and high temperature peaks).

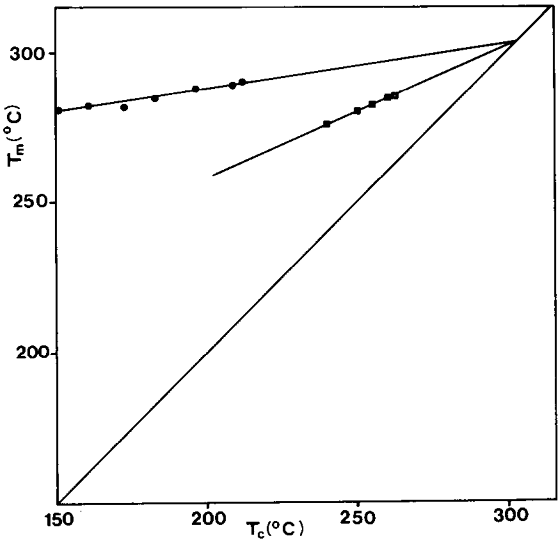

Fig. 5. Hoffman–Weeks plot for PPS samples crystallized from solution (●) and from the molten state (■).

latter authors [12], who correlate $T_m^{\ominus}$ with molecular weight $\langle M_w \rangle$, it is possible to derive a $\langle M_w \rangle$ of 17000 for our PPS samples.

The melting behaviour of the PPS crystallized from solution has also been investigated after fusion, by reheating the samples crystallized from the melt. Figure 6 shows the dependence of the temperature of melting and of the heat of fusion after fusion and recrystallization upon the temperature of the first crystallization from solution. A decrease has been observed in both T_m and ΔH_m with increasing T_c from solution, which may indicate that samples treated at higher temperatures are more difficult to recrystallize. This was also shown by the crystallization temperature from the melt (T_c^f). These data were obtained in non-isothermal crystallization experiments carried out at constant cooling rate (10 K min^{-1}) on samples precipitated from solution at different values of T_c. Figure 7 shows the results of such an experiment. As can be seen, a decrease in the T_c^f is observed when the T_c from solution rises. The data of Figs. 6 and 7 could be interpreted by assuming that the higher the T_c the higher the number of defects introduced into the chain by a mechanism of formation of dibenzothiophenic structures and of interchain cross-linking. This is also in agreement with the investigation into the dependence of the dissolution temperature of such crystals on T_c, already discussed in a previous paper [7]. In fact, in that case the dissolution temperature of the crystallized PPS was shown to increase with increasing T_c.

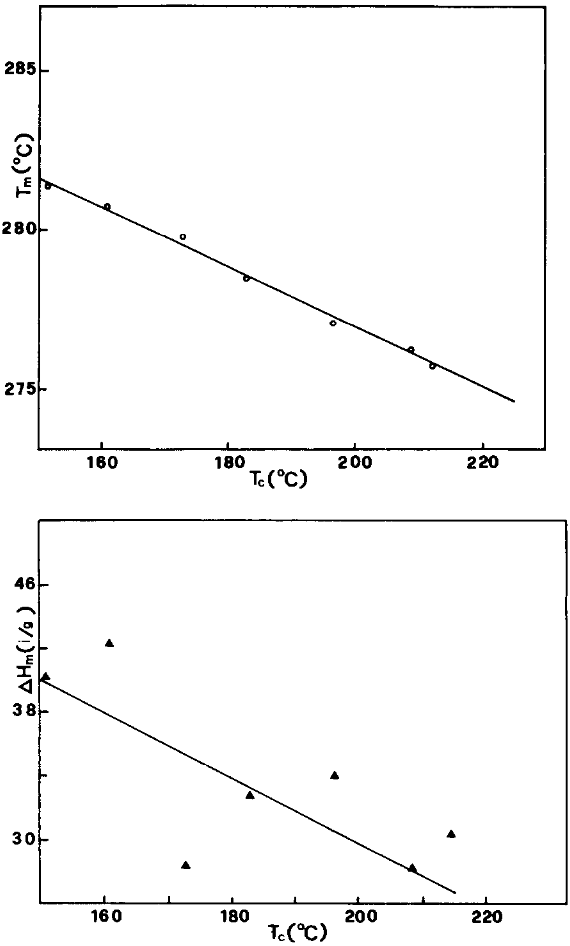

Fig. 6. Dependence upon the temperature of crystallization from solution (T_c) of the temperature of melting (T_m) and of the enthalpy of fusion ($\Delta H_m'$) after fusion and recrystallization from the melt of PPS samples.

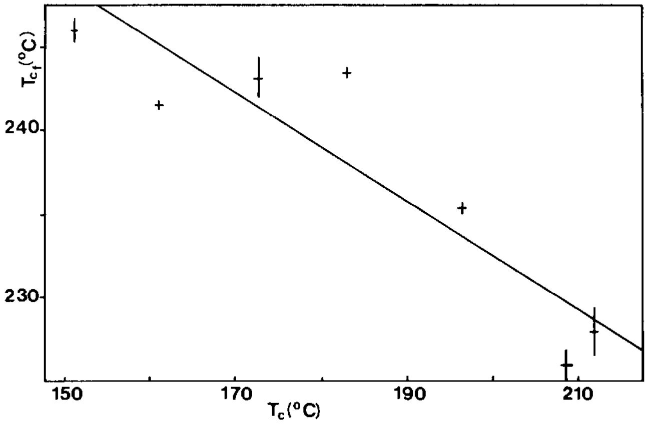

Fig. 7. Relationship between the temperature of crystallization from the melt and the T_c from solution in non-isothermal crystallization experiments of PPS crystallized from solution and then from the melt.

CONCLUSIONS

The melting behaviour of PPS crystallized from a dilute solution of diphenyl ether has been investigated by DSC as a function of the heating rate. The two melting peaks observed have been explained in terms of recrystallization rather than of reorganization processes. A value of the equilibrium melting temperature $T_m^\ominus = 303°C$ has been derived by the Hoffman–Weeks method, using data relative to samples crystallized from solution and from the molten state. The melting behaviour of the PPS precipitated from solution, which was melted and then recrystallized, has also been investigated, as well as the dependence of the crystallization temperature from the melt of these samples upon the temperature of crystallization from solution. The data have been interpreted in terms of chemical modifications induced by the high temperature on the PPS chains, i.e. formation of dibenzothiophenic structures and of interchain cross-linking.

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