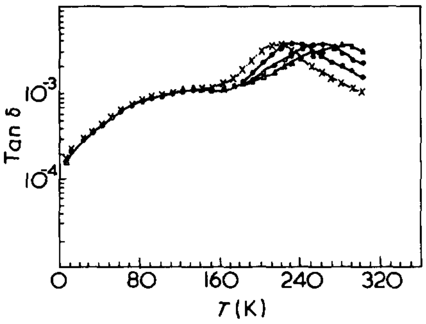

Figure 3 Dielectric loss in polyethersulphone, showing a β region above 170K and a γ region below 170K. A, 100 kHz; B, 10 kHz; C, 1 kHz; D, 0.1 kHz

cess in the polysulphones is given in the following paragraph.

The nature of the second (low temperature) transition around T_{g2} 170K is not known in great detail; but in having two T_g's the polysulphones resemble graft and block copolymers. They behave as though they were a two phase mixture, in which one phase undergoes a transition roung T_{g1} and the other phase undergoes a transition around T_{g2}.

The position of T_{g2} falls within the region of the γ process, and two things then become apparent: the fact that the height of the γ region increases with increasing crystallinity would suggest that the relaxation itself takes place in the crystalline phase. Secondly the location of the γ region in the neighbourhood of T_{g2} suggests a possible connection between the two. In fact, the author has proposed a hypothesis to account for the general occurrence of multiple relaxations in any organic solid (polymeric or monomeric)[3]. According to this hypothesis, the lower transition (around T_{g2}) leads to an apparent two phase nature of the polysulphones. The two 'phases' then provide two environments in which the β and the γ losses occur. The effect of crystallinity on the γ region then suggests a possible connection among the lower phase transitions, the presence of a small degree of crystallinity in the polymer and the occurrence of the γ process in the crystalline phase.

Future work should investigate the detailed nature of the lower transitions and the possible connections cited above.

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Comments on Paper 'Residual solvent removal and n-hexane sorption in blends of atactic and isotactic polystyrene'

(D. L. Faulkner, H. B. Hopfenberg and V. T. Stannett *Polymer* 1977, 18, 1130–1136)

In a recent paper, Faulkner *et al.*[1] presented an alternative mechanism for the sorption of organic vapours by atactic and isotactic polystyrene (APS and IPS, respectively). In this Letter we should like to make some comments on their explanation in view of the interpretation in our paper[2].

Faulkner *et al.*[1] observed a maximum in the sorption kinetics of n-hexane in unannealed samples of both IPS and APS. A final weight lower than the initial sample weight was found in some cases. The absorption of n-hexane was generally much slower in IPS compared with APS (unannealed and annealed samples). The maxima were explained by a liberation of trapped casting solvent as a consequence of the absorption of n-hexane. The presence and loss of the trapped solvent was proved by gravimetric and neutron activation analysis. After desorption, the resorption kinetics of these dried samples do not show a maximum. Based on these observations, the authors proposed an alternative interpretation of our observations with IPS.

Different experimental facts, however, allow us to conclude that the desorption (maximum in the kinetics) in our work is only due to crystallization and not to any rejection of trapped solvent. Some of these facts were not reported in our publication because they were considered to be of secondary importance in our study.

The samples used in our work were free of solvent. The polymer was synthesized in n-heptane and purified several times by dissolving in *o*-dichlorobenzene followed by reprecipitation in methanol. The atactic material was extracted by refluxing in butanone-2 for several hours. The purified polymer was then dried under vacuum at 80°C for several weeks. Films for the absorption measurements were prepared by compression moulding at 260°C, well above the melting point of IPS. The resulting films were amorphous as deduced from X-ray, d.s.c. and density measurements. After this treatment, no traces of solvent could be detected. Consequently, rejection of residual solvent during absorption of organic vapours (acetone or dichloromethane) is to be excluded as an explanation of the maximum in the absorption kinetics. Furthermore, starting with samples of IPS and APS prepared in this manner, complete superposition of the absorption curves is observed until IPS crystallizes. At every temperature, a critical vapour pressure is needed to reach a minimum

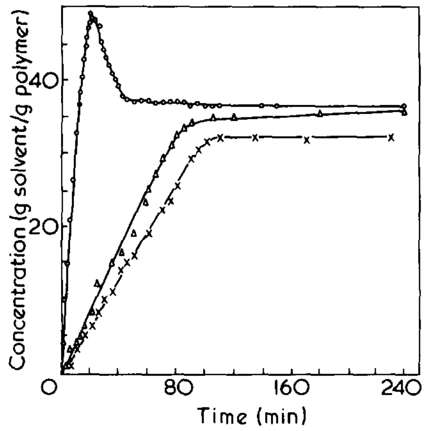

Figure 1 Integral dichloromethane absorption kinetics of IPS at 25°C, P/p_0 = 0.85 (sample thickness 0.25 mm). Starting material: ○, amorphous IPS; △, resorption kinetics of the previous film crystallized in dichloromethane vapour (crystallinity fraction = 0.23); x, IPS thermally crystallized at 127°C for 2 weeks (crystallinity fraction = 0.27)

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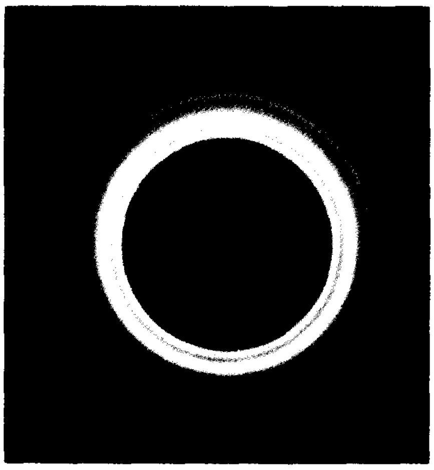

Figure 2 WAXS pattern of an IPS film, cast from a mesitylene solution, as described in ref 1

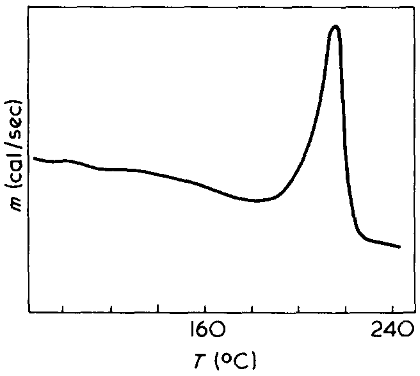

Figure 3 D.s.c. thermogram of the IPS film, cast from a mesitylene solution, scan rate 20° C/min

solvent concentration allowing crystallization.

When samples of IPS crystallized by this technique are dried under vacuum and are brought again in contact with dichloromethane or acetone, no maximum in the absorption curves is observed (*Figure 1*). This corresponds to an absorption of Case II of ref 1. This absorption behaviour is also obtained with thermally crystallized samples (*Figure 1*). We conclude therefore that when completely dried, semicrystalline samples are used, the degree of swelling increases continuously until an equilibrium value is reached. No maximum can be seen in the curves. It is also clear from these remarks that the desorption reported by us (ref 2) is only the consequence of crystallization.

The situation is completely different when IPS samples are prepared by casting films from solutions of the polymer in high boiling solvents as mesitylene or *o*-chlorotoluene. Samples prepared as described in ref 1 are crystalline. This can be easily shown by X-ray diffraction (*Figure 2*) and d.s.c. (*Figure 3*). This is due to the very slow rate of evaporation of the solvent. It is also possible that the residual solvent concentration is high enough to allow further crystallization at room temperature. Annealing of these samples can even increase the crystallinity. The presence of this crystalline fraction can be directly deduced from the densities reported in ref 1, *Figure 1*. After annealing for 48 h, pure IPS has a crystallinity fraction of 0.18, calculated from the density reported in this Figure, using 1.057 and 1.125 g/cm^3 as the densities of amorphous and completely crystalline IPS. Starting then with an already crystallized sample, a maximum in the absorption kinetics of their dried samples cannot be expected. Furthermore, we have observed that n-hexane is unable to crystallize IPS by swelling at 35°C. Probably the maximum degree of absorption at this temperature is too low to allow any crystallization.

From these observations and remarks, we can reach the following conclusions. Samples partly crystalline and containing some amount of casting solvent, will show a maximum in the absorption kinetics as a consequence of desorption of trapped casting solvent. The difference in absorption rate can be explained by the presence in IPS of a crystalline fraction. Starting with amorphous, dried samples, a maximum is only observed when crystallization is possible. This requires a minimum concentration of solvent in the sample depending on the partial vapour pressure and the temperature. This is clearly illustrated in ref 2, *Figure 2*.

The fundamental difference between the results of Faulkner *et al.* and our work results from the difference in the sample preparation techniques. They also used an organic liquid that is incapable of crystallizing IPS under the reported experimental conditons.

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Fine structure of the low temperature relaxation in linear polyethylene

In linear polyethylene the low temperature (γ) relaxation occurs at about −120°C (depending upon the frequency of measurement) and is thought to consist of components from both amorphous and crystalline parts of the polymer. Illers[1] identified three separate relaxations termed γ_{I}, γ_{II} and γ_{III} centred (at 1 Hz) at −110°, −135° and −165°C, respectively. The interpretation of these relaxations has led to considerable difference of opinion[2] and in addition, in a paper published in 1972, Cooper and McCrum[3] pointed out the importance of thermal history on the position and magnitude of these low temperature relaxations.

In this Letter we give results of some preliminary studies on the low temperature mechanical behaviour of ultra-high drawn polyethylene which suggest that there may indeed be multiple γ relaxations in these materials.

Sample preparation

The samples used in this work were from a batch previously prepared during the work reported elsewhere[4]. They had been made from Rigidex 50 which had been moulded at 160°C into a sheet, cooled at 1.5°C/min to 110°C and then quenched in cold water. Tensile test samples, 20 x 4 x 1 mm, had

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