

Dissolution of polyethersulphone in chloroform

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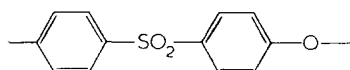
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Polyethersulphone (PES) is soluble in a number of organic solvents. Some of the solutions so formed have unusual properties and the dissolution process has features not hitherto reported. The present paper describes experiments with PES and chloroform and forms part of a more general investigation involving other solvents.

When PES dissolves in chloroform the rate of dissolution shows a maximum when plotted against temperature. The length of the induction period, which precedes a steady rate of dissolution, is also temperature dependent but displays a minimum. These results, together with the occurrence of a lower critical solution temperature, are discussed in terms of competing effects.

INTRODUCTION

Polyethersulphone, (PES), is a high temperature engineering thermoplastic with the repeat unit



Mainly due to the presence of the sulphone group which increases the stiffness of the chain, the polymer shows very good mechanical and electrical¹⁻³ properties even at relatively high temperatures. PES is a glassy polymer and all attempts to crystallize it by heat treatment have so far failed. In spite of the fact that some of the technology associated with manufacturing and processing PES hinges on getting the polymer into and out of solutions, the kinetics and thermodynamics of PES-solvent interactions are not understood. Chloroform is one of the solvents whose behaviour towards PES is to some extent peculiar and unusual.

In general, solvent imbibed by a polymer behaves as a plasticizer and reduces the strength associated with entanglement of the macromolecules. This, in turn, results in changed mechanical properties, a lower glass transition temperature, and a lower melt flow point. The higher the solvent concentration the more pronounced are these effects.

In the PES-chloroform system, in some ranges of temperature, the amount of solvent imbibed by the polymer at high activities of the solvent vapour is large enough to depress the melt flow point of the mixture below the sorption temperature, thus producing a liquid phase. A preliminary study on PES-chloroform mixtures revealed that the mutual solubilities decrease with increase in temperatures. That is, the higher the temperature the lower will be the concentration of the imbibed solvent at equilibrium. In order to investigate the phase boundaries of this system it was found necessary to use three different techniques for three ranges of temperature and concentration according to the state of the mixture.

(i) At low temperatures with higher concentrations of the

solvent the polymer-solvent mixture is fluid and one can observe the cloud point at different compositions.

(ii) At higher temperatures with lower solvent concentrations the mixture is too viscous for observation as in (i). Instead, the equilibrium sorption of the solvent vapour for different vapour activities can be obtained and extrapolated to unit activity.

(iii) To study the solubility of PES in chloroform one has to look at mixtures where the solvent-saturated phase, in the form of globules, is dispersed throughout the very dilute polymer-saturated solution containing those polymer molecules, if any, which have been truly dissolved and freely floated in the solvent. For this purpose spectrophotometry was found to be convenient.

In order to study the kinetics of PES-chloroform interaction one can look at the rate of dissolution of this polymer in liquid chloroform. Rotating PES discs were used as the pattern of the fluid flow is well known⁴.

As will become evident the word 'solution', as used in this paper, is not to be taken to mean a completely homogeneous phase on every occasion. It is being used very generally to describe the liquid-like parts of the system even though these normally consist of fine dispersions of solvent-saturated polymer globules in an exceedingly dilute true solution.

EXPERIMENTAL

Materials

Polymer. The polymer used in this work was polyethersulphone grade 200P which was kindly supplied by ICI Plastics Division. It was received in the form of discs of 11.4 cm diameter and 0.35 cm thickness. It was specified as having a glass transition temperature of 220°C and density of 1370 kg/cm³. For the dissolution measurement smaller discs of 4.82 cm diameter and 0.35 cm thickness were cut using a hole cutter. Care was taken not to overheat the polymer. The maximum water uptake under at-

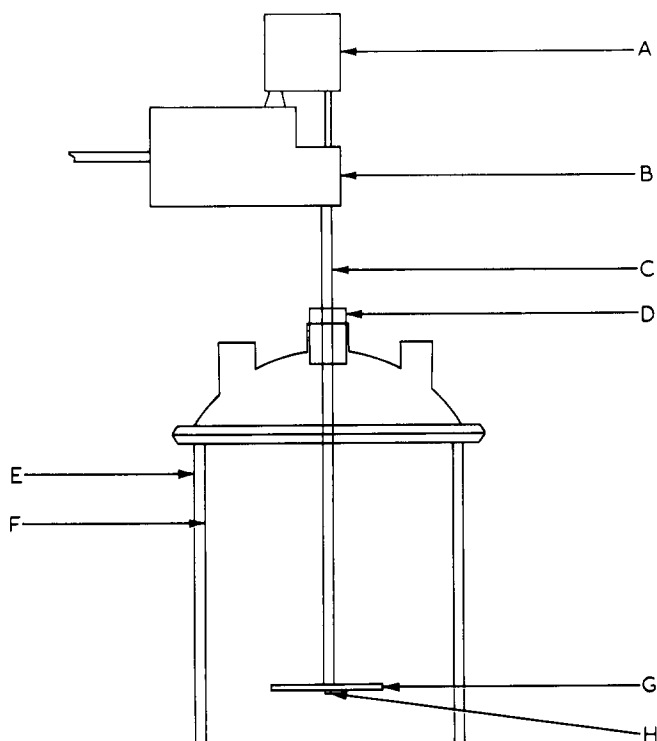


Figure 1 The dissolution apparatus. A tachometer, B stirrer motor, C stirrer shaft, D Teflon seal, E glass tank, F steel baffles, G polymer specimen, H supporting screw

mospheric conditions was reported to be of the order of 1 wt%. The polymer samples were therefore dried at 190°C for 5 h prior to any experiment. Following the drying process, the discs were quenched to room temperature between two thick iron sheets.

For the vapour sorption study thin films were produced by casting a solution of the polymer on a glass sheet trimmed by masking tape strips along the edges to provide the desired thickness. The solvent used was a 50:50 mixture of chloroform and dichloromethane by volume. The solution had a polymer concentration of 22 wt%. Solutions with either higher or lower concentrations of polymer were not suitable for this method of casting. During casting a glass rod was pushed across the solution on the glass sheet and immediately followed by another glass sheet to cover the cast film. This covering was to avoid rapid evaporation of the solvent which would have resulted in the production of bubbles in the film. The cover was removed after 15 min to let a slow evaporation take place. After 2 h at room temperature and 1 h at 40°C in an oven the film was peeled off from the surface of the plate using a few drops of distilled water as release agent. At this stage the amount of solvent in the polymer film was up to 30 wt%. (Due to the high cohesion between glass and PES it is not possible to pull the polymer film off the glass plate without damaging it unless water is applied. The cohesion is so great that in some instances patches of glass retain their bond with the polymer film and thin layers break off the surface of the sheet. Water molecules seem able to penetrate the interface and weaken the forces between polymer molecules and the glass). The polymer was then heated under vacuum at a steady rate of 10°C/h until it reached 230°C which is 10°C above its glass transition temperature. A katharometer was used to check the completeness of the solvent removal by analysing the gas above the liquid polymer at 350°C. The density of the film was measured and found to be identical to that of as-

received-polymer. The thickness of the polymer films could be varied from 50 to 250 μm and samples could be selected so that the thickness variation throughout a sample was less than ±3% of the average thickness.

Solvents. Chloroform and dichloromethane were both of AR grade and were used as received.

Apparatus

Vapour sorption. For the sorption experiments a quartz spring balance with a sensitivity of 267 mm/g was used. The polymer sample was laid in an aluminium basket which was hooked to the spring. The spring was hung in a glass column the temperature of which was controlled by water circulating through the column jacket. The column could be either connected to a vacuum line or to the vapour generator as required. The vapour generator was a small tank of solvent the temperature of which was controlled by circulating water and always kept below the column temperature. The water temperature of the column and the vapour generator were controlled separately to better than ±0.05°C. The connecting tubes and the column were calmped in a perspex box with control of the circulating air temperature. As chloroform attacks high vacuum greases very easily PTFE taps had to be used.

Spectrophotometry. A Pye spectrophotometer SP 500 was used to examine the dilute mixtures.

Dissolution. The apparatus for the dissolution measurements consisted of a 1.5 litre tank with a rotating shaft connected to a motor, as shown in Figure 1. The tank was held in a water bath. The polymer discs were screwed to the shaft through a central hole and all faces of the discs were in contact with the solvent.

Procedure

Absorption experiments. For the absorption measurements polymer samples were cut with dimensions of 19 mm by 14 mm. The nominal thickness of 150 μm varied by ±5 μm from one sample to another. The weight of the aluminium basket was about 50 mg. The solvent was degassed prior to any experiment by freezing and melting it repeatedly in liquid nitrogen. The surface area of film open to solvent diffusant depended on the way the specimen was resting in the basket. Furthermore in the course of the experiment the solid polymer gives way to a liquid due to the high solvent concentration. The liquid tends to accumulate in the corners of the basket, because of interfacial tensions, and therefore changes the surface area. For the above reasons the rate of absorption is not meaningful and only the amount of solvent uptake at equilibrium is significant. In order to obtain the maximum uptake at unit solvent activity for a given temperature, the equilibrium uptakes at lower solvent activities were obtained and extrapolated to unit activity. The activity of the solvent is defined as usual as the ratio of the saturated vapour pressure at the temperature of the vapour generator to the saturated vapour pressure at the temperature of the polymer specimen.

Cloud point experiments. For the cloud point experiments a pre-weighed polymer sample and a suitable amount of solvent were mixed in a stoppered conical flask. The flask was vibrated for 24 h to produce two well-saturated phases. The temperature of the mixture was then lowered gradually to produce a clear solution. The transition was found to be very fast and very similar to those of systems consisting

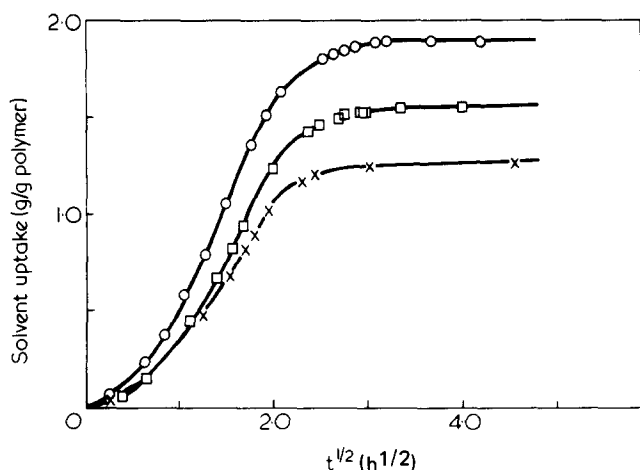


Figure 2 Chloroform uptake by PES at 25°C as a function of \sqrt{t} for different vapour activities. X 0.957, \square 0.978, \circ 0.991

of small molecules only such as aniline with hydrocarbons⁵. This resemblance was expected as the diffusion of the chloroform molecules into and out of the solution governs the kinetics of the cloud point, not the disentanglement of the macromolecules. The upper and lower temperatures reached by cooling and heating were as close as 0.5°C and averages are reported here.

Spectrophotometry. The study of the cloud point was found to be impossible in very dilute 'solutions' of the polymer. In this case it is the disentanglement and diffusion of the macromolecules from the globules that governs the kinetics of the cloud point and much time is required if equilibrium is to be achieved. As the temperature of the experiment is very low gelation occurs *before* the equilibrium is reached. The process of gelation is far different from the simple polymer-solvent mixing and as the polymer molecules undergo some reorientation the thermodynamic equilibrium of the system will also be different. Spectrophotometry was found to be very useful, being much more rapid. The wave length of 2950 Å was selected on the evidence of the complete absorption spectrum. The dilute solutions were filtered repeatedly through glass wool and their extinctions ($\log I_0/I$) were measured after each filtration. A calibration curve was also obtained by measuring the extinctions at known *total* concentrations.

Dissolution measurements. The progress of the dissolution of the rotating discs was followed by removing samples of the solution at intervals and analysing these gravimetrically. One litre of solvent was used in each run, the volume being measured at the temperature of the experiment. In order to have a clear-cut zero time for the experiment, the solvent was added to the system through the sampling inlet and the clock was started when the level of the solvent in the tank reached the rotating disc. The total time for the introduction of the solvent to the system was about 30 sec. The initial temperature of the solvent was always set somewhat above the desired temperature of the dissolution experiment to compensate for the loss of heat during the handling. The temperature of each experiment was subsequently controlled to better than $\pm 0.1^\circ\text{C}$ using a water bath. A 25 cc safety pipette with syringe was used for sampling and the sampling time was only 10 ± 1 sec. Samples were transferred to pre-weighed aluminium dishes where the solvent was evaporated. The final drying was done in an oven in such a way as to avoid any splashing of the samples. After

each sampling the pipette was washed with dichloromethane to remove the polymer globules adhering to the glass. The washings were added to each dish prior to drying. It must be emphasized that dissolution of the polymer discs does not produce a homogeneous solution but a dispersion of fine polymer-rich globules in what is virtually pure solvent.

RESULTS AND DISCUSSION

Polymer-solvent compatibility

The kinetics and thermodynamics of solvent sorption by polymers have been much studied⁶ and some conclusions at least are of high reliability. In the present work, however, the kinetics of vapour sorption have not been studied because of problems associated with variation in the surface area of the sample in the course of each experiment. Figure 2 shows a set of results at 25°C for different activities of solvent vapour where the uptake is plotted against the square root of time.

When it is not possible to expose polymer to solvent of unit activity, one can always extrapolate to unit activity using results from lower activities. This procedure is subject to some error which arises from the curvature of the extrapolated line⁷. Nevertheless, since the activities used here were quite high, this uncertainty is not serious. Figure 3 represents the chloroform uptake versus activity for different temperatures. The lower the temperature the steeper is the extrapolating line and it can be predicted that at low enough temperatures the uptake would tend to infinity in the absence of complications associated with the freezing of the solvent and gelation of the polymer. The results from the cloud point measurement which are shown in Table 1 are consistent with this conclusion and confirm the trend.

For the dilute mixtures, using the spectrophotometer, it was found that virtually *all* the polymer molecules in the system were in the form of globules which could be filtered off. The globules (of diameter around 10 μm) constitute

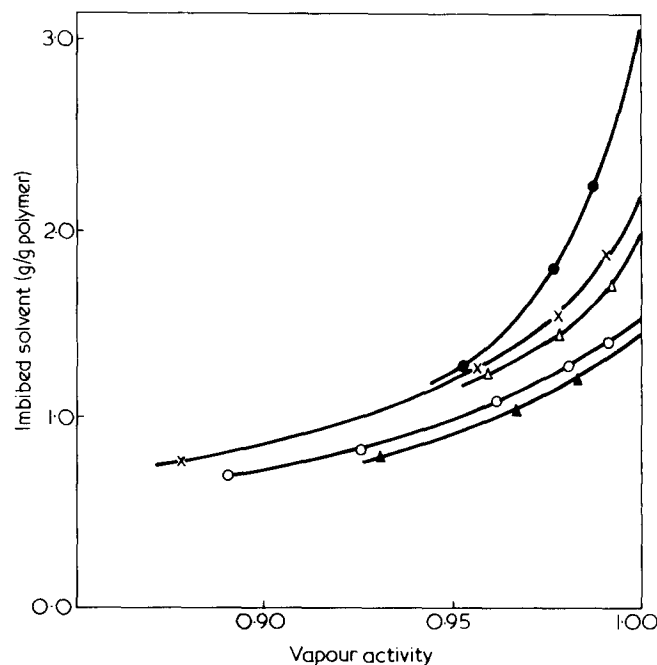


Figure 3 Effect of chloroform vapour activity on equilibrium uptake by PES at various temperatures. \bullet 15°C, X 25°C, \triangle 30°C, \circ 40°C, \blacktriangle 50°C

Table 1 Cloud points

Composition (g solvent/g polymer)	Separation temperature (°C)
8.39	-1.9
7.01	-1.1
6.67	1.8
4.21	8.0

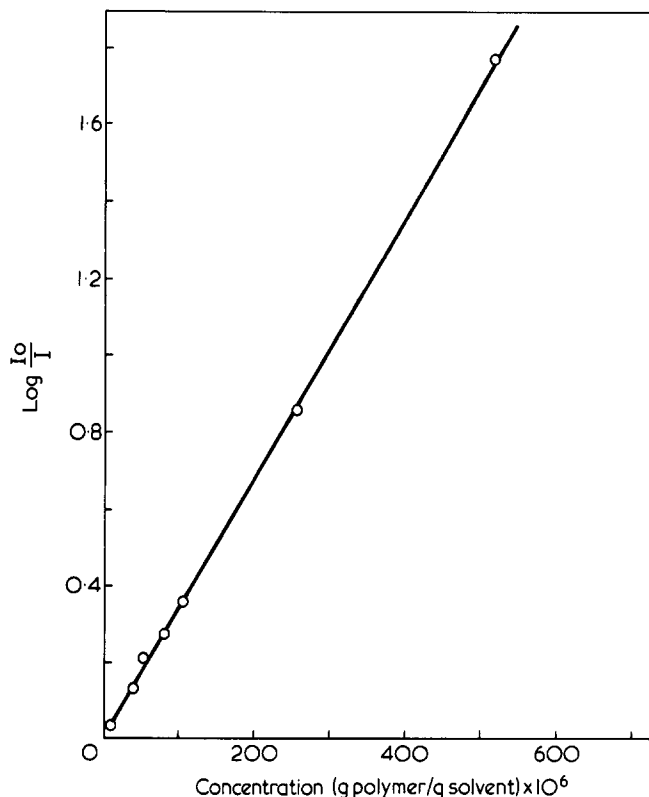


Figure 4 Spectrophotometer calibration plot for dilute mixtures of PES and chloroform

the polymer rich phase. The amount of polymer truly dissolved was so small that it could not be detected in the filtered solutions. The calibration curve shown in Figure 4 indicates that total polymer concentrations of 10 PPM are easily detectable. Putting all the results together the phase boundary for this system can be plotted as is shown in Figure 5. According to the results there exists a lower critical separation temperature (LCST) around -10°C . As mentioned before, the gelation of the polymer at low temperatures is the reason for failure to identify the exact position of the LCST. As chloroform is a polar molecule and a proton donor, its interaction with ether groups in the polymer chain⁸ is likely to be the dominating factor and responsible for the existence of the LCST.

Dissolution

Dissolution of a few macromolecular substances has been studied in great detail⁹⁻¹⁵. An induction period preceding a steady rate of dissolution has been observed in all cases and is dependent on the nature of the polymer and solvent and the conditions of the experiment. Figure 6 shows the dissolution of PES discs in chloroform at different temperatures where $M(t)$, the mass of polymer dissolved up to time t , is plotted against time. The stirring speed is 200

revolutions per minute. Figure 7 shows the results of similar experiments at a higher rate of stirring. There is evidently a regime of constant rate which can be extrapolated back to zero mass dissolved thus fixing the length of an induction period or swelling time.

Ueberreiter and Asmussen^{9,10} have shown that the rate of dissolution is a function of temperature and rate of stirring for a given polymer and solvent. As has been confirmed by many authors the rate of dissolution increases with the rate

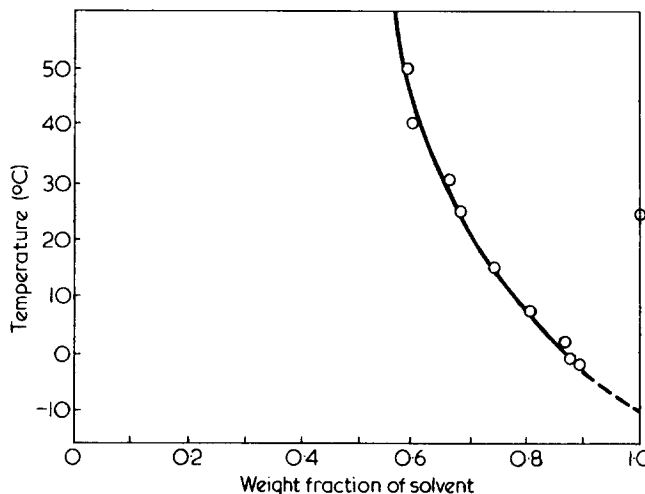


Figure 5 Phase diagram for PES-chloroform system

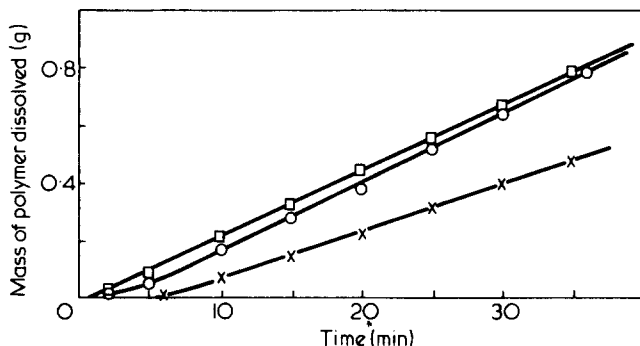


Figure 6 Dissolution of PES in chloroform at three temperatures; stirring speed 200 rev/min. \square 20°C , \circ 30°C , \times 40°C

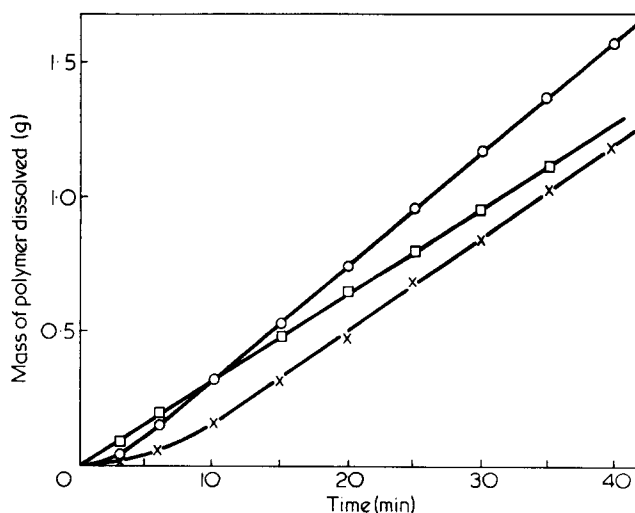


Figure 7 Dissolution of PES in chloroform at three temperatures; stirring speed 300 rev/min. \square 20°C , \circ 30°C , \times 40°C

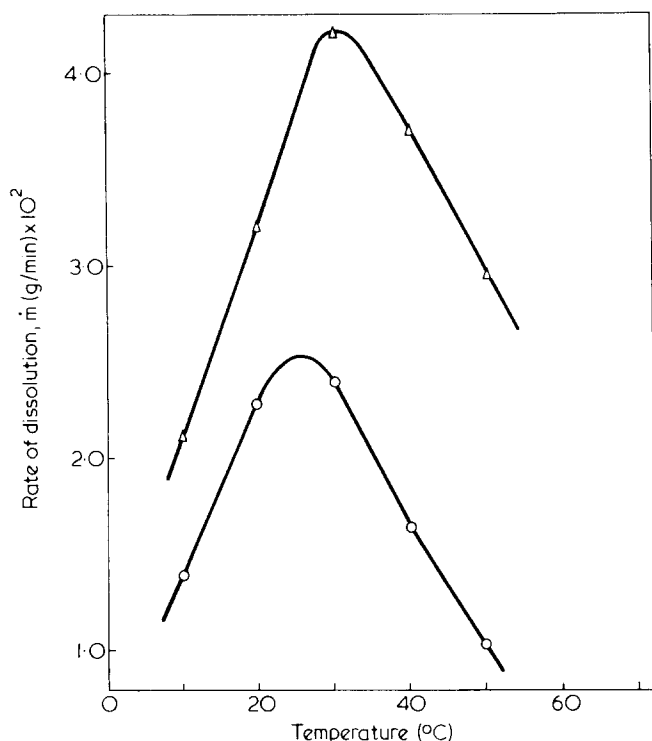


Figure 8 Effect of temperature on the rate of dissolution of PES in chloroform: ○ stirring speed 200 rev/min. △ stirring speed 300 rev/min.

of stirring as can be seen in Figure 8. However, the present results are not in accord with the expectation that the rate of dissolution should increase with temperature according to an expression of the Arrhenius type¹⁰. The maxima in Figure 8 are due to two opposing factors, namely, the temperature and the concentration of the imbibed chloroform.

The kinetics of the dissolution of macromolecules is governed by the diffusivity of the solvent and the mobility of the macromolecules as well as by the thickness of the swollen layer. According to Ueberreiter and Asmussen¹⁰ the thickness of the swollen layer increases with temperature which is reasonable provided that the increase in temperature results in an increase in the mobility of the polymer molecules. This does not apply uniformly to the PES-chloroform system. Solvent molecules are lubricants which increase the mobility of the anchored macromolecules. The lower the solvent concentration the lower will be the mobility of the polymer molecules when other conditions are fixed, and Figure 5 shows that the higher the temperature the lower will be the weight fraction of chloroform imbibed by PES at equilibrium. On the other hand the polymer molecules have a higher thermal mobility at higher temperatures. The thickness of the swollen layer will therefore change with temperature in the direction of the dominant factor over a given temperature range and the diffusional resistance of the mixture of PES and chloroform need not fall with rising temperature since it contains progressively less solvent.

Others have shown^{12,13} that the induction period decreases with increase in the rate of stirring due to a decrease in the final thickness of the swollen layer. This can be observed in Figure 9 where the swelling time is shorter at all temperatures for the higher stirring rate. The induction period, t_Q , has been represented as a function of temperature¹⁵

$$t_Q = A \exp(\Delta E_s/RT)$$

where ΔE_s is the activation energy and A is a weak function

of temperature but strongly dependent upon the physical properties of the solvent and polymer. Not surprisingly this expression is not in accord with our results because it takes no account of the imbibed solvent concentration which is itself temperature dependent.

It is noteworthy that the maximum in Figure 8 is shifted towards a higher temperature as the rate of stirring is increased. In the region where the rate of dissolution is increasing with temperature, both the thickness of the swollen layer and the diffusivity of the solvent through this layer are also increasing with temperature, but the latter effect is dominant. In the second region where the rate of dissolution falls with increasing temperature the importance of the two factors is presumably reversed. If the stirring rate is increased, the swollen layer becomes thinner and a higher temperature is attained before the turn down in rate.

The minimum in Figure 9 for a given stirring rate does not coincide with the corresponding maximum in Figure 8. During the swelling time the resistance of the matrix to the diffusion of the solvent changes less rapidly with temperature than it does in the steady state because, at any given temperature, there is necessarily less solvent present in the polymer during the swelling period than when the steady state is attained. On the other hand the driving force represented by the concentration of solvent at the surface varies with temperatures exactly as in the steady state. The net result is that the maximum steady state rate of dissolution for a given stirring rate does not occur at the same temperature as the minimum in the swelling time even though both are governed by the same factors.

It is to be expected that the rate of dissolution should increase with the rate of stirring more rapidly at high than at low temperatures and this is observed in Figure 8. The preceding general discussion implies that the swollen layer is thinner at higher stirring rates: the effect of any increase in its resistance with temperature is thereby minimised.

CONCLUSIONS

- (i) The PES-chloroform system shows a lower critical solution temperature.
- (ii) When plotted against temperature the rate of dissolution of PES in chloroform passes through a maximum while the swelling time passes through a minimum.

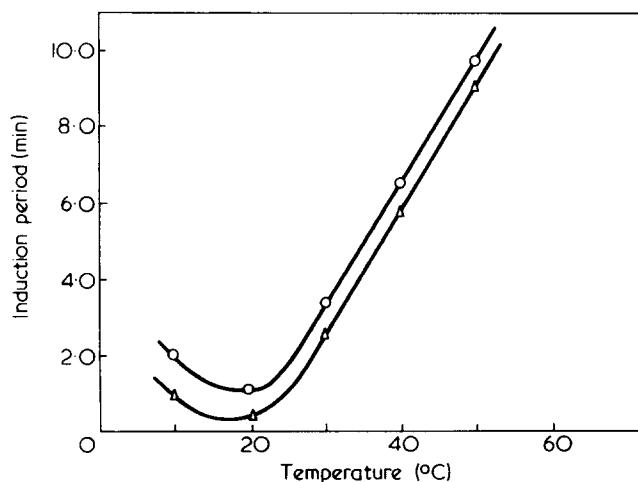


Figure 9 Effect of temperature on the swelling time of PES dissolving in chloroform: ○ stirring speed 200 rev/min. △ stirring speed 300 rev/min.

In order to interpret these results it is necessary to appreciate how a thermodynamic phenomenon, the equilibrium uptake of solvent by polymer, affects a kinetic process, the dissolution of the polymer.

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