Dissolution of polypropylene in organic solvents: 4. Nature of the solvent

D. A. Blackadder
University of Cambridge, Department of Chemical Engineering, Cambridge CB2 3RA, UK
and G. J. Le Poidevin
Electricity Council Research Centre, Capenhurst, Chester, UK
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The rate of dissolution of solid polypropylene in organic solvents is affected by intrinsic properties of both polymer and solvent as well as by the experimental conditions such as temperature and the degree of stirring. It is to be expected that the rate of dissolution will be connected in some way with the rate of penetration of the polymer by solvent molecules. Semi-empirical correlations lead to the conclusion that kinetic and thermodynamic factors are operating and that they jointly determine the effectiveness of a given solvent for dissolution of the polymer.

INTRODUCTION

Previous papers[1-3] have described the effect of temperature, stirring speed, crystallinity and molecular weight on the rate of dissolution of polypropylene in *p*-xylene. The steady state dissolution of macromolecular substances can be considered as a special case of diffusion with a moving frame of reference. It is to be expected that the rate of polymer dissolution will be linked to the rate of penetration of solvent molecules into the polymer. It is therefore important to seek an equation, empirical if necessary, which will relate some intrinsic properties of the polymer–solvent system to the rate of dissolution. This paper considers the effectiveness of several solvents including *p*-xylene.

Diffusion *without* dissolution is the natural starting point and has been discussed by many authors. One of the simplest relationships[4] involves the mobility of a solvent, B, the viscosity of the polymer–solvent mixture, η_m, and a quantity d which is a distance comparable to the jump length in the transition state[5] and zone theories[6] of diffusion:

$$B = \frac{1}{\eta_m d} \tag{1}$$

The mobility, B, is related to the concentration-dependent diffusion coefficient, D, by:

$$D = BRT\frac{\delta \ln a}{\delta \ln c} \tag{2}$$

where a and c are the activity and concentration of sorbed penetrant. Another approach to the problem of correlating a diffusion coefficient with a viscosity is described by Rogers and Machin in their review monograph[7]. The Stokes–Einstein equation is written in the modified form:

$$D = \frac{kT}{6\pi r \eta_m} \tag{3}$$

where r is the radius of a diffusing molecule and η_m the viscosity of the mixture through which it moves. This equation has provided a basis for some partly successful attempts to describe the diffusion of organic solvents and oils through natural rubber. Free volume theories[7] have also been used with some degree of success and are conceptually helpful. Small penetrant molecules in a polymer would be expected to increase the average free volume and hence the mobility of the polymer chains which in turn control each diffusion step.

For a diffusion process accompanied by dissolution, however, it is unfortunately not possible to evaluate a diffusion coefficient at zero penetrant concentration, nor is it possible to vary the concentration of solvent in the dissolving system. Concentration gradients are set up across the swollen polymer–solvent layers during dissolution and the exact nature of these will depend on the temperature and hydrodynamic conditions. There would therefore appear to be little point in trying to make use of the more complicated treatments in the context of polymer dissolution. Equations (1) to (3) represent the most promising approach.

Ueberreiter and Asmussen[8,9] dissolved amorphous polystyrene of fixed molecular weight in various solvents at constant temperature and under uniform stirring conditions. They used the Stokes–Einstein equation in the form of equation (3) to establish a relationship between a diffusion coefficient, D, and the viscosity of the pure solvent, η, together with the mean radius of the solvent molecule, r. If the solvent molecule is assumed to be roughly spherical then r will be proportional to $V^{1/3}$ where V is the molar volume of the solvent. Assuming also that the rate of dissolution, $\dot{m}$, will be proportional to D, whatever its definition, it follows that:

$$\dot{m} = \frac{A}{\eta V^{1/3}} \tag{4}$$

where A is a proportionality constant. If a plot of $\dot{m}$ against $1/(\eta V^{1/3})$ is an appropriate correlation for kinetic aspects of

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dissolution then all points should fall on a straight line passing through the origin provided that no other factors are in operation. In fact the solvents investigated by Ueberreiter and Asmussen covered a wide thermodynamic range as well as a wide kinetic range. They chose to join the origin to the single point representing that solvent which, on thermodynamic grounds discussed below, seemed most favourable. All other points lay below this line with the poorest solvents lying furthest from it.

Now strictly speaking the Stokes–Einstein equation should only apply to free diffusion of spherical particles in dilute solution and clearly these conditions are not met in the dissolution of macromolecular solids where there is a high concentration of polymer in all parts of the swollen surface layer. At best equation (4) must be regarded as semi-empirical and the fact that it applies so well to the new results in this paper is perhaps a matter for gratified surprise.

It is necessary to distinguish clearly between the thermodynamic and kinetic suitability of any given solvent for dissolving a particular polymer. The former will depend on the intermolecular forces between solvent and polymer, commonly measured by the Flory–Huggins parameter χ. In this work the thermodynamic dissolution temperature, T_s, is used instead of χ. Subject to certain conditions it may be shown that χ is largely dependent on T_s. On thermodynamic grounds alone the most suitable solvent for the dissolution of polypropylene at a given temperature will be that giving the lowest value of T_s. Kinetic suitability for dissolution, on the other hand, is chiefly connected with the size and viscosity of the penetrant molecules.

The main aim of the present work was to extend the approach of Ueberreiter and Asmussen to cover the dissolution of a semicrystalline polymer.

EXPERIMENTAL

Materials

Polymer. The polymer used was a polypropylene homopolymer, GXM43, kindly supplied by Imperial Chemical Industries Limited, Plastics Division. It was quoted as having a melt flow index of 2.16 and a melt viscosity of 5.0×10^3 N sec/m at 190°C.

Solvents. The *p*-xylene was a 99% product obtained from Imperial Chemical Industries Ltd. The other organic solvents, of SR or AR grade, were used as received.

Standard procedures

Fabrication of specimens. Quenched discs of polypropylene were prepared as described previously[2].

Viscosities. The viscosities of the pure solvents were determined whenever literature values were unavailable or doubtful. A Schurz–Immergut suspended-level viscometer was used both for pure solvents and for mixtures of solvents.

Theremodynamic dissolution temperature. The value of T_s for bulk quenched polypropylene in a pure solvent was determined by a method based on that of Jackson, Flory and Chiang[10]. Small thin shavings were cut with a razor blade from the interior of a disc which had a density of 904.7 kg/m^3. A guess was first made as to the probable value of T_s for a given solvent. A shaving was placed in 20 cm^3 of solvent in a test tube immersed in an oil bath set about 2°C below the guessed temperature. A first approximation to the true T_s was obtained by raising the temperature of the bath until the specimen just dissolved in the solvent. To aid dissolution agitation was applied with a glass rod. In the light of the approximate T_s, the experiment was repeated at a number of fixed temperatures until a temperature was found at which a fresh shaving of polymer just dissolved, while at 0.2°C below this temperature complete dissolution did not occur no matter how long the tube was kept in the oil bath. By this means the effect of molecular reorganization was eliminated.

A slightly different procedure was adopted to obtain reliable values of T_s for binary solvent mixtures. It will be shown that there is a tendency for the components of a solvent mixture to be absorbed at different rates depending on their molecular sizes and on their relative thermodynamic compatibilities with the polymer. The composition of the binary mixture inside a disc of dissolving polymer will thus be different from the bulk solution. If this should happen during a measurement of T_s an incorrect value might be obtained. To avoid such an occurrence the test shavings were made extremely thin ($\approx$50 μm) so as to facilitate the attainment of the bulk solvent composition throughout the dissolving polymer.

The attainment of this situation was demonstrated directly using a 50:50 mixture (weight basis) of *p*-xylene and 1-chloronaphthalene. About 0.2 g of dry polypropylene in the form of thin strips were added to 50 cm^3 of solvent mixture held at 118°C. From *Table 1* it will be seen that this temperature is about 0.7°C above the appropriate T_s. After 10 min the polymer was observed to fragment, indicating that substantial dissolution had occurred. The remaining polymer was removed from the tube with tweezers and transferred rapidly to a weighed test tube which was stoppered and immersed in liquid nitrogen. The combined weight of polymer and frozen solvent was noted, then the test tube was inserted in a dural block at 150°C. The solvent mixture was vacuum distilled for 6 h and the *p*-xylene collected in a tube cooled with liquid nitrogen. The 1-chloronaphthalene, having a very much higher boiling point, remained in the tube containing the polymer. Refractive index measurements showed that the *p*-xylene was 99.9% pure and the 1-chloronaphthalene was 99.8% pure. Further weighings showed that 49.9% of the total mass of solvent mixture consisted of 1-chloronaphthalene which is not significantly different from the bulk concentration, and T_s values obtained with thin specimens are therefore likely to be reliable.

The above experiments prompted a direct demonstration of the fact that differential solvent absorption does indeed occur during dissolution of thick disc-shaped specimens. A quenched disc 22 mm in diameter was immersed in 500 cm^3 of 50:50 *p*-xylene and 1-chloronaphthalene at 120°C for 8 min. The partly swollen disc was then removed and subjected to the solvent analysis described above for thin specimens. The results showed that 55 wt % of the imbibed solvent consisted of *p*-xylene. Evidently the better solvent was preferentially absorbed.

Dissolution rates. All dissolution rates were determined in the apparatus described in a previous paper[2]. Except where otherwise stated, all runs were carried out at 120°C and the rotation speed of the 50 mm discs was 1000 rev/min. At most 40% of the original disc weight dissolved during the runs which varied in duration from 7 min to 15 min depending on the rate.

Table 1 The dissolution of polypropylene in various solvents and solvent mixtures at 120°C

Solvent or solvent mixture (volume ratio)	Dissolution rate, $\dot{m}$ (g/min)	Solvent viscosity $\eta \times 10^3$ (N sec/m^2)	Molar volume $V \times 10^6$ (m^3/mol)	$\frac{10^{-5}}{\eta V^{1/3}}$	Thermodynamic dissolution temperature T_s (°C)
p-Xylene	0.383	0.281	137.3	0.692	106.4
Ethylbenzene	0.393	0.265	136.7	0.733	107.2
Cumene	0.268	0.312	155.0	0.596	110.8
Decahydronaphthalene	0.155	0.653	171.2	0.275	102.7
Tetrahydronaphthalene	0.134	0.608	148.0	0.310	111.2
n-Octane	0.312	0.208	184.9	0.843	114.5
n-Decane	0.135	0.307	220.2	0.538	117.5
Chlorobenzene	0.355	0.313	113.1	0.660	107.6
Bromobenzene	0.189	0.422	115.8	0.486	112.0
40/60 n-Octane/decahydronaphthalene	0.212	0.424	167.8	0.428	108.5
60/40 n-Octane/decahydronaphthalene	0.232	0.334	179.3	0.530	110.0
35/65 n-Decane/decahydronaphthalene	0.158	0.490	185.3	0.358	107.8
60/40 n-Decane/decahydronaphthalene	0.156	0.405	198.4	0.430	111.6
20/80 1-Chloronap/*p*-xylene	0.310	0.337	139.8	0.572	110.7
40/60 1-Chloronap/*p*-xylene	0.190	0.417	142.3	0.459	115.0
50/50 1-Chloronap/*p*-xylene	0.146	0.468	143.9	0.407	117.3
20/80 Decahydronaphthalene/*p*-xylene	0.318	0.312	143.9	0.612	104.4
50/50 Decahydronaphthalene/*p*-xylene	0.261	0.397	155.8	0.466	103.5
75/25 Decahydronaphthalene/*p*-xylene	0.194	0.508	160.7	0.362	103.3

RESULTS AND DISCUSSION

Effect of solvent type on the rate of dissolution of quenched polypropylene

Figure 1 shows the rate of dissolution of quenched polypropylene at 120°C as a function of $(1/V^{1/3})$, where V is the molar volume of pure solvent. The variable in the abscissa is therefore the reciprocal of the radius of the solvent molecule, assumed to be spherical. This exceedingly simple correlation gives three distinct lines representing: (i) n-alkanes (ii) aromatics and naphthenics (iii) halogenated solvents. The central aromatics and naphthenics line also carries three different mixtures of *p*-xylene and decahydronaphthalene. The value of $(1/V^{1/3})$ for each of these points is an appropriate average of the molecular dimensions. Two points on the n-alkane line (n-dodecane and n-decane) were determined at 127°C for practical reasons rather than at 120°C. Values of the rates at 120°C were estimated.

It is possible to identify common features of the results and those obtained by other workers using vapour sorption techniques. Brown *et al.*[11] studied the sorption of the vapours of dichloromethane, benzene, chloroform and 2,2,4-trimethylpentane by polybutadiene at 25°C. They found that the diffusion coefficient at zero penetrant concentration, D_0, decreased with increasing molecular size, in the order given above. However, the decrease between chloroform and 2,2,4-trimethylpentane was relatively small even though the change in molar volume is by far the largest in the series. It was argued that the larger of the two molecules, 2,2,4-trimethylpentane, was also the more flexible, the fact that molecular shape and flexibility can be more important than molar volume in determining a diffusion coefficient having been known for some time. The diffusion of linear and branched hydrocarbons in polyisobutylene[12] and asymmetric small molecules in polystyrene[13] show how important these effects can occur. It therefore appears that in the present work the higher rate of dissolution of polypropylene in n-alkanes, compared with naphthenics and aromatics for any given molar volume, might be interpreted in terms of the greater flexibility of the n-alkanes. It is unlikely that the rightward displacement of the line for halogenated solvents can be explained in steric terms, nor the curious displacement of the tetrahydronaphthalene point away from the naphthenics and aromatics line. Although solvent radius is evidently extremely important, other factors must be taken into account.

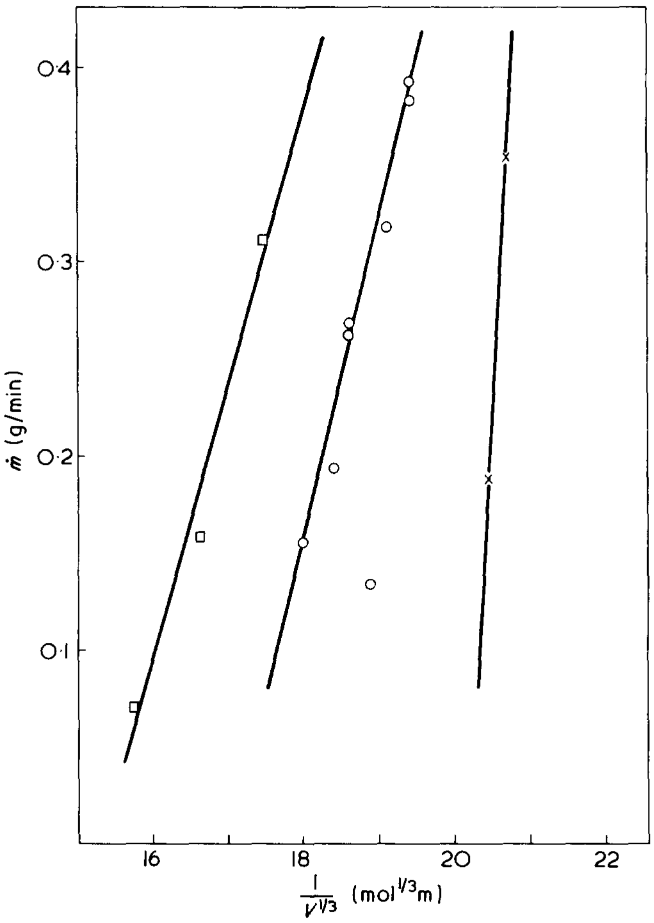

Figure 1 Effect of size of solvent molecules on the rate of dissolution of polypropylene at 120°C. Polymer disc diameter 50 mm, stirring speed 1000 rev/min. □, n-Alkanes; ○, aromatics and naphthenics; X, halogenated solvents

Figure 2 shows rate of dissolution plotted against $1/(V^{1/3}\eta)$ in accordance with equation (4). There is very

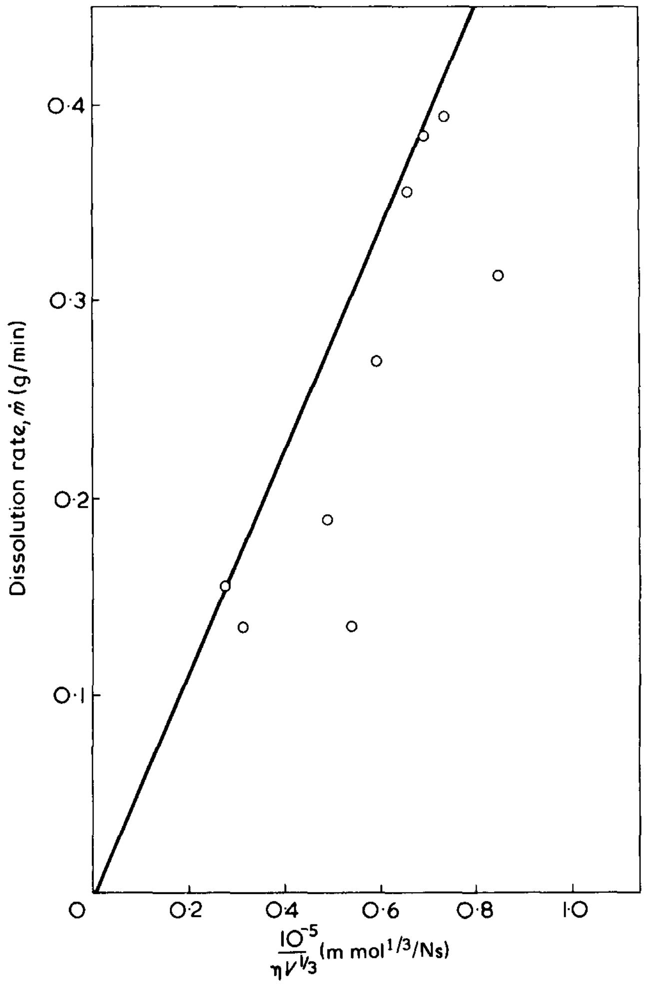

Figure 2 Combined effect of size and viscosity of solvent molecules on the rate of dissolution of polypropylene at 120° C. Polymer disc diameter 50 mm, stirring speed 1000 rev/min

considerable scatter in the data, but *Table 1* shows that the thermodynamic dissolution temperature of polypropylene, T_s, varies quite considerably with solvent. If, in *Figure 2*, a straight line is drawn through the decahydronaphthalene point and the origin, all other points lie below this line. Since decahydronapthalene is thermodynamically the best solvent, having the lowest T_s, a new similarity between the dissolution behaviour of polypropylene and that of the amorphous polymers investigated by Ueberreiter and Asmussen[9] is clear. (It was shown previously[2] that although polypropylene is a semicrystalline polymer there is a tendency for it to behave very much like an amorphous polymer under appropriate conditions). The straight line in *Figure 2* will be referred to as the 'best solvent line' using the adjective in a thermodynamic sense.

The Hildebrand Solubility Parameter for decahydronaphthalene is 17.2 $(\mathrm{MJ/m^3})^{1/2}$ compared with the polypropylene value of about 16.7 $(\mathrm{MJ/m^3})^{1/2}$. However, this parameter can be misleading as a guide to the relative effectiveness of solvents[1]. Chlorobenzene, for example, has a solubility parameter of 19.9 $(\mathrm{MJ/m^3})^{1/2}$, yet it is a very good solvent for polypropylene as evidenced by the fact that the experimental point on *Figure 2* comes very close to the 'best solvent line'. On the other hand, T_s for chlorobenzene is close to T_s for decahydronaphthalene and it therefore seems better to use T_s, rather than the Solubility Parameter, as a basis for correlating the data.

Figure 3 shows $(\underline{\dot{m}} - \dot{m})/\underline{\dot{m}}$ plotted against $(T_s - 102.7)$ for polypropylene dissolving in various solvents at 120°C. Here $\dot{m}$ is the experimentally determined dissolution rate and $\underline{\dot{m}}$, the hypothetical dissolution rate for the solvent concerned, is obtained from the 'best solvent' line on *Figure 2* for the appropriate abscissa. The thermodynamic dissolution temperature, T_s, is expressed in °C and 102.7°C is the value for decahydronaphthalene. The ordinate of *Figure 3* is a measure of deviations from the 'best solvent' line predictions, and it increases with T_s. In the limit as T_s approaches 120°C, the temperature of the actual dissolution experiments, $\dot{m}$ tends to zero and $(\underline{\dot{m}} - m)/\underline{\dot{m}}$ approaches unity. A feature of *Figure 3* is the fact that pure solvents and mixtures of solvents fall on separate curves, and it is necessary to explain the displacement of the mixture curves from the central curve representing pure solvents.

Consider first a mixture of p-xylene and 1-chloronaphthalene. On thermodynamic and kinetic grounds the former is a good solvent while the latter is a poor solvent on both grounds. The p-xylene molecule is the smaller of the two and would be expected to secure preferential absorption, the departure from bulk liquid composition being greatest at the point of deepest penetration of the solid by solvent. The elevated concentration of p-xylene in the liquid within the polymer will tend to reduce T_s for thick discs below the value measured for thin shavings. The values of $(T_s - 102.7)$ for these mixtures on *Figure 3* are therefore likely to be somewhat too high and the rightward shift of the curve for p-xylene/1-chloronaphthalene mixtures is understandable.

The opposite effect is shown by mixtures of decahydronaphthalene and n-decane where the curve is shifted leftwards. The n-decane is preferentially absorbed into the dissolving discs and has a relatively high value of $1/(\eta V^{1/3})$. However, it is thermodynamically inferior to decahydronaphthalene and the effective T_s in the dissolving discs is now higher than the value obtained for thin shavings. The values of $(T_s - 102.7)$ are therefore too low when these mixtures are plotted on *Figure 3* and the curve lies to the left of that for pure solvents.

To understand precisely why thermodynamic factors should affect the rate process it is important to recall the mechanism of the dissolution process[2]. It was shown previously that there are two dissolution regimes, one in which the dissolution rate is strongly dependent on density (crystallinity) and another in which the rate is largely independent of any ordered structures which may be present in the dry

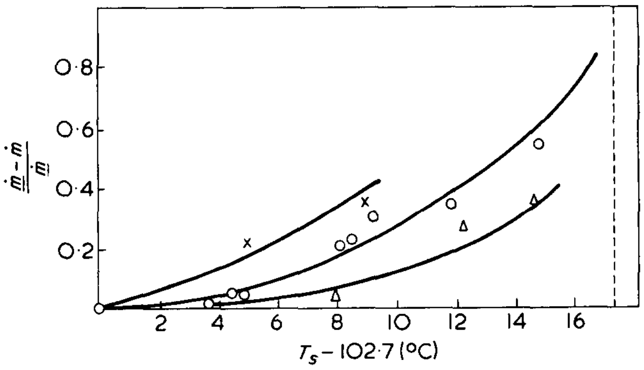

Figure 3 Effect of thermodynamic dissolution temperature on the rate of dissolution expressed as a deviation from the 'best solvent line'. ○, Pure solvents; △, mixtures of 1-chloronaphthalene and p-xylene; X, mixtures of decahydronaphthalene and n-decane

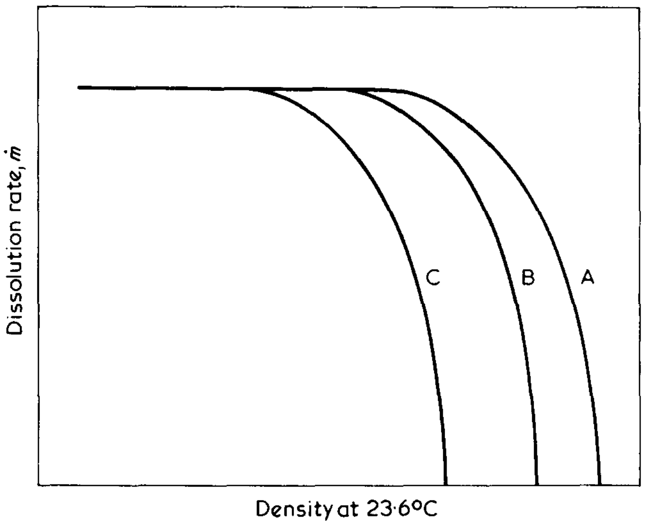

Figure 4 Schematic representation of the effect of density on the rate of dissolution of polypropylene in solvents of different thermodynamic suitability but having the same value of $1/(\eta V^{1/3})$ at a selected temperature

polymer. *Figure 4* shows schematically the dependence of dissolution rate on sample density for polypropylene dissolving in three different solvents at a fixed temperature, each solvent having the *same* value of $\eta V^{1/3}$. Curve A, based on previous work[2], is for decahydronaphthalene, the best solvent, while curves B and C represent hypothetical solvents which are progressively less suitable on thermodynamic grounds. At low densities the curves coincide and are virtually parallel to the density axis, indicating that structural factors are unimportant. The dissolution rate falls off with increasing density and the separation of curves A, B and C may be attributed to the thermodynamic factor. This is essentially the key both to the scatter on *Figure 2* and the correlation in *Figure 3*.

It is interesting to note (*Table 1*) that $\dot{m}$ changes very little with composition for mixtures of decahydronaphthalene with n-decane containing from 0 to 60 vol % of the latter. The thermodynamic and kinetic factors are certainly changing but in such a way as to nearly compensate one another.

Effect of temperature on the rate of dissolution of polypropylene in dissimilar solvents

The dissolution of amorphous polymers depends on temperature according to the equation:

$$\dot{s} = \dot{s}_0 \exp(-E_s/RT) \qquad (5)$$

where $\dot{s}$ is the velocity of penetration of polymer by solvent and E_s is the apparent activation energy for the process[14]. The formula can also be applied to polypropylene with the minor modification of replacing $\dot{s}$ by $\dot{m}$ which is the actual rate of dissolution of polymer. Provided that the density of the polypropylene is sufficiently low, that the temperature is sufficiently high and that the speed of stirring is low, the behaviour approximates to that of amorphous polymer.

Figure 5 shows log $\dot{m}$ plotted against $1/T$ for quenched polypropylene dissolving in *p*-xylene and in decahydronaphthalene. Taking only the straight portion of each curve E_s is found to be 31.4 and 58.0 kJ/mol. Ueberreiter and Asmussen[14] obtained values of 16.0 and 25.2 kJ/mol for amorphous polystyrene dissolving in toluene and in amyl acetate. The fact that the dissolution of semicrystalline polymer demands a higher activation energy seems entirely reasonable, and the very high value for decahydronaphthalene is probably best explained in terms of the large holes which such a molecule would require for diffusion through the polymer.

Effect of polymer density on the dissolution rate in dissimilar solvents

Figure 6 shows the effect of density (measured at 23.6°C) on the rate of dissolution of polypropylene in *p*-xylene and in decahydronaphthalene at 120°C. It was shown previously[2] that the intersection on the density axis of a curve showing $\dot{m}$ as a function of the density can be taken as the density at which all of the polymer will just dissolve at the given temperature of dissolution. In other words it gives T_s for a bulk specimen of polymer prepared in a certain way and having a particular density. It is not at all surprising that the curve for decahydronaphthalene interesects the density axis at a higher density than *p*-xylene because the former is the better solvent thermodynamically speaking, as evidenced by the lower T_s value (*Table 1*). *Figure 6* also shows a certain density at which the dissolution rates are the same in the two solvents. A solvent which dissolves quenched polypropylene rapidly is not necessarily the most effective solvent for specimens of higher density. Only if a given solvent is kinetically and thermodynamically the best for the polymer in its amorphous state will it give the fastest dissolution rate over the entire density range.

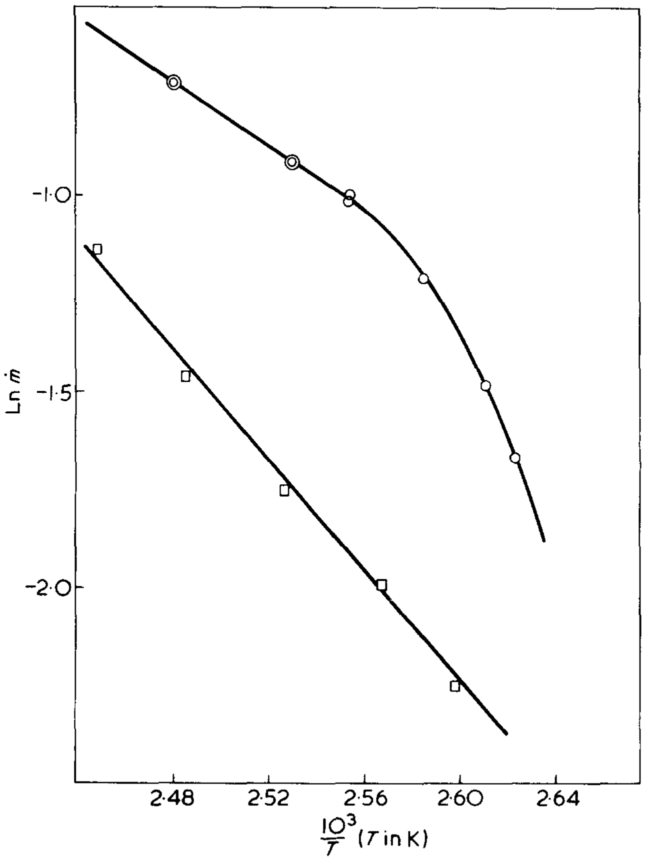

Figure 5 Effect of temperature on the rate of dissolution of quench-cooled polypropylene in *p*-xylene and decahydronaphthalene. Polymer disc diameter 50 mm, stirring speed 1000 rev/min. ○, *p*-Xylene; □, decahydronaphthalene

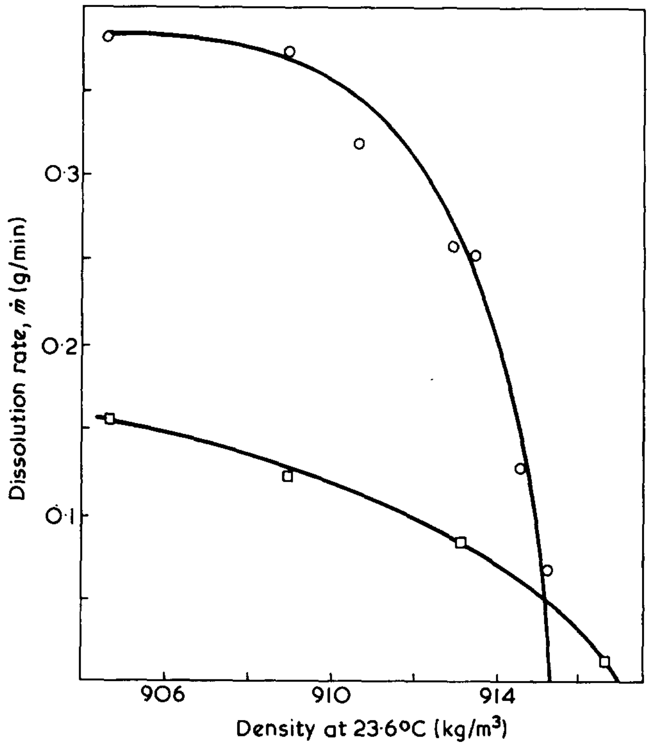

Figure 6 Effect of polymer density on the rate of dissolution of polypropylene in *p*-xylene and decahydronaphthalene at 120°C. Polymer disc diameter 50 mm, stirring speed 1000 rev/min. ○, *p*-Xylene; □, decahydronaphthalene

CONCLUSIONS

(1) The approach of Ueberreiter and Asmussen, which correlates rate of dissolution with solvent viscosity and molecular radius, is applicable to quenched polypropylene as well as to amorphous polymers. Scatter in the data can be explained in terms of the thermodynamic compatibility of polypropylene with the solvents concerned.

(2) The effectiveness of a binary solvent mixture in dissolving polypropylene is influenced by the relative size, flexibility and thermodynamic suitability of each component. The observed rate of dissolution is conveniently referred to the value predicted by averaging the results for pure solvents on the basis of the composition of the mixture. Mixtures containing a notable proportion of a fast-diffusing species which has a higher compatibility with the polymer than does the other component will always show a rate of dissolution higher than predicted. If, conversely, the fast-diffusing species is of low thermodynamic compatibility the rate of dissolution in the mixture will be lower than predicted.

(3) At temperatures sufficiently in excess of T_s a linear relationship is obtained when log $\dot{m}$ is plotted against $1/T$, and the activation energies can be interpreted in terms of the size of the solvent molecules.

(4) Solvents which dissolve quenched polypropylene rapidly are not necessarily as effective for specimens of higher density. Only when a solvent is kinetically and thermodynamically outstanding for quenched polymer will it retain its kinetic superiority over other solvents for all values of the polymer density.

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