

Dissolution of poly(ethersulphone) in dichloromethane

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The dissolution of poly(ethersulphone), PES, in dichloromethane has been studied. Rotating discs of the polymer were allowed to dissolve in a large volume of solvent. The rate of dissolution is a function of temperature and passes through a maximum at about 17°C. This feature can be explained with the help of the polymer-solvent phase diagram which has a lower critical solution temperature. The dissolution rate is also affected by the viscosity of the solvent and by the rate of stirring. All of these effects are discussed in the context of previous findings concerning the dissolution of PES in chloroform and a detailed interpretation is now possible. The effect of imbibed water in PES is to reduce the rate of dissolution in dichloromethane.

INTRODUCTION

The study of polymer solutions occupies a central position in polymer science, yet the actual formation of solutions by dissolution of bulk polymer in appropriate organic solvents has received surprisingly little attention. Ueberreiter and Asmussen¹⁻³ laid the foundations for an understanding of the dissolution process by their detailed examination of the dissolution of amorphous polystyrene. Blackadder and Le Poidevin⁴ then described the dissolution of polypropylene, a semicrystalline polymer. Certain features are shared by the two systems, notably a swollen surface layer of dissolving polymer which plays an important role. In the case of polypropylene, experiments with a variety of solvents have shown that there are thermodynamic and kinetic aspects of solvent power which jointly affect the rate of dissolution⁵.

Recently Blackadder and Ghavamikia⁶ reported on the dissolution of poly(ethersulphone), PES, in chloroform. This system presents features not previously encountered. The rate of dissolution is naturally dependent upon temperature but, surprisingly, it passes through a maximum. The explanation for this phenomenon appears to lie partly in the phase diagram for the polymer and solvent which displays a lower critical solution temperature.

Morphological studies have shown that PES-chloroform and PES-dichloromethane mixtures share some unusual features concerning order in the polymer^{7,8}. It seemed appropriate to investigate the dissolution of PES in dichloromethane as part of a general unravelling of dissolution processes.

EXPERIMENTAL

Materials

Polymer. The polymer used in this work was polyethersulphone grade 200P which was kindly supplied by ICI

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Plastics Division. It was specified as having a glass transition temperature of 220°C and a density of 1370 kg m⁻³. Discs of 48.2 mm diameter and 3.5 mm thickness were cut out of larger as-received discs using a hole cutter. The polymer samples were dried at 190°C for 5 h, and then quenched to room temperature between two thick iron sheets prior to each experiment.

Solvent. Dichloromethane was of AR grade and used as received.

Apparatus

The apparatus⁶ consisted of a 1.5 l tank, held in a water bath, and fitted with a rotating shaft connected to a motor. 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

The progress of the dissolution of the rotating discs were followed by removing samples of the solution at intervals and analysing these gravimetrically. A 25 cm³ pipette was used which gave a sampling time of about 10 ± 1 s. One litre of solvent was used in each run, the volume being measured at the temperature of the experiment.

RESULTS AND DISCUSSION

Phase diagram of PES and dichloromethane

Unlike the PES-chloroform system studied previously⁶ it was possible to determine all the phase boundaries using the cloud point method. *Figure 1* shows the phase diagram and a lower critical solution temperature is in evidence at about 19°C. This feature was also observed for the PES-chloroform system⁶ and proves to be the key to the dissolution experiments. At room temperature, in contrast to chloroform which could not dissolve the PES as single molecules, dichloromethane can produce true solutions containing up to 1.7 g dm⁻³.

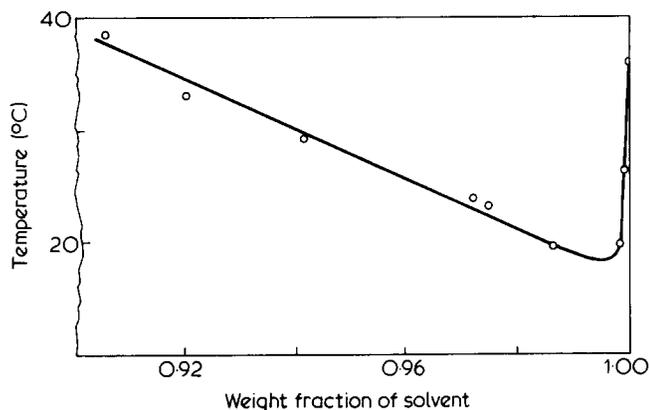


Figure 1 Phase diagram for PES-dichloromethane system

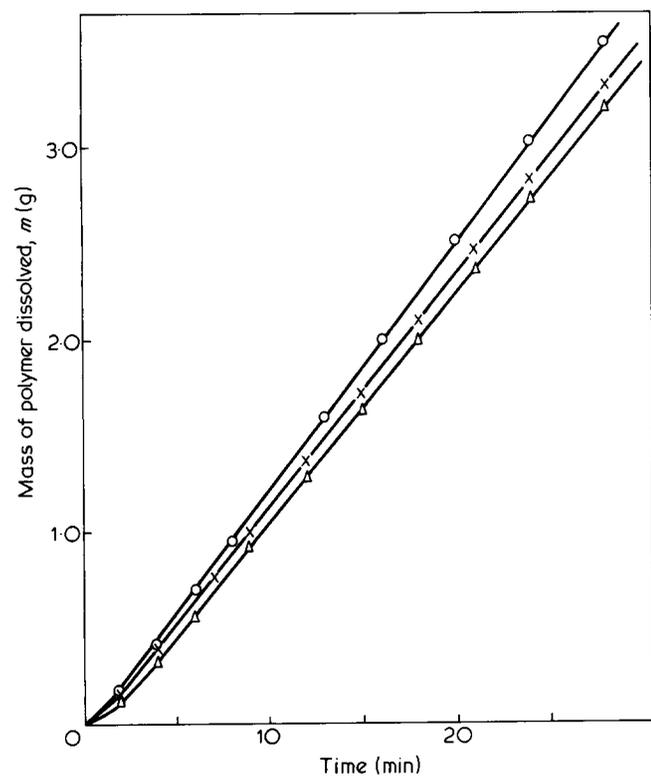


Figure 2 Dissolution of PES in dichloromethane at a stirring speed of 200 rpm. X, 5°C; O, 20°C; Δ, 35°C

Dissolution of PES in dichloromethane

The amount of polymer, $m(t)$, dissolved from a disc by time t , is plotted in Figure 2 for three temperatures and at a stirring speed of 200 rpm. After a short induction period each curve is linear, the rate of dissolution, \dot{m} , having become constant. The induction period is so short as to be comparable with the experimental timing error at the start of a run. The effects of temperature and stirring rate were therefore analysed only with respect to the rate of dissolution.

Figure 3 shows \dot{m} plotted against temperature, T , for 200 rpm and 300 rpm stirring speeds. The curves show maxima at about 17°C. This curious feature was first noted and explained in an earlier paper⁶ concerning the dissolution of PES in chloroform which should be consulted for an account of the origins of the maximum. In both systems the effect of stirring is most pronounced at higher temperatures though the dissolution rates in dichloromethane are at least

five times greater than those in chloroform. It is now possible to advance a more detailed interpretation of the results.

For both solvents it is important to consider the composition of the surface layers of the dissolving polymer. It appears that the solvent to polymer ratio does not range from 0 to ∞ (pure bulk solvent) or even to the limiting value represented by the ambient bulk solution. This has implications for the general dissolution equation¹

$$\dot{s} = \frac{\bar{D}^v}{\Delta} (\phi_1 - \phi_2) \tag{1}$$

where \dot{s} is the velocity of solvent penetration, \bar{D}^v the concentration averaged diffusion coefficient and Δ the thickness of all the surface layers after establishment of the steady state. The volume fractions ϕ_1 and ϕ_2 refer to solvent at the outer and inner boundary surfaces. During dissolution it is clear that ϕ_2 is zero, representing dry bulk polymer. The value of ϕ_1 may be read off the phase diagram, Figure 1, and equation (1) reduces to

$$\dot{s} = \frac{\bar{D}^v}{\Delta} \phi_1 \tag{2}$$

In other words, the concentration of solvent at the interface where disengagement occurs plays a crucial role.

Now clearly the polymer molecules must either leave the surface as individuals or as globules of polymer-rich, viscous liquid. Having become detached such globules may dissolve completely later on or else equilibrate with the bulk liquid by taking up more solvent. Consider the dissolution of PES in dichloromethane at, say, 20°C. On solubility grounds it would be possible for the first 1.7 g of polymer to dissolve directly into true solution as individual molecules though the bulk solution would then be saturated. After 1.7 g have dissolved, however, all subsequent 'dissolution' must neces-

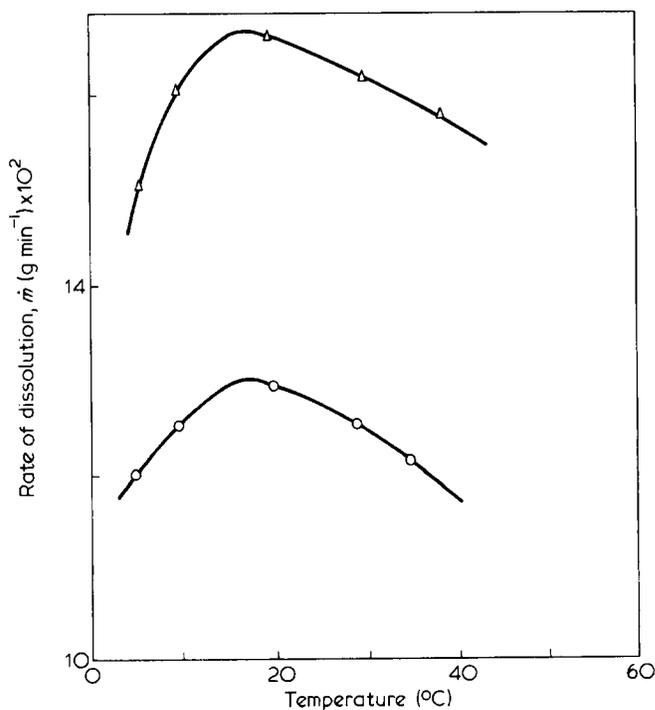


Figure 3 Effect of temperature on the rate of dissolution of PES in dichloromethane. O, 200 rpm; Δ, 300 rpm

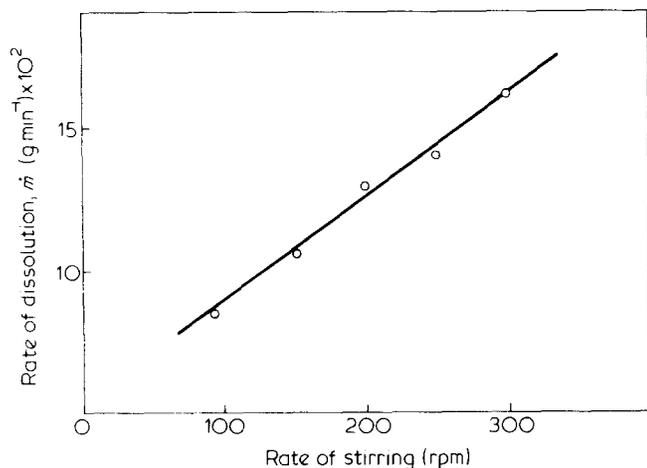


Figure 4 Effect of stirring speed on the rate of dissolution of PES in dichloromethane at 20°C

sarily be in the form of globules. In Figure 2 there is no evidence of a change in mechanism, either gradual or abrupt, around 1.7 g dissolved and this suggests that throughout its progress the dissolution occurs largely by the single mechanism of globule detachment. The polymer molecules in these globules would subsequently dissolve or equilibrate, depending on the concentration of already-dissolved polymer. This second stage could not, in any event, affect the dissolution process and it is the viscosity of the swollen surface layer which is crucial at a given stirring speed. The viscosity of the surface layer, on which the thickness depends, is naturally affected by temperature *per se* as well as on composition, though the latter is itself temperature dependent. The dissolution of PES, a kinetic phenomenon, is therefore influenced by the thermodynamics of polymer-solvent mixtures.

Figure 3 shows that dissolution rate is strongly affected by rate of stirring and this can be understood in terms of the shear stress applied to the polymer disc. This shear stress is instrumental in detaching globules of polymer and it is a function of the kinematic viscosity of the liquid as well as the rate of stirring. The kinematic viscosity of the solvent changes at most by 30% in the temperature range of the experiment. As the temperature goes up the kinematic viscosity falls and so the rate of dissolution also falls. The applied shear stress is related to stirring speed and kinematic viscosity by powers of 1.8 and 0.2 respectively⁹. If the stirring speed is changed from 200 rpm to 300 rpm the shear stress will rise by 107%, resulting in an increase in the observed dissolution rate of up to 30%. The 30% decrease in kinematic viscosity causes a 5% decrease in shear stress which would represent a decrease in dissolution rate of less than 1.5% over the whole temperature range. It therefore follows that although the changing kinematic viscosity of the solvents plays a role in reducing the rate of dissolution with increasing temperature its effect is minor.

From all of the above a prediction is now possible. For any given polymer-solvent system where mutual solubility decreases with temperature increase it is likely that the rate of dissolution will pass through a maximum as in Figure 3.

In Figure 4 the effect of stirring speed on the dissolution of PES in dichloromethane is shown in detail for experiments at 20°C. The results are compatible with the general equation¹⁰.

$$\dot{m} = pn^x + \dot{m}_0 \quad (3)$$

where n is the stirring rate, x a pure number, p a proportionality constant, and \dot{m}_0 the dissolution rate at zero stirring rate. For the present results x is unity which indicates turbulent flow in the system and this is compatible with the calculated Reynolds' number.

Effect of water on the dissolution of PES

Experiments have shown that PES absorbs about 2.2 wt % water when immersed in liquid water and this uptake is almost constant over the temperature range 3°C to 85°C. It seemed possible that this amount of water might affect the dissolution of the polymer in dichloromethane. A disc of PES was annealed at 190°C for 5 h and thus completely dried before being weighed and immersed in water at room temperature for three weeks to equilibrate. Figure 5 shows the usual plot of amount dissolved against time for the subsequent dissolution experiment, and the dissolution of a normal dry sample at the same temperature is included for comparison. The rate of dissolution, \dot{m} , is reduced by 5.5% when water is present. This observation is probably incompatible with the occurrence of clusters of water molecules as the major component of water uptake by the polymer. Instead it appears altogether more likely that the water molecules are uniformly and individually dispersed through the polymer matrix, each interacting strongly with particular segments of polymer and resisting displacement by the invading organic solvent.

CONCLUSIONS

The dissolution of PES in dichloromethane bears a marked resemblance to the dissolution of the polymer in chloroform.

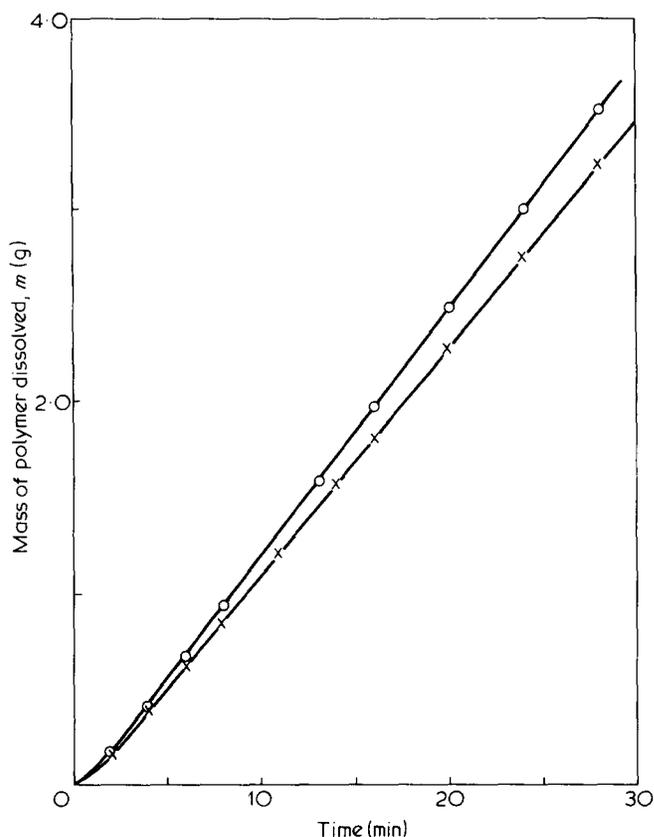


Figure 5 Effect of imbibed water on the rate of dissolution of PES in dichloromethane at 20°C, stirring speed 200 rpm. O, dry specimen; X, wet specimen

In both systems the phase diagram shows a lower critical solution temperature and this is responsible for a maximum in the rate of dissolution expressed as a function of temperature. Similar correlations are to be expected in other polymer-solvent systems.

The rate of dissolution in dichloromethane is always more than five times greater than in chloroform under similar conditions of temperature and stirring.

The effect of stirring can best be understood in terms of the stress applied to the swollen surface of the rotating polymer discs. This stress is influenced to only a minor degree by the variation in the kinematic viscosity of the solvent with temperature.

When PES contains 2.2 wt% absorbed water, the rate of dissolution in chloroform is reduced by 5.5%. This suggests that the water molecules, dispersed through the PES matrix, offer some resistance to being dislodged by the chloroform.

ACKNOWLEDGEMENT

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