Solvent sorption and swelling in poly(ethersulphone)

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The sorption of carbon disulphide, methanol and chloroform by poly(ethersulphone), PES, has been studied on a time-scale which excludes the crystallization effects reported previously. The thermal history of this glassy polymer has a marked effect on the sorption kinetics which are non-Fickian. Ancillary measurements concern the dimensional changes undergone by specimens of PES during solvent sorption and desorption. Each solvent has a constant partial specific volume in mixtures with PES.

INTRODUCTION

The prior history of a glassy polymer is known to have a marked effect on the kinetics and equilibria of solvent sorption. Barrer *et al.*[1] were among the first to examine the time-dependence of sorption curves. Ethyl cellulose samples subjected to a swelling agent before annealing at temperatures below the glass transition showed different sorption curves from those which had not been annealed. It was concluded that the initial sorption produces a swollen and rearranged structure. The subsequent desorption, which occurs more rapidly than sorption, is not accompanied by a complete return to the original configuration since some intersegmental bonds reform with different participants. Raising the temperature of such specimens after removal of solvent accelerates the relaxation process and the modified configuration will return more quickly to the initial configuration.

Berens[2,3] studied the solubility of vinyl chloride monomer in PVC powders and found that equilibrium sorption follows the Flory–Huggins relation above the glass transition whereas at lower temperatures there is an additional component of solubility attributable to hold-filling in the glassy polymer. Changes in solubility with time and sample history parallel the volume relaxation processes occurring in the polymer.

Enscore *et al.*[4] studied the sorption of n-hexane into glassy microspheres of polystyrene. They also showed that pre-swelling at a high vapour activity increases both the rate and amount of sorption at lower activities. Conversely, thermal annealing reduces the rate and amount of sorption relative to fresh samples. The apparent equilibrium concentration of permeant converges to a single value upon repeated cycling for all samples at a given high activity of solvent vapour. It was suggested that a true glassy state equilibrium can be approached by the conditioning effect of repeated cycling.

Any adequate description of glassy state behaviour must take account of the slow relaxation processes which occur in polymers. In particular, deviations from Fickian sorption behaviour are associated with the time taken by polymer chains to respond to a swelling stress and rearrange themselves to accommodate the molecules of permeant. For non-Fickian diffusion, neither sorption nor desorption curves are linear with the square root of time and a sigmoidal shape is typical of such plots. Crank and Park[5] offered an explanation for these shapes. This involves a tension between swollen and unswollen parts of a specimen since the latter tend to resist further swelling. In the early stages of sorption, the surface may fail to reach the true equilibrium concentration of permeant for some time; the rate of sorption builds up slowly to give a sigmoidal curve. More recently, it has been shown that for some systems the sorption data give nearly linear plots of weight gain against time. In such cases the transport is entirely controlled by polymer relaxation and is known as Case II diffusion.

Since sorption is normally accompanied by dimensional changes, it is surprising that most workers have not considered this additional source of information about the behaviour of polymer–solvent systems.

Dimensional changes during sorption and desorption have been investigated for few systems. Park[6] studied the swelling of polystyrene sheets in methylene chloride at 25°C. The change in thickness was calculated from the rate of sorption, assuming a constant partial specific volume for methylene chloride. During sorption, the thickness of a specimen increased more rapidly than the area. For 50% of the equilibrium weight gain, more than half of the final thickness swelling had occurred but less than 20% of the final area swelling. During the later stages of sorption, the area began to increase rapidly while the thickness reached a constant value. Overall, the swelling was non-isotropic and a total change in thickness of 4% was accompanied by a change in each lateral dimension of only 2%. After a complete sorption–desorption cycle, the area was slightly reduced. Michaels *et al.*[7] measured changes in the dimensions of 2 mm thick sheets of polystyrene when these were swollen in n-heptane at 40°C. The system showed Case II diffusion: there was an initial increase in thickness at constant area, followed by an increase in area at constant thickness as the fronts approached each other. No thickness decrease was reported after the fronts had met; all changes in dimensions were complete by that stage. Thomas[8] studied the swelling of 1 mm and 3 mm thick poly(methyl methacrylate) sheets in methanol at different temperatures. In general, sample thickness increased linearly with time until the fronts met; then there was a discontinuity in a plot of thickness against

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weight gain with a fall of about 50% in the thickness swelling, precisely compensated by a sharp increase in area. For sorption at 24°C, just above the glass transition of the swollen polymer, the original specimen shape was restored entirely at the end of the sorption process. At higher temperature, however, the specimens did not revert to their original shapes after non-isotropic swelling in the early stages. Typically, a 20% increase in thickness accompanied a 10% increase in lateral dimensions. The sparse literature concerned with dimensional changes in polymers during solvent sorption prompts further investigation to discern a general pattern of behaviour.

The detailed study of partial specific volumes in polymer–solvent systems has been neglected. Although partial molar volumes of many polymers have been measured in dilute solutions, not much information is available on the behaviour of polymer-rich mixtures. Park[9] investigated the methylene chloride–polystyrene system. He found that for less than 15 wt% of solvent, the partial specific volume of the methylene chloride was constant at 0.67 $cm^3\ g^{-1}$, compared with the pure liquid value of 0.75 $cm^3\ g^{-1}$. The polymer had a partial specific volume equal to its own specific volume. In a similar investigation, Thomas and Windle[10] studied the sorption of methanol by poly(methyl methacrylate) sheets at 24°C and obtained a constant value of the methanol partial specific volume of 1.07 $cm^3\ g^{-1}$ over the whole composition range up to 21 wt% methanol. The specific volume of pure methanol is 1.26 $cm^3\ g^{-1}$ and that of the polymer was assumed to be unchanged in the mixtures.

There appears to be a strong case for investigating polymer–solvent systems by several different techniques which complement one another. In the present work, conventional sorption studies are allied to measurements of dimensional changes. From the latter, it is possible to extract useful information about partial specific volumes. The polymer studied is poly(ethersulphone), PES. This paper forms part of a wide-ranging investigation of its interaction with organic solvents. Previous papers[11–13] have drawn attention to its unusual dissolution behaviour and to its capacity for forming crystallites in the presence of certain solvents. It is normally regarded as an amorphous polymer and, therefore, the general category of the work is the sorption of vapours and liquids by a glassy polymer.

EXPERIMENTAL

Materials

Polymer. The polymer used in this work was poly(ethersulphone) grade 200P, kindly supplied by ICI Plastics Division. The sample was specified as having a glass transition temperature of 220°C and a density of 1370 kg m^{-3}.

Solvents. These were of AR grade and used as received.

Fabrication of specimens. The casting of PES films was described in a previous paper[11]. For the present work an additional stage was introduced for the purpose of imposing a uniform and reproducible thermal history on each specimen. The treatment involved heating to 240°C for 1 h under vacuum, followed by quenching to room temperature. Pieces of film used in the experiments were 19 mm wide and between 40 and 80 mm long. The three thicknesses were: 40 ± 2 μm, 170 ± 4 μm, 210 ± 4μm

Procedures

The study of the sorption of vapours and liquids has been well documented with respect to the experimental techniques[11,14,15] and no radically new apparatus was used here.

Measurement of dimensional changes. To obtain accurate values for the thicknesses of PES films, a micrometer was constructed which had a sensitivity better than ±0.5 μm. Specimens were placed between two anvils and the displacement of a push rod in a transducer changed the output voltage which was displayed by a digital voltmeter. Standard resistance wires were used to calibrate the unit. The spring loading was kept as low as possible to avoid any undue compression of samples with a high solvent concentration. The change in thickness of a sample was based on the average of two readings taken at chosen spots at a fixed distance from the edges. A horizontal travelling microscope was used to follow changes in the lateral dimensions of specimens held between two microscope slides. This ensured flatness at the time of reading. The change in the diagonal of a rectangular specimen was used as a measure of lateral dimensions and an accuracy of better than 5 μm was possible in a length of about 50 mm.

Due to a variety of practical difficulties, the changes in swelling of PES by carbon disulphide, methanol and chloroform could only be measured for the desorption process. The measurements take up to 3 min for each sampling, during which time the specimens lose considerable amounts of solvent, causing significant errors. With carbon disulphide and methanol, PES samples with pre-measured dimensions were equilibrated first with liquid solvent at room temperature and then exposed to vacuum for 10 min. Thus the first reading was taken when the solvent concentration was about 60% of the equilibrium value for carbon disulphide and about 80% of the equilibrium value for methanol. The amount of swelling could be based on the dimensions of dry samples either before or after exposure to the solvent.

A somewhat different approach was necessary to follow the swelling of PES in chloroform. Instead of the usual solvent mixture, the film was cast from pure chloroform and appropriate samples were cut when the solvent content had fallen to below 30 wt %. The amount of swelling could only be expressed in terms of the final dimensions of the dry samples.

For each solvent the swelling of up to 6 different samples was studied and the reproducibility was very good.

RESULTS AND DISCUSSION

Sorption of methanol as liquid

A gravimetric experiment showed that PES is not soluble in methanol. Liquid methanol sorption curves at three temperatures for PES samples of thickness 170 μm are compared in *Figure 1.* The rate of sorption is strongly dependent on temperature (apparent activation energy for the diffusion coefficient is 44 kJ mol^{-1}), whereas the final uptake falls only slightly with increasing temperature. (These liquid sorption measurements are not subject to significant error on account of rapid evaporation. This was confirmed by equilibrating some samples of PES with methanol vapour of activity 0.99. During subsequent desorption under vacuum at room temperature the weight loss in the first few seconds was negligible).

The effect of cycling on the rate and uptake of liquid methanol at 45°C is shown in *Figure 2.* It is possible to remove all of the solvent from a sample by keeping it under vacuum for a few days at 45°C. This means that the second

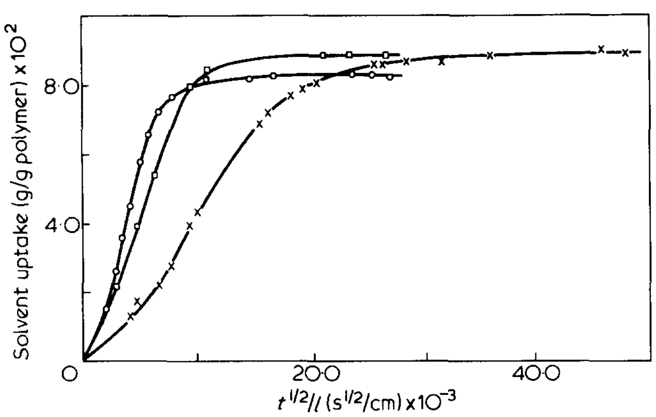

Figure 1 Sorption of liquid methanol in 170 μm thick PES films. ○, 65°C. □, 45°C; x, 25°C

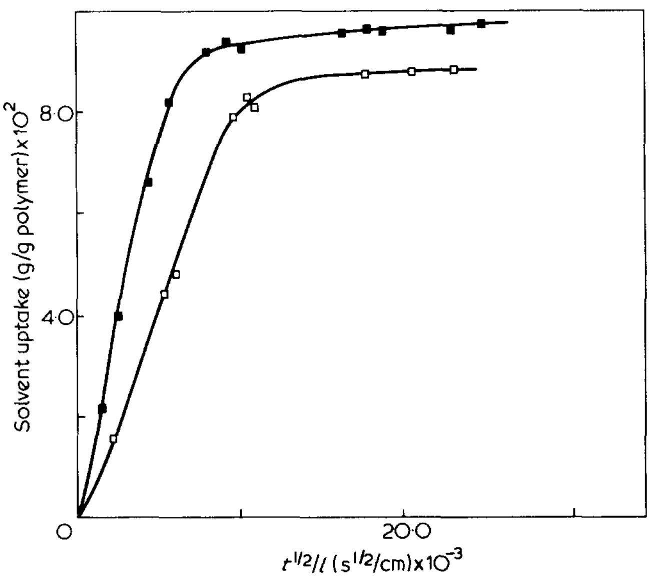

Figure 2 Repeated sorption of liquid methanol in 170 μm thick PES films. □, first sorption; ■, second sorption

subjection of a sample to solvent is a truly integral sorption like the first; the increased rate can be attributed unambiguously to the effect of conditioning by solvent in the first sorption. No further increase in rate is observed in subsequent sorptions.

Sorption of carbon disulphide as vapour

The sorption of carbon disulphide vapour at four temperatures was studied using PES samples with a thickness of 170 μm. When plotted as for the methanol data in *Figure 1,* again the curves are characteristically sigmoidal and the diffusion is essentially non-Fickian. Over the narrow temperature range of the experiments, the rate of sorption increases with temperature (apparent activation energy for the diffusion coefficient is 13 kJ mol^{-1}).

Again, the effect of cycling is to increase the sorption rate and the third and subsequent sorptions are identical to the second. Evidently, the presence of a large amount of solvent at the end of the first sorption ensures a short relaxation time for the polymer molecules and one cycle is enough to create a specimen with a reproducible response.

Figure 3 shows equilibrium uptake as a function of temperature for the first and second runs at each temperature. Although the uptake is always larger for the second run, it appears that the values are converging at higher temperatures. This may simply be because, with the higher mobility associated with the presence of solvent at higher temperatures, most of the changes which can take place actually occur during the very first encounter with solvent. On the other hand, it may also be that the glass transition of the polymer is so much reduced by the presence of solvent as to be almost achieved in some of the experiments, with a consequent obliteration of the effects of history.

Sample history. Figure 4 shows the effect of annealing at 190°C on the sorption of carbon disulphide vapour at 25°C, for 170 μm thick PES specimens. In order to ensure a rapid achievement of the annealing temperature, specimens were placed on a hot glass plate in a pre-heated oven (190°C). Annealing for ½ h produces no detectable effect but after 4 days the sorption of vapour is slower. The effect is increased by annealing for 7 days. These experiments identify upper and lower limits for the relaxation time at 190°C.

Figure 5 concerns the effect of other annealing temperatures. At 100°C, the polymer molecules are not mobile enough to rearrange in 4 days. Annealing at 240°C does not alter the characteristics of specimens which had already spent 1 h at 240°C. (It will be recalled that the standard procedure for preparing samples involved heating them under vacuum at 240°C for 1 h before quenching them to room temperature). These experiments inspire confidence in the procedure

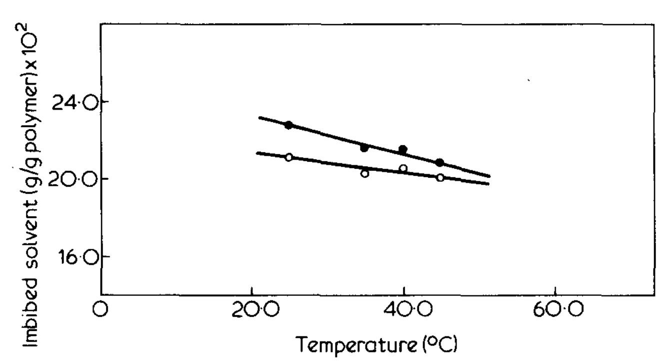

Figure 3 Effect of temperature on first and second final uptakes of carbon disulphide vapour in 170 μm thick PES films. ○, first sorption; ●, second sorption

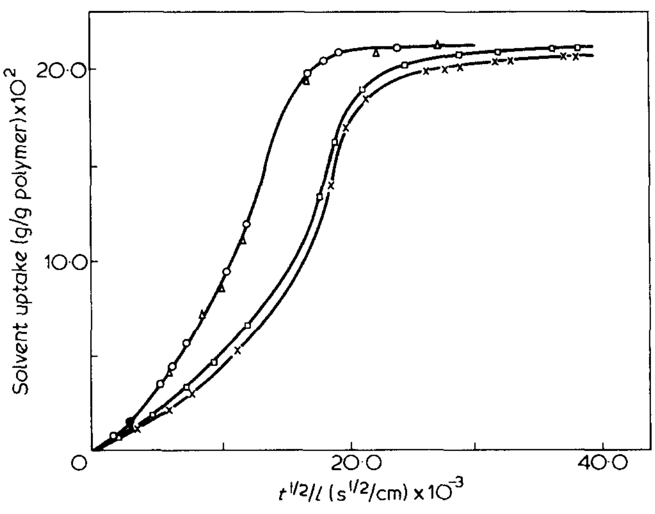

Figure 4 Effect of annealing at 190°C for different periods on sorption of carbon disulphide vapour at 25°C in 170 μm thick PES films. x, one week; □, four days; △, half hour; ○, unannealed

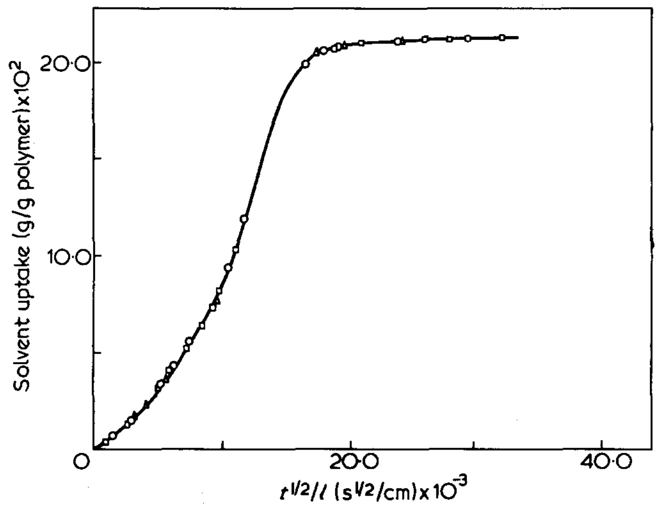

Figure 5 Effect of annealing for four days on sorption of carbon disulphide vapour at 25°C in 170 μm thick PES films. ○, unannealed; □, four days at 100°C; △, four days at 240°C

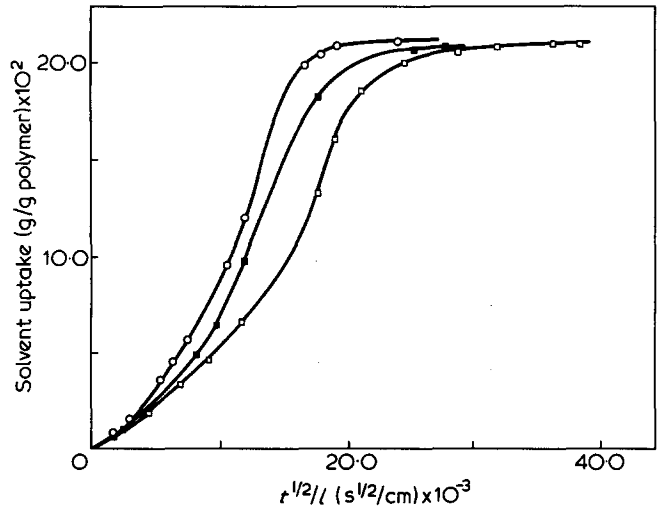

Figure 6 Effect of different histories on sorption of carbon disulphide vapour at 25°C in 170 μm thick PES films. ○, untreated; □, annealed at 190°C for four days; ■, treated with liquid carbon disulphide, then annealed at 190°C for four days

used for conditioning all specimens. At or above 240°C, it appears that the full effect of annealing is secured after a very short time.

The possibility of obliterating the effect of one form of treatment by another is explored in *Figure 6*. A sample of PES, 170 μm thick, was treated with liquid carbon disulphide at 25°C for 7 days. After removal of the solvent, it was annealed at 190°C for 4 days. The rate of sorption is lowered relative to the untreated specimen: a specimen which had been treated with solvent and not annealed would have had an enhanced rate of sorption. It is clear that solvent pretreatment and annealing act oppositely. If the mechanism of solvent action is to increase the number of cavities in the polymer structure capable of accommodating solvent molecules, it is not surprising that annealing reverses the effect.

Other experiments were devised to reveal the effect of pre-treatment with one solvent on subsequent sorption of a different solvent. *Figure 7* shows the sorption of carbon disulphide vapour by specimens of PES (40 μm) pre-treated with liquid methanol and liquid carbon disulphide, respectively. The pre-treatment involved contact with the appropriate liquid at 25°C for 7 days, followed by thorough drying under vacuum at 45°C for 3 days. *Figure 7* indicates that pretreatment with carbon disulphide had the larger effect. This is either because the equilibrium uptake of methanol, being lower (9 wt% as against 21 wt%), affects less of the polymer matrix, or because the sites occupied by the two sorts of solvent molecules are not identical.

Sorption of carbon disulphide as liquid

A gravimetric experiment involving prolonged contact of PES with carbon disulphide over a range of temperatures confirmed that the polymer was not soluble. Curves showing the sorption of carbon disulphide from the liquid state gave equilibrium uptakes lower than those recorded previously at the same temperature for sorption of carbon disulphide vapour at an activity of 0.99. This alarming and thermodynamically nonsensical observation can be understood by reference to *Figure 8*. In the first 10 s of desorption, a specimen losses more than 2 wt% solvent. Now, the procedure for following *sorption* from a liquid involves removal of specimens for weighing from time to time. The surface of each specimen must be dried with tissue and this cannot take less than 10 s, which means that the measured uptake could be too low by up to 2 wt%. This could not have been established simply by extrapolating to time zero the changing weight of specimens while on the balance pans in air.

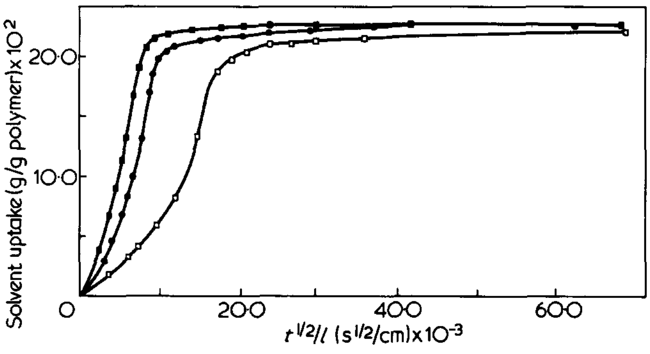

Figure 7 Effect of different histories on sorption of carbon disulphide vapour at 25°C in 40 μm PES films. □, untreated; ●, treated with liquid methanol; ■, treated with liquid carbon disulphide

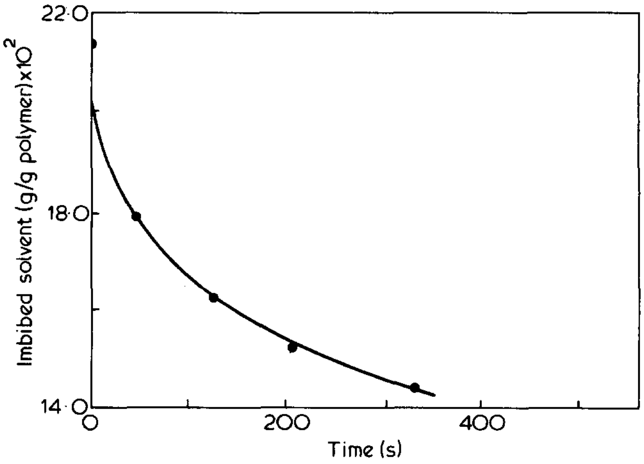

Figure 8 Desorption of carbon disulphide from a 170 μm thick PES film at 25°C

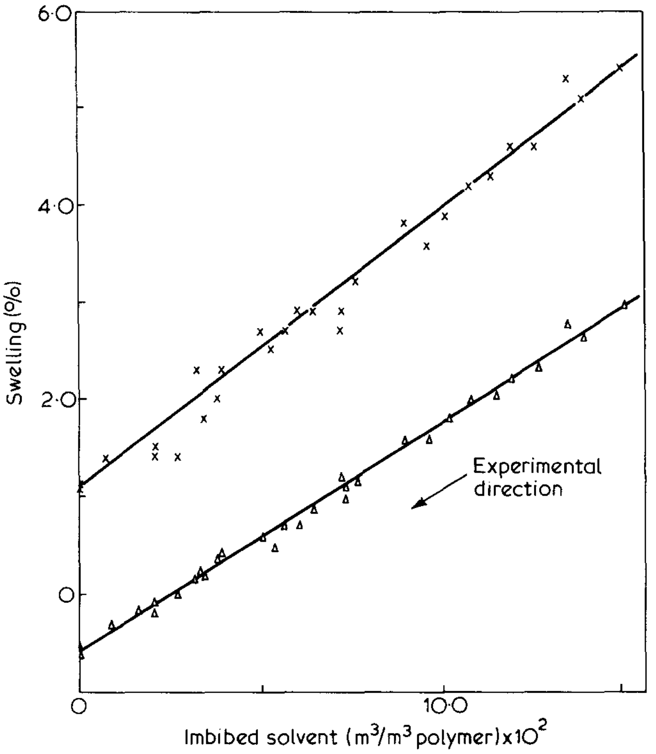

Figure 9 Dimensional changes in a sample of PES desorbing carbon disulphide. x, thickness; △, diagonal

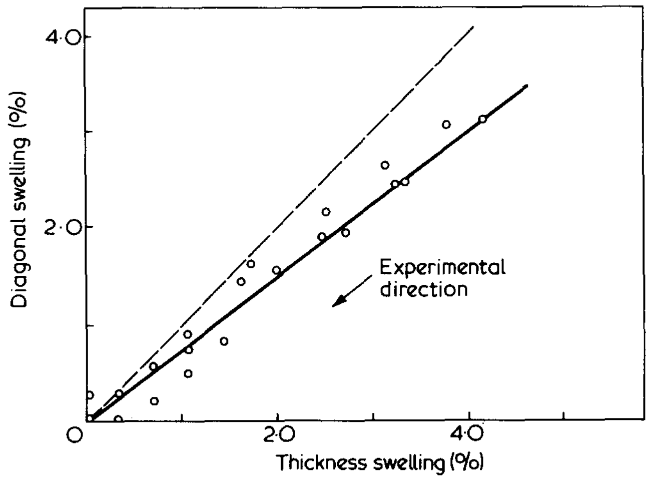

Figure 10 Dimensional changes in a sample of PES desorbing methanol. Dotted line represents isotropic behaviour

Effect of sample thickness on sorption characteristics

The effect of sample thickness was investigated for the sorption of carbon disulphide vapour. The conventional plot against $t^{1/2}/l$ showed the rate of sorption to increase with thickness. However, a plot against t/l discriminates between thick specimens (210 μm or 170 μm) which show Case II sorption and thin specimens (40 μm) where there is no sign of Case II sorption as observed by Enscore *et al.*[4].

Dimensional changes during desorption

Figure 9 compares the decrease in the thickness and diagonal of PES specimens desorbing carbon disulphide under vacuum at room temperature. At very low concentrations (1 or 2 vol% solvent), short heat treatments at 50°C were required to drive off more solvent. At equilibrium with carbon disulphide, the starting point of the experiment, the specimen had lost its original shape due to anisotropic swelling, the thickness having increased proportionally more than the diagonal. On desorption, the thickness decreases 20% more than the diagonal. This can be explained by an argument concerning the tension between fully swollen and less swollen parts of a specimen. During *desorption* the outer layers of the samples are necessarily lower in solvent content than the interior, and it is these less swollen outer layers which tend to restrict lateral contraction. In comparison, the thickness can reduce more easily. Over a complete sorption–desorption cycle, there is no volume change when carbon disulphide is used. A 1% net gain in thickness is offset by a decrease in the lateral dimensions.

Similar experiments with methanol as the solvent appear in *Figure 10*. Diagonal swelling is plotted against the thickness swelling for desorption. There is obviously less loss of shape when PES is in equilibrium with the solvent. At the end of a complete cycle, the original shape is recovered. Thickness swelling reduces 30% more than diagonal swelling (cf. 20% for carbon disulphide) which implies a greater resistance to lateral contraction.

Experiments on the desorption of chloroform from PES are shown on *Figure 11*. Diagonal swelling is again plotted against thickness swelling. The changes are based necessarily on the final dimensions of the dried specimens because the films as cast necessarily contain chloroform. Two desorption régimes are in evidence. At high solvent concentrations, the shrinkage is isotropic. Later on, the thickness decreases 50% more rapidly than the diagonal. Evidently, there is a particular overall solvent composition at which the effect of the outer, still swollen layers, becomes important in restricting lateral contraction.

Taking the results for the three solvents together, there is a wide spectrum of possible states at the end of a sorption–desorption cycle. For a given system, the elasticity of the polymer and the tension between the swollen and unswollen (or less swollen) regions are sensitive to solvent concentration and to temperature. Furthermore, controlled sorption or

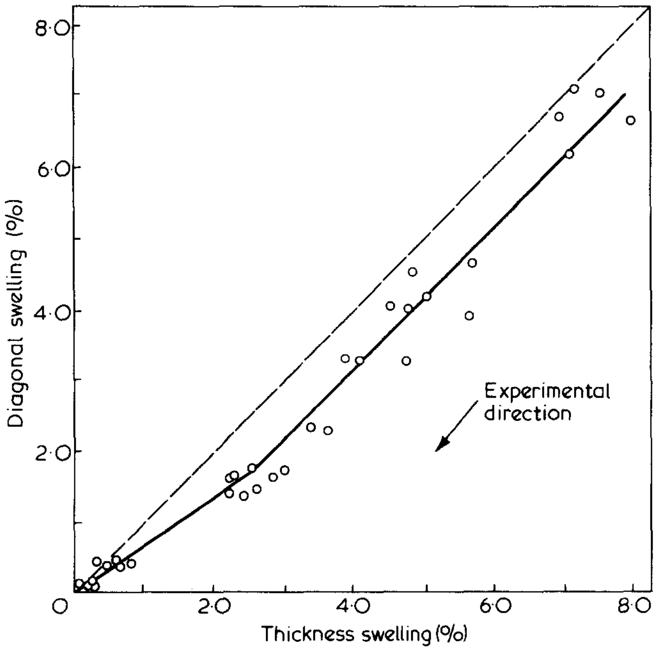

Figure 11 Dimensional changes in a sample of PES desorbing chloroform. Dotted line represents isotropic behaviour

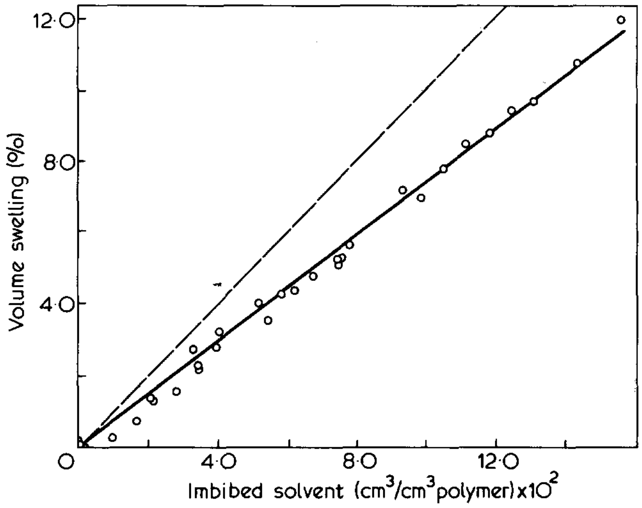

Figure 12 Swelling of PES sample by carbon disulphide. Dotted line represents ideal mixing

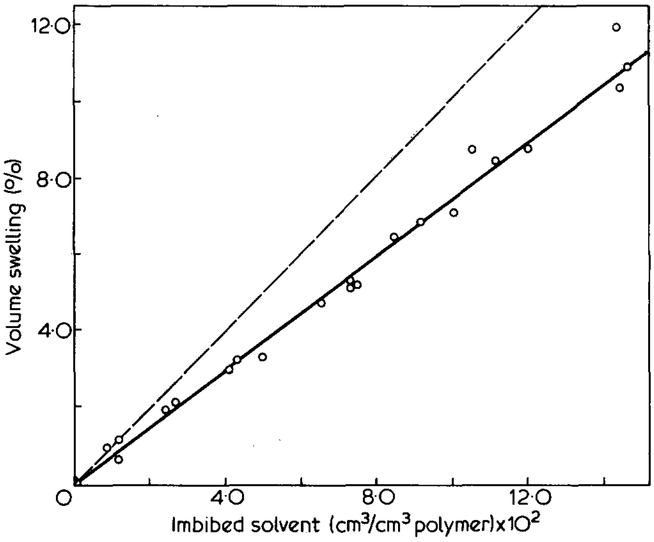

Figure 13 Swelling of PES sample by methanol. Dotted line represents ideal mixing

desorption experiments involving discrete steps and intermediate equilibria correspond to lower interlayer tensions. Thus, a wide range of deformations may be achieved in polymer–solvent systems, depending on the experimental procedures for sorption and desorption. In conclusion, any sample deformation brought about by sorption and/or desorption is a non-intrinsic property of the system, merely a consequence of the experimental conditions.

Specific volumes in polymer–solvent mixtures

For experiments on the desorption of solvent from PES, % volume swelling is plotted against % imbibed solvent for carbon disulphide, methanol and chloroform respectively (*Figures 12–14*). The well-fitting straight line plots permit calculation of the partial specific volume of each solvent when mixed with polymer.

The calculation involves the assumption that both polymer and solvent have a *constant* partial specific volume independent of composition. The rationale for the assumption emerges from the plots themselves. It is scarcely conceivable that the straight lines are the result of a perfect compensation between individual variations in partial specific volume affecting both polymer and solvent. As the major component of all the mixtures studied, the polymer may be assumed to have a partial specific volume identical to its pure state specific volume. The solvents have partial specific volumes as follows, with the pure solvent specific volumes in brackets for comparison:

carbon disulphide 0.56 $cm^3 g^{-1}$ (0.79)
methanol 0.92 $cm^3 g^{-1}$ (1.26)
chloroform 0.55 $cm^3 g^{-1}$ (0.67)

The first number is always lower than the second, in agreement with other work. This is attributed to the compressive effect of the polymer matrix which resists swelling by solvents. The constancy of each partial specific volume over the composition range indicates that the molecules of solvent are imbibed as individuals. There is no evidence of clustering of imbibed molecules nor is there any sign that sorption occurs by a 'hole-filling' mechanism. It would appear that each solvent molecule creates space for itself and makes an appropriate contribution to the overall volume change, being 'oblivious' of all other solvent molecules.

The results of the experiments with chloroform throw light on the following observation for which an *erroneous* explanation might otherwise have been proposed. A fresh specimen of PES floats in chloroform, the densities being 1.37 and 1.48 g cm^{-3} respectively, but it later sinks having imbibed some solvent. Although rearrangement of the polymer molecules certainly does occur on a long time scale, such rearrangement is not the primary cause of the observed densification. This is merely due to the imbibed chloroform having a partial specific volume which is lower than the specific volume of the pure ambient solvent.

PES–solvent systems manifest different types of behaviour (sorption, crystallization, dissolution) on different time-scales. These differences can be examined separately by devising experiments of appropriate duration at selected temperatures.

CONCLUSIONS

(1) The sorption of organic liquids and vapours by glassy PES is affected strongly by the history of each specimen.

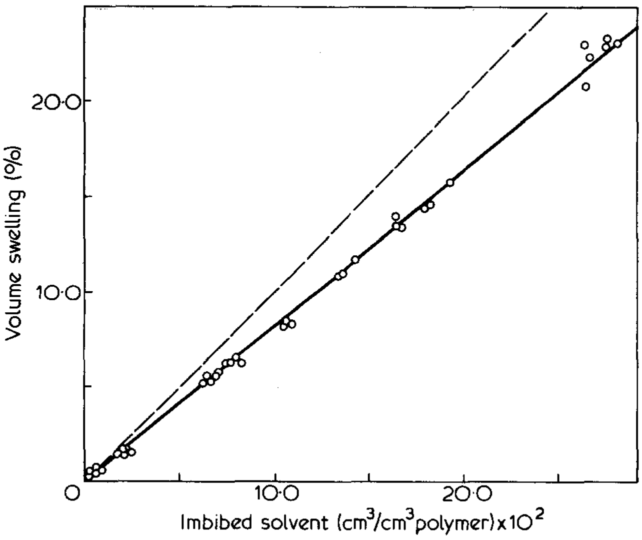

Figure 14 Swelling of PES sample by chloroform. Dotted line represents ideal mixing

The rate of sorption is increased by pre-treatment with solvent and decreased by annealing at appropriate temperatures. The 'equilibrium' uptake is also influenced by the history of a specimen, but repeated sorption–desorption cycling leads to a reproducible response. The relaxation time, which underlies the explanation of all these effects, is quite long. This might be expected of a polymer with such a stiff chain. Non-Fickian diffusion is characteristic of the sorption kinetics.

(2) The swelling and contraction of PES specimens when solvent is added or removed may be isotropic or non-isotropic. At equilibrium with the solvent, and at the end of a sorption–desorption cycle, the specimens may or may not have changed in shape. The particular behaviour observed in a given experiment is dependent on the temperature, the solvent and the circumstances of solvent removal. Generalizing, it is the unswollen core of a specimen which controls the expansions caused by sorption and it is the solvent-denuded outer layers which exercise control during desorption.

(3) Each of the three solvents studied has a constant partial specific volume in mixtures with PES. For each solvent, the value is less than that for the pure liquid specific volume. The solvent molecules appear to be sorbed independently. There is no evidence of hole-filling or of clustering. The results permit a simple explanation of an otherwise puzzling observation.

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