Dissolution of polypropylene in organic solvents: 3. Effect of molecular weight of polymer

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Previous papers in this series have described the main features of the dissolution of solid polypropylene in organic solvents. The molecular weight of the polymer is now considered in connection with the rate of dissolution, the density of the specimens and the temperature of the dissolution experiments. A straight line relationship is obtained on plotting the log of the rate of dissolution (for fixed temperature and specimen density) against the log of the viscosity-average molecular weight.

INTRODUCTION

Previous papers[1,2] described the effects of temperature, stirring speed and density on the rate of dissolution of polypropylene in *p*-xylene. The rate depended on polymer density in quite a complicated way and it seems likely that chain length will have some bearing on the rate of dissolution.

Only two other groups of investigators[3,4] have considered the dissolution kinetics of polymer fractions in any detail and both were concerned with amorphous polymer. Their results could be represented by the general relation:

$$\dot{s} = K^{\dagger} M^{-\alpha} \tag{1}$$

where $K^{\dagger}$ and α are constants. M is the number-average molecular weight and $\dot{s}$ the rate of solvent penetration into the solid. For polystyrene dissolving in toluene, Asmussen and Ueberreiter[4] found that α, unlike $K^{\dagger}$, was independent of temperature and the conditions of stirring. They also proposed[5] that the dissolution rate could be expressed as:

$$\dot{s} = \frac{\bar{D}^{\nu}}{\delta} \tag{2}$$

where $\bar{D}^{\nu}$ is the mean mutual diffusion coefficient and δ the thickness of the boundary layer of solvent-swollen polymer. $\bar{D}^{\nu}$ was independent of molecular weight, and at constant temperature and stirring speed the effect of chain length was manifested in δ only.

The previous paper[2] showed many similarities between the dissolution of quenched unfractionated polypropylene and the dissolution of amorphous polymer. The aim of the present paper is to show if quenched fractionated polypropylene obeys a relationship like equation (1), and to establish the extent to which it behaves like an amorphous polymer.

EXPERIMENTAL

Materials

Polymer. The polypropylene used was a homopolymer, GXM 43, kindly supplied by ICI Plastics Division. It was quoted as having a melt flow index of 2.16 and a melt viscosity of 5.0 x 10^3 Nsec/*m* at 190°C.

Solvent. The *p*-xylene was a 99% product obtained from ICI.

Procedures

Fractionation of polymer. Fractions of polypropylene were prepared by a fibrous deposition method based on that used by Pennings[6] and by Salovey and Hellman[7]. Polypropylene chips (20 g) were dissolved at 130°C under a nitrogen atmosphere in 2 x 10^{-3} m^3 of *p*-xylene containing 0.005% w/v of BHT anti-oxidant. The polymer was precipitated in fibrous form by cooling to 72°C with constant stirring, and the clear solution was decanted from the vessel. Methanol was added at room temperature to precipitate all the polymer still in solution. After filtering and washing with acetone the fraction was dried in a vacuum oven at 60°C for 24 h. Fresh *p*-xylene was added to the vessel containing the fibrous polymer and the temperature was raised to 102°C with continuous stirring. After 2 h at this temperature the process of decanting the clear solution and recovering the dissolved polymer was repeated. Other fractions were obtained at higher temperatures up to 113°C and numbered 1 to 8 in ascending order of temperature of extraction. All the solid polymer remaining at 113°C was dissolved at 125°C, precipitated with methanol and set aside as the fraction of highest molecular weight. The whole fractionation was repeated with four more 20 g quantities of polypropylene.

Certain of the fractions thus obtained were combined. All fractions 1 from the five separate preparations were used to form fraction A, while fraction E consisted of all the polymer not dissolved at 113°C. Fractions B, C and D were obtained by combining all the fractions 2 and 3, 4 and 5, 6 and 7 respectively. To make the lettered fractions 'homogeneous' they were each re-dissolved in *p*-xylene and preci-

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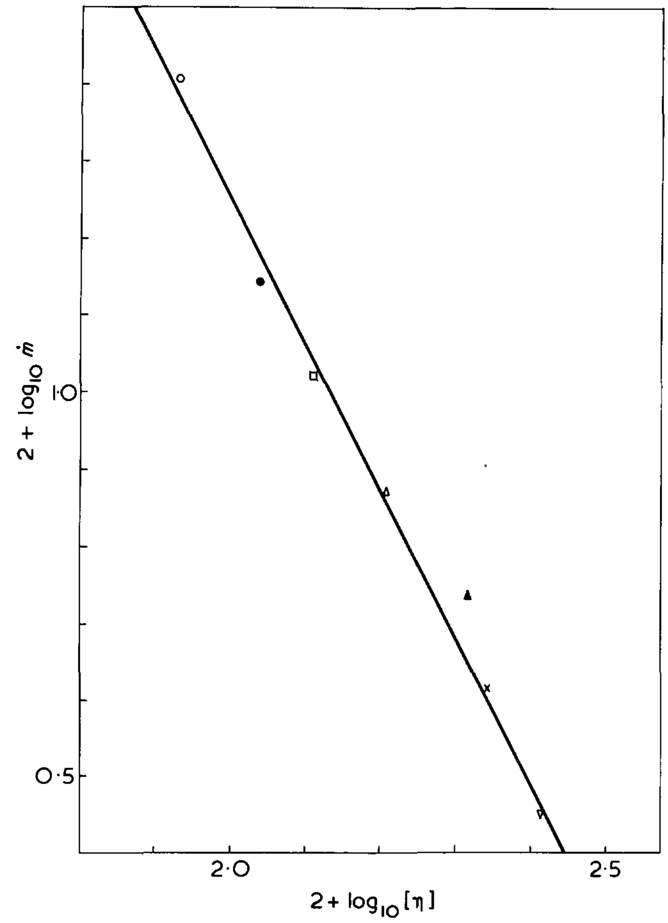

Figure 1 Dissolution of polypropylene specimens of constant density in *p*-xylene at 120°C (specimen diameter 25 mm, stirring speed 500 rev/min). Logarithmic relationship between rate of dissolution and limiting viscosity number

Symbol	Specimen	2 + log$_{10}$(η)	$\bar{M}_v$ (equation 7)
○	Fraction B	1.93	82 100
□	Fraction C	2.12	142 200
△	Fraction D	2.21	183 100
▽	Fraction E	2.41	330 000
●	Mixture F (50–50 B and C on weight basis)	2.04	112 400
▲	Mixture G (50–50 D and E on weight basis)	2.32	249 100
X	Unfractionated	2.34	267 600

pitated with methanol.

Characterization. The specific viscosity, η_{sp}, was determined for 0.25 g/dl solutions of each fraction in decahydronaphthalene at 135°C. The limiting viscosity number (η) was then calculated from Chiang's formula[8]:

$$\log_{10}(\eta_{sp}/c) = \log_{10}(\eta) + 0.18(\eta)\,c \qquad (3)$$

where c is the concentration in g/dl (concentration in kg/m^3 = 10c).

Rate of dissolution. The rate of dissolution of each fraction was measured using the apparatus and procedures described in the previous paper[2]. The specimens were in the form of discs 25 mm in diameter rotated at 500 rev/min in *p*-xylene. Each disc was prepared by quench cooling the melt and weighed about 2 g. The density of a specimen was increased as required by annealing it for 2 h at an appropriate temperature. Each dissolution run lasted for between 5 and 30 min.

Density. Densities were measured in a density gradient column at 23.6°C using chlorobenzene and *p*-xylene as column liquids. Precautions and corrections were as described previously.

RESULTS AND DISCUSSION

Effect of molecular weight of polypropylene on rate of dissolution

Suppose that the rate of dissolution follows equation (1) in a slightly modified form.

$$\dot{m} = K^{\ddagger}M^{-\alpha} \qquad (4)$$

Here $\dot{s}$ has been replaced by $\dot{m}$, the mass rate of dissolution used in the present work, and the replacement of $K^{\dagger}$ by $K^{\ddagger}$ preserves the proportionality.

The Mark–Houwinck equation relates limiting viscosity number and molecular weight, where K and α are constants for a particular polymer, solvent and temperature:

$$(\eta) = KM^{a} \qquad (5)$$

Combining equations (4) and (5):

$$\log_{10}\dot{m} = \log_{10}K^{\ddagger}K^{\alpha/a} = (\alpha/a)\log_{10}(\eta) \qquad (6)$$

In *Figure 1* $\log_{10}\dot{m}$ is plotted against $\log_{10}(\eta)$ for quenched specimens, all of the same density, dissolving in *p*-xylene at 120°C. The caption to the Figure gives $\bar{M}_v$ values calculated from Chiang's formula[8].

$$(\eta) = 1.00 \times 10^{-4}\bar{M}_w\ 0.8 \qquad (7)$$

The molecular weight calculated from this formula is taken to be $\bar{M}_v$ rather than $\bar{M}_w$ for the following reason.

The excellent straight line in *Figure 1* shows that the limiting viscosity number is a very appropriate parameter with which to correlate the rate of dissolution under specified conditions. Now equation (5) is normally taken to apply to viscosity-average molecular weights unless, of course, the materials concerned are all such sharp fractions that $\bar{M}_v$ and $\bar{M}_w$ are indistinguishable. The fractions used here were not particularly sharp as a result of mixing portions from different fractionation runs, and the results actually include two mixtures of lettered fractions. These would certainly not have a sharp distribution.

Effect of temperature and density of specimen on rate of dissolution

Figure 2 is typical of the results and shows the rate of dissolution of fraction C plotted against density (measured at 23.6°C) for various dissolution temperatures. The curves are similar to those for unfractionated polymer presented in the previous paper[2]. Each curve tends to flatten out at the lower densities but becomes progressively steeper as it approaches its intersection with the density axis.

The significance of the intersections with the density axis was discussed previously[2].

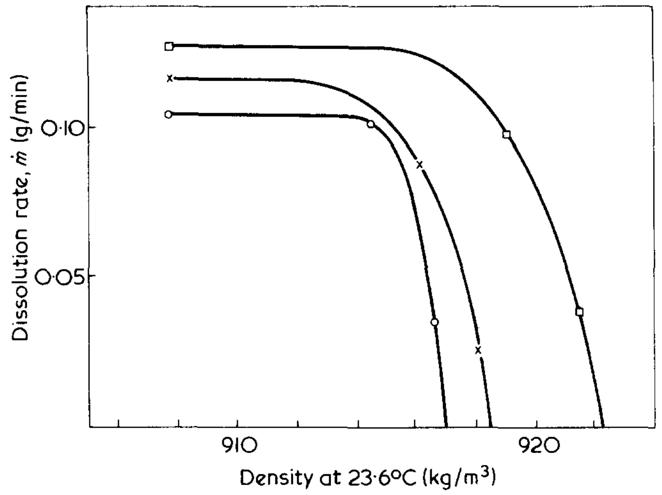

Figure 2 Dissolution of fraction C in *p*-xylene at various temperatures. Rate of dissolution as a function of specimen density: □, 126.9°C; X, 122.5°C; O, 118.9°C

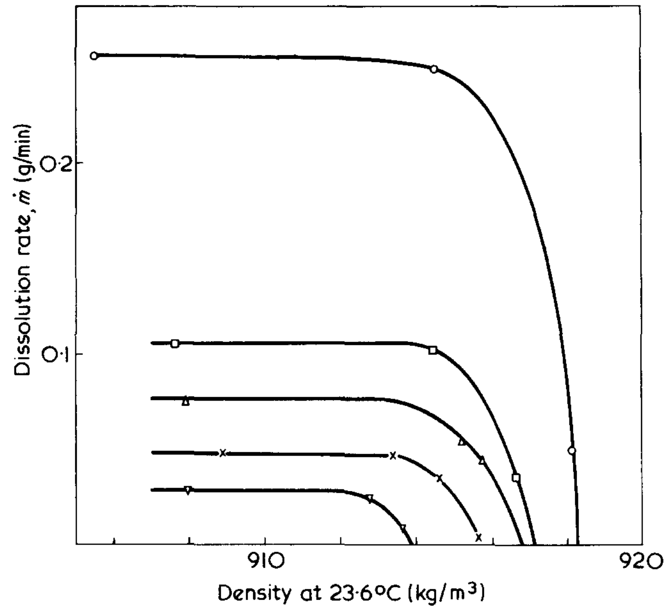

Figure 3 Dissolution of various specimens in *p*-xylene at 118.9°C. Rate of dissolution as a function of specimen density. For key to symbols see caption to *Figure 1*

Figure 3 shows dissolution rate plotted against density for various fractions at a fixed temperature of 118.9°C. This plot brings out other features of the results. The intersection of each curve with the density axis occurs at a density which increases as the molecular weight decreases. The curve for unfractionated polymer falls neatly between those for fractions D and E as expected on the basis of the molecular weights in the caption to *Figure 1*. The same features are shown by experiments at 122.5° and 126.9°C.

It is not surprising that fractions with similar densities may have different dissolution rates at a given temperature or the same dissolution rate at different temperatures. This probably arises from the familiar observation that for fixed annealing conditions of time and temperature the density of a specimen decreases with increasing molecular weight. *Figure 4* shows the effect clearly for the polypropylene fractions annealed at various temperatures for 2 h each.

It is clear that density has to be used with care when describing the dissolution behaviour of fractions and, indeed, annealing temperature may be the more useful property. It is certain, however, that the dissolution rate at a given temperature will always be greater for polymer of lower molecular weight at any given density, provided that the annealing times are held constant during the specimen preparation stage.

CONCLUSIONS

(1) As for amorphous polymer, the rate of dissolution of quenched isotactic polypropylene is dependent upon its molecular weight. There is an excellent linear relationship between the log of the rate of dissolution and the log of the limiting viscosity number of the polymer for fixed conditions of dissolution and specimens of constant density.

(2) At a specified temperature of dissolution the rate of dissolution extrapolates to zero at a density which increases as the molecular weight decreases provided that the annealing time is constant. Over the whole range of densities available the rate of dissolution is always greater for lower molecular weight samples, the annealing time again being held constant.

(3) For a given temperature of annealing the density of the specimen is dependent upon its molecular weight. The higher the molecular weight, the lower the resultant density.

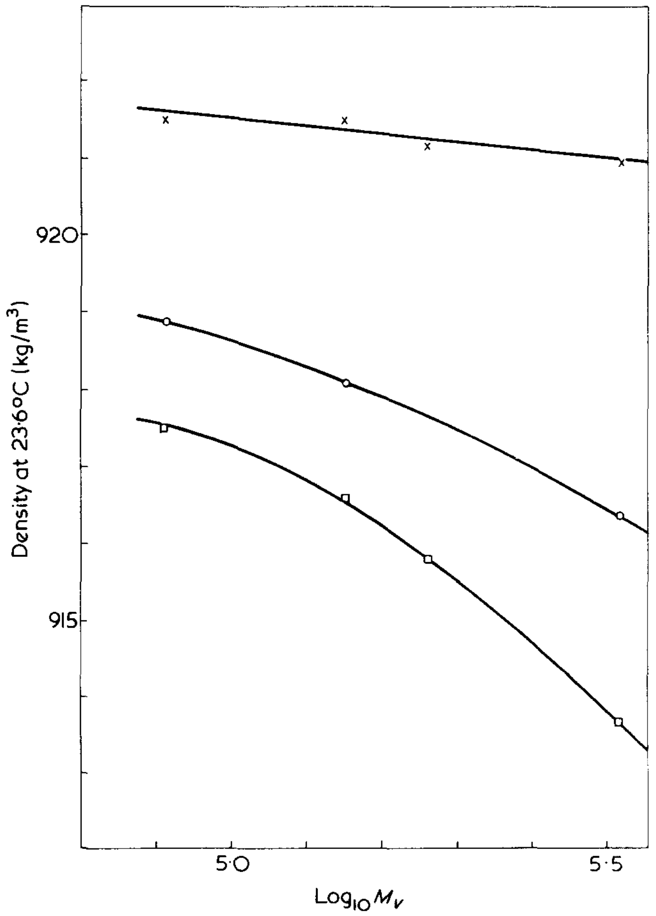

Figure 4 Effect of molecular weight and annealing temperature on the density of polypropylene specimens (annealing time 2 h throughout): X, annealing temperature 161°C; O, annealing temperature 158°C; □, annealing temperature 151°C

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