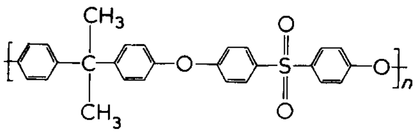
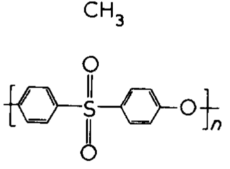
Letters

Dielectric γ losses in polysulphone and polyethersulphone

Polysulphone (PS) and polyethersulphone (PES) are linear polyphenylenes with structural formulae, respectively:





The main difference between these two members of the 'polysulphone' family is that the repeat unit in PS, which contains a bisphenol-A group, is twice the length of the repeat unit in PES. Since the densities of the two polymers are approximately equal, PES is therefore approximately twice as polar as PS, with the result that PES has a higher glass–rubber T_g (503K) than PS (468K). Somewhat unexpected for linear polymers, the polysulphones are also known to undergo a phase transition[1] at a lower temperature, T_{g2}, which is 173K for PS and 203K for PES.

Although a good deal of study has been undertaken on the thermomechanical properties of the polysulphones[1,2], little has been done on the low temperature dielectric properties of these relatively new polymers. The purpose of this article is to report the unexpected occurrence of dielectric γ losses in these linear, supposedly amorphous, polymers in which α peaks are known to occur above 460K.

The dielectric loss (log tan δ) in commercial grade thin films of PS and PES was measured as a function of temperature on a General Radio type 1615 A transformer ratio-arm bridge, using a McCammon and Work type of dielectric cell. ***Figures 1*** and ***3*** show the results for PS and PES, respectively, at 0.1, 1, 10 and 100 kHz, in the temperature range 4.2 to 320K.

In *Figure 1* (PS), two relaxation regions are visible. The β peak occurs around 226K (at 1 kHz), where it reaches its maximum height of 1.5×10^{-3} in tan δ. A second loss region occurs around 120K, joining the low temperature limits of the β peak as a shoulder. This region was termed γ. Unlike the β peak, whose position (but not height) is highly frequency dependent, the γ region is practically insensitive to frequency changes, maintaining the same position and height as the frequency is increased from 100 Hz to 100 kHz. Its intensity, of the order of 10^{-4} in tan δ, is quite low.

The experiment was repeated with a fresh PS film sample which was subsequently heat treated in a vacuum chamber by evenly depositing a hot aluminium film on both surfaces. Over the period of heat treatment of about 4 min, the average temperature (of heat treatment) may be estimated at ~833K, the temperature of molten aluminium. The aluminium film served further as an efficient maximal-contact electrode. Dielectric loss measurement was performed in the usual way (as described above), precautions being taken to ensure that the film did not interfere with the normal operation of the guard electrode (on one side aluminium was deposited only over the central disc, which came into contact with the measuring electrode; the circular region coming into contact with the guard was left uncoated).

Figure 2 shows log tan δ *versus* temperature at 1 kHz for a PS film sample before and after heat treatment. The loss curve of the untreated sample is a good reproduction of the one shown in *Figure 1*. However, in the heat treated sample the β peak has shifted from 226 to 240K; it is broader, but reduced in height. The γ region, on the other hand, has shifted only slightly to a higher temperature, but its intensity has increased from about 4×10^{-4} in tan δ, in the untreated sample, to about 6.5×10^{-4} in tan δ, in the heat treated sample. This represents a 50% increase in γ losses. The main difference between the two samples is that the heat treated sample has gained a higher degree of crystallinity, as was verified using an X-ray diffractometer.

In *Figure 3* for PES it can be seen that the loss curves very closely resemble those for PS (*Figure 1*), except that in PES the dielectric losses are twice as high (PES is twice as polar) as in PS and that the β peak occurs at a higher temperature (230K) at 1 kHz. The γ shoulder is located in the same temperature region as in PS, also being centred aroung 120K. As in PS, it is practically frequency independent over the whole temperature range 4.2 to 160K.

The high temperature α peaks in both PS and PES are believed to be associated with the glass–rubber transition. The occurrence of β peaks in the glassy region is not surprising. However, the occurrence of γ losses in these linear polysulphones is unexpected, since a third 'degree of freedom' in the mechanical motions os segments of the polymer chains cannot be found. While other interpretations of the results may be put forward (ref 4), a possible explanation for the occurrence of the γ pro-

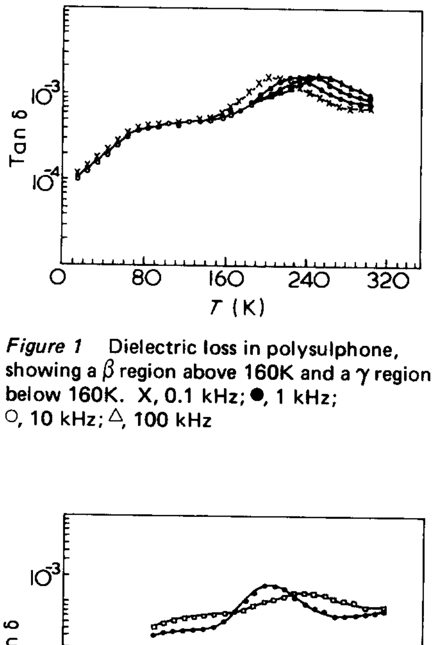


Figure 1 Dielectric loss in polysulphone, showing a β region above 160K and a γ region below 160K. X, 0.1 kHz; ●, 1 kHz; ○, 10 kHz; △, 100 kHz

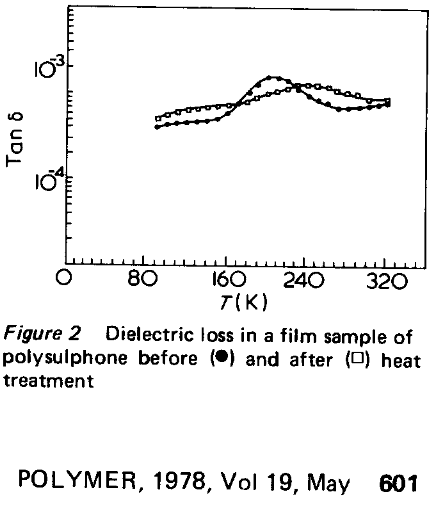


Figure 2 Dielectric loss in a film sample of polysulphone before (●) and after (□) heat treatment

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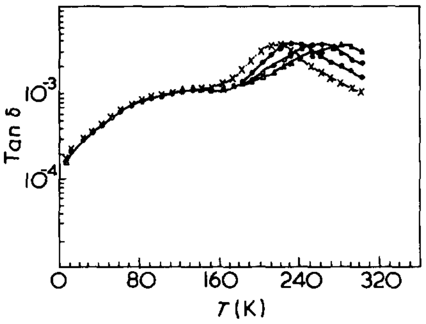

Figure 3 Dielectric loss in polyethersulphone, showing a β region above 170K and a γ region below 170K. A, 100 kHz; B, 10 kHz; C, 1 kHz; D, 0.1 kHz

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

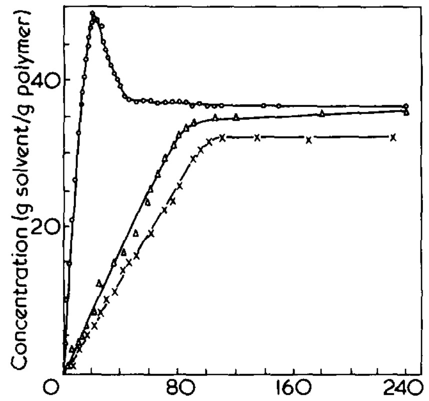

Figure 1 Integral dichloromethane absorption kinetics of IPS at 25°C, $P/p_0 = 0.85$ (sample thickness 0.25 mm). Starting material: ○, amorphous IPS; △, resorption kinetics of the previous film crystallized in dichloromethane vapour (crystallinity fraction = 0.23); x, IPS thermally crystallized at 127°C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

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