Dissolution of polypropylene: differential solubility

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Isotactic polypropylene is a polydisperse semicrystalline polymer. Observation of the molecular weight, morphological and crystallinity changes which occur on immersion of film samples in tetrachloroethylene at temperatures $<T_s$ (95°C) and $>T_s$ (100°C) have been made. The results show that the polymer exhibits differential solubility of the crystalline and amorphous phases and of the various molecular weight fractions. The results are augmented by scanning electron micrographs which confirm the dissolution processes.

Keywords Polypropylene; solvent; tetrachloroethylene; crystallinity; differential solubility; thermodynamic dissolution temperature (T_s)

INTRODUCTION

The dissolution of macromolecules in organic solvents has been dealt with in detail by Ueberreiter and by Blackadder.

At least three factors are known to determine the solubility of a polymer in a solvent[1]:

(i) The combinatorial entropy of mixing.

(ii) An enthalpic effect arising from any difference in contact energies and intermolecular forces between the polymer and the solvent.

(iii) An effect due to the difference in free volume between the polymer and the solvent.

The solution process is a result of two opposing influences:

(i) the diffusion of solvent molecules into the polymer, which is caused by the chemical potential gradient set up, the rate of diffusion being determined by the molecular volume and chemical structure of the solvent;

(ii) the setting up of a swollen layer on the surface of the polymer, which acts as a resistance to diffusion by diminution of the concentration gradient in the region of this layer[2].

In the case of semicrystalline polymers such as polypropylene there exist diversified aggregations of molecular chains ranging from perfectly crystalline to completely amorphous. In the crystalline regions the polymer chains are laid down in an orderly fashion. The non-crystalline regions consist of whole molecules (largely of low molecular weight) and portions of molecules partly incorporated in one or more crystalline lamellae. The conditions of crystallization determine the number and length of these ties. In a quenched melt there are a large number of ties having a wide distribution of lengths, as the chains have little time to disentangle themselves from configurations typical of the melt. In a slowly cooled sample there should be fewer ties of more uniform length[3].

It is not unreasonable, in the light of these structural differences, to expect the dissolution behaviour of semicrystalline polymers to differ from that of totally amorphous polymers. Differential solubility may be expected where some regions of the polymer are more soluble than the remainder under given conditions[4].

Important factors when considering the dissolution of semicrystalline polymers are solvent temperature, polymer density and molecular weight. Semicrystalline polymers dissolve less readily than amorphous polymers and few solvents are suitable. At temperatures well below their melting points, semicrystalline polymers do not completely dissolve in organic solvents. The positive entropy changes associated with fusion and mixing do not compensate sufficiently for the large heat of fusion and so overall the free energy change for crystallite dissolution is positive. With semicrystalline polymers, the activation energy for dissolution varies considerably with temperature and polymer density resulting in a more complicated situation than that for amorphous polymers. A graph of log dissolution rate against reciprocal dissolution temperature generally results in a curved plot, and the curvature of the Arrhenius plot is attributed to the controlling influence of crystallite destruction in polymer dissolution[5].

As mentioned, density is another important factor. A significant difference between amorphous and crystalline polymers is that at any given temperature the density of an amorphous polymer is more or less fixed while that of a semicrystalline polymer is dependent upon its thermal history. The dissolution rate of polypropylene has been

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observed to increase with decreasing polymer density, although not in a simple manner[5]. The effect of density on dissolution is further complicated by the fact that exposure of a polymer to a solvent at high temperatures for a long time results in considerable morphological changes in the polymer. However, the influence of density is best explained by the increase in fold length of the polymer chains which accompanies an increase in density.

Finally one must consider the polymer molecular weight. The entropy per unit volume of a solution at constant volume or weight fraction decreases with increasing size of the solute molecules. The free energy will thus increase and the solution stability will decrease with the result that increasing the molecular weight of the polymer makes dissolution more difficult[1].

Semicrystalline polymers such as polypropylene can thus be considered to be composite materials, consisting of purely amorphous and purely crystalline regions, with a wide morphological spectrum inbetween. It is expected that the dissolution behaviour of such a polymer is complex, with contributions from each region.

This paper attempts to illustrate this point by observing the molecular weight, morphological and crystallinity changes which occur on exposure of polypropylene film samples to a kinetically and thermodynamically good solvent (tetrachloroethylene)[6], both above and below the thermodynamic dissolution temperature, T_s, of the polymer in this solvent.

EXPERIMENTAL

Materials

The polymer film was prepared from stabilized polypropylene granules (Shell KY61) by slit film extrusion, with a 5:1 draw ratio, as described previously[7]. Tetrachloroethylene was purchased from Hopkin and Williams Ltd.

Solvent extraction of polypropylene film

Solvent extraction of the polymer films involved introducing film samples (150 mm lengths) into a solvent container housed in a thermostatically controlled oil bath. Following exposure, excess solvent was removed by pressing the samples lightly between filter paper. The samples were then dried to constant weight, at 40°C, in an oven.

Crystallinity measurements

(a) A Perkin Elmer DSC 1B Differential Scanning Calorimeter was used to determine the melting points and heats of fusion of the samples. The value for heat of fusion of 100% crystalline polypropylene was taken as 59 cal g^{-1}.

(b) The method of Natta *et al.*[8] was used to determine the percentage crystallinity from data obtained from wide-angle X-ray diffraction patterns. The equipment used was a Philips Wide-Angle X-ray Diffractometer, Model P.W. 1050 with a Rigaku-Denki 2c X-ray tube.

(c) Density measurements were carried out using a Techne D C-1 Density Gradient Column with TE7 thermoregulator. The density of amorphous phase polypropylene was accepted as 0.855 g cm^{-3} and that of crystalline phase polypropylene as 0.936 g cm^{-3}.[9]

Viscosity measurements

Viscosity average molecular weights for the samples were calculated using the Mark–Houwink correlation using intrinsic viscosity data. Decalin at 135°C was used as the solvent for the polypropylene. The viscometer used was an ASTM No. 1 Ubbelohde type. Values of constants used in the Mark–Houwink equation were $K = 1.1 \times 10^{-4}$, $a = 0.8$.

Molecular weight distribution

The molecular weight distributions of the film samples were determined by gel permeation chromatography. This work was carried out by RAPRA using a Waters 200 GPC with a differential refractometer as the detector. The chromatograms obtained were computer analysed and the results obtained enabled plots of molecular weight distribution to be made and values of number, viscosity, weight and Z-average molecular weights to be determined.

RESULTS AND DISCUSSION

Short term exposure of polypropylene film samples (i.e. immersion in solvent for 10 min) at temperatures from 25° to 90°C had no noticeable effect, as determined by electron microscopy. However, exposure at 95°C, (just below the T_s for the polymer–solvent combination, i.e. 98.8°C,[6]) and at 100°C produced marked effects, and samples exposed at these temperatures were investigated in terms of molecular weight and molecular weight distribution changes, and changes in crystallinity as measured by density, differential scanning calorimetry, and wide angle X-ray scattering methods.

Table 1 illustrates the change in crystallinity occurring in film samples exposed at 95°C, for increasing exposure times.

Generally, film crystallinity is observed to increase with exposure time. The initial fall in crystallinity as measured by WAXS is attributed to the relaxation of draw and orientation which occurs on exposure to the solvent and the resultant change in the scattering pattern as shown by *Figures 1* and *2*. The general increase in crystallinity may be attributed to the selective dissolution under these conditions of atactic and amorphous material, although solvent induced recrystallization may also play a part.

Table 2 records the molecular weight changes as measured by viscometry. The exposure conditions are such that the dissolution of atactic, amorphous, and perhaps low molecular weight crystalline material is possible, with the dissolution of low molecular weight polymer chains being favoured.

The viscometry results support the thesis that under the above conditions of exposure, selective dissolution occurs. The viscometry results are supported by the results of gel

Table 1 Crystallinity changes

	Percentage crystallinity		
Film exposure	d.s.c.	WAXS	Density
Control film (zero exposure)	44	60	60
95°C, 1 min	51	52	66
95°C, 5 min	56	56	68
95°C, 10 min	53	63	72

permeation chromatography shown in *Table 3* and *Figure 3*. From these results the extraction of the low molecular weight tail of the molecular weight distribution with increasing exposure time is obvious. As low molecular weight material is removed the distribution curves sharpen as shown by the values of the $\bar{M}_w/\bar{M}_n$ and $\bar{M}_z/\bar{M}_n$ ratios. Crosslinking may also be a possibility, given the shift of the distribution curves to the higher molecular weight zone observed with increasing exposure time.

Electron micrographs obtained for the various treated films are included as *Figures 4–7*. The electron micrographs were obtained using the scanning mode with the samples coated directly in gold. The virgin polymer film is virtually featureless except for some draw induced striations, which indicate the partial fibrillar nature of the film. However, the micrographs of the exposed films bear some similarity to micrographs of photooxidized polypropylene film, obtained by Blais *et al.*[10] In their work, degraded polymer was stripped-off prior to producing the micrographs. The similarity may be understood if one accepts their proposal that photo-oxidative degradation occurs more readily in the amorphous regions.

Exposure of polypropylene film to tetrachloroethylene solvent at 100°C will rapidly result in polymer dissolution. However, if exposure is terminated after five or ten seconds the film is still intact. The crystallinity and viscometry results obtained here are recorded as *Tables 4* and *5*. At 100°C complete polymer dissolution can occur. The time scale of events is shortened drastically as compared to the previous exposure conditions and film integrity is destroyed rapidly.

The results in *Table 4* show that there is an initial increase in crystallinity as measured by d.s.c. and density methods. This increase, which is possibly due to the preferential loss of amorphous material, is followed by a

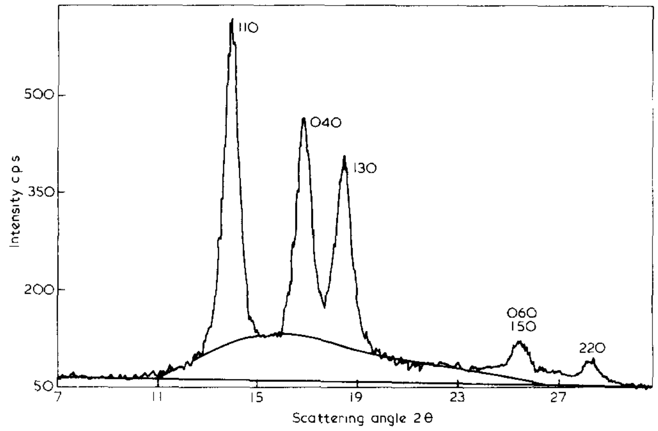

Figure 1 WAXS on control film (5:1 draw ratio)

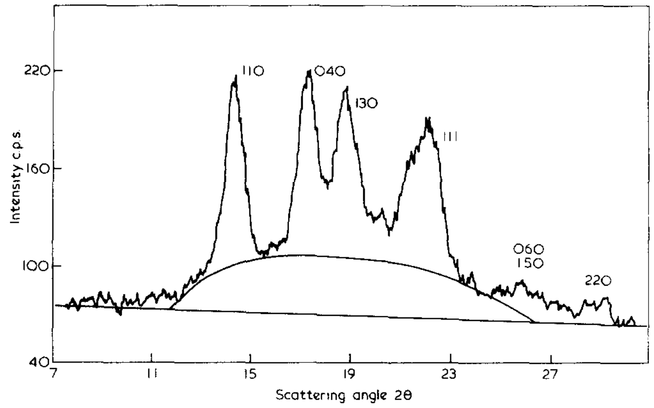

Figure 2 WAXS on film exposed at 95°C for 1 min

Table 2 Viscosity average molecular weight changes

Film exposure	$\bar{M}_v$ of film after exposure	$\bar{M}_v$ of extract	Sample % weight loss
Control film	238 x 10^3	–	–
95°C, 1 min	260 x 10^3	55 x 10^3	34
95°C, 5 min	313 x 10^3	66 x 10^3	47
95°C, 10 min	333 x 10^3	68 x 10^3	58

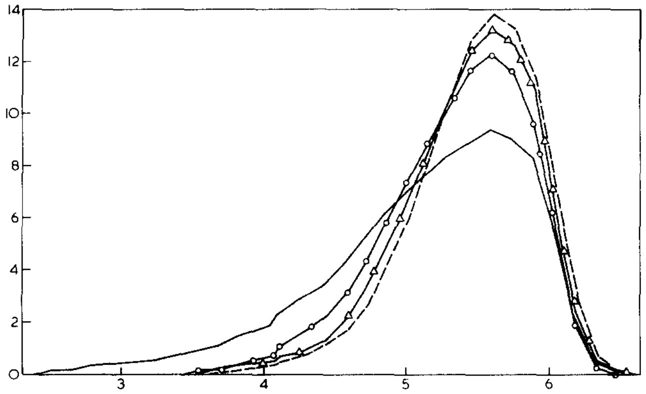

Figure 3 Differential molecular weight distributions for selective polymer dissolution. (——) control; (–○–○–○–) 95°C for 1 min; (–△–△–△–) 95°C for 5 min; (– – – –) 95°C for 10 min

Table 3 Molecular properties of exposed films

Film exposure	$\bar{M}_n$ x 10^5	$\bar{M}_v$ x 10^5	$\bar{M}_w$ x 10^5	$\bar{M}_z$ x 10^5	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_n$
Control film	0.1957	2.894	3.311	7.790	16.92	39.80
95°C, 1 min	0.9892	3.446	3.772	7.044	3.81	7.12
95°C, 5 min	1.1950	3.917	4.260	7.872	3.56	6.59
95°C, 10 min	1.1570	4.318	4.667	8.296	2.97	5.28

decrease in crystallinity as low molecular weight material begins to be leached out of the crystalline regions. Thus, above T_s, all fractions of the polymer are thermodynamically soluble but, in the short time used, amorphous and low molecular weight crystalline fractions are kinetically preferred. The crystallinity results obtained by WAXS are again confused due to changes in scattering pattern brought about by changes in orientation due to relaxation occurring when the drawn film is exposed to the solvent.

While the results for $\bar{M}_v$ of the exposed film samples, *Table 5* do not show the marked increase in $\bar{M}_v$ observed in the previous case (i.e. below T_s, *Table 2*), the increase in the molecular weight of the extracted fraction with exposure time supports the implication of the crystallinity results shown in *Table 4*, that at a temperature at which all molecular weight fractions are soluble, preferential dissolution can still be observed. This is further supported by the results obtained by gel permeation chromatography shown in *Table 6*. From these results it can be clearly seen that on initial exposure the values of $\bar{M}_n$, $\bar{M}_v$ and $\bar{M}_w$ all increase and, more significantly, the

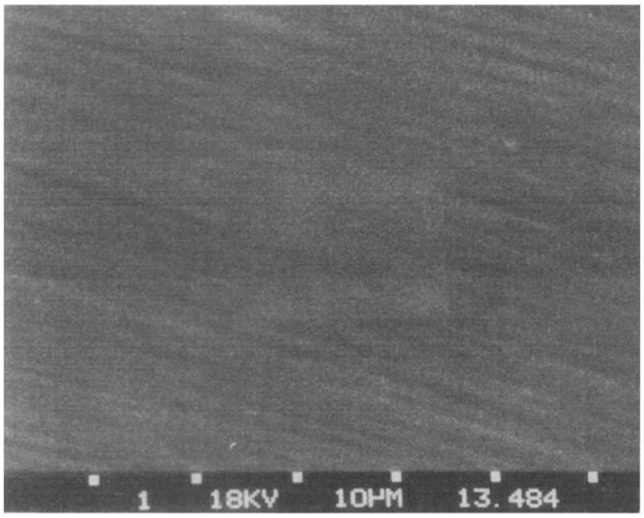

Figure 4 PP film zero exposure (x1600)

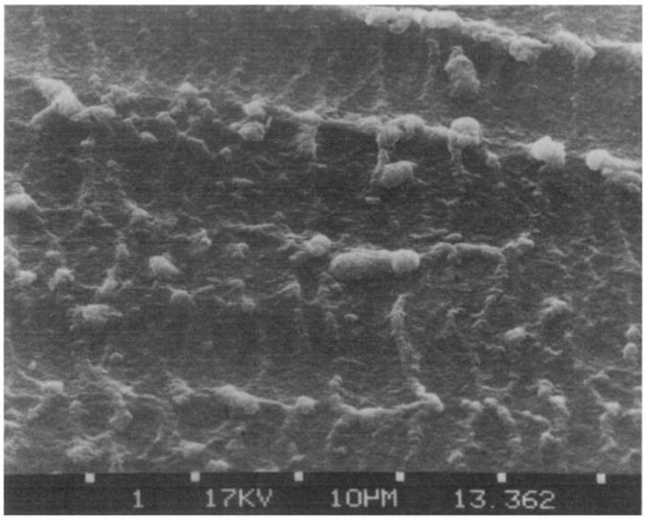

Figure 5 PP film exposed 95°C, for 1 min (x1600)

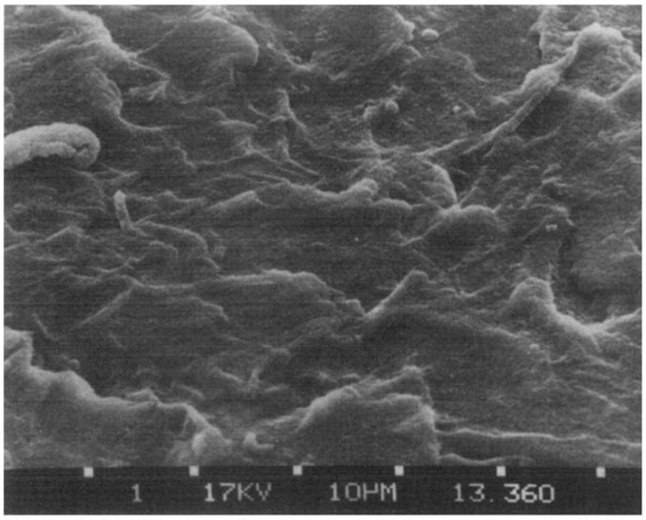

Figure 6 PP film exposed 95°C, for 5 min (x1600)

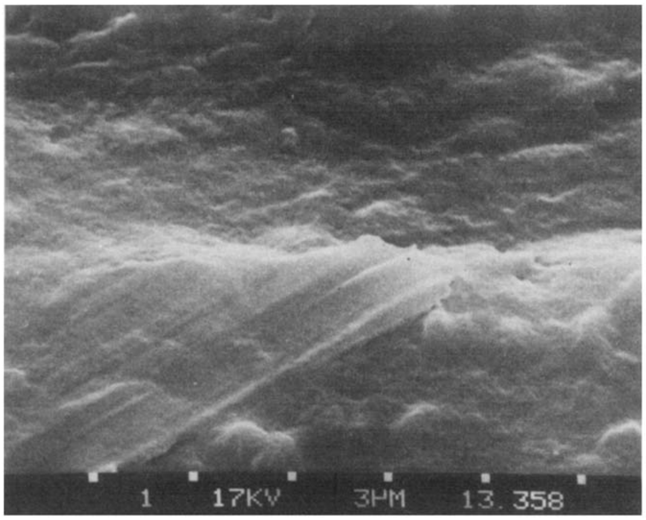

Figure 7 PP film exposed 95°C, for 10 min (X1600)

Table 4 Crystallinity changes

	Percentage crystallinity		
Film exposure	d.s.c.	WAXS	Density
Control film	44	60	60
100°C, 5 s	56	56	63
100°C, 10 s	42	60	59

Table 5 Viscosity average molecular weight changes

Film exposure	$\bar{M}_v$ of film after exposure	$\bar{M}_v$ of extract	Sample % weight loss
Control film	238×10^3	–	–
100°C, 5 s	237×10^3	99×10^3	10
100°C, 10 s	240×10^3	126×10^3	13

Table 6 Molecular properties of exposed films

Film exposure	$\bar{M}_n \times 10^5$	$\bar{M}_v \times 10^5$	$\bar{M}_w \times 10^5$	$\bar{M}_z \times 10^5$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_z/\bar{M}_n$
Control film	0.1957	2.894	3.311	7.790	16.92	39.80
100°C, 5 s	0.4611	2.972	3.359	7.556	7.28	16.39
100°C, 10 s	0.4295	2.637	3.207	7.175	7.47	16.70

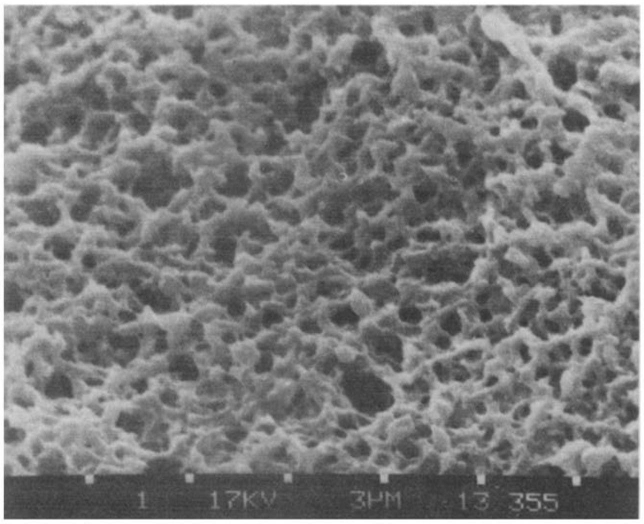

Figure 8 PP film exposed 100°C, 5 s (x5200)

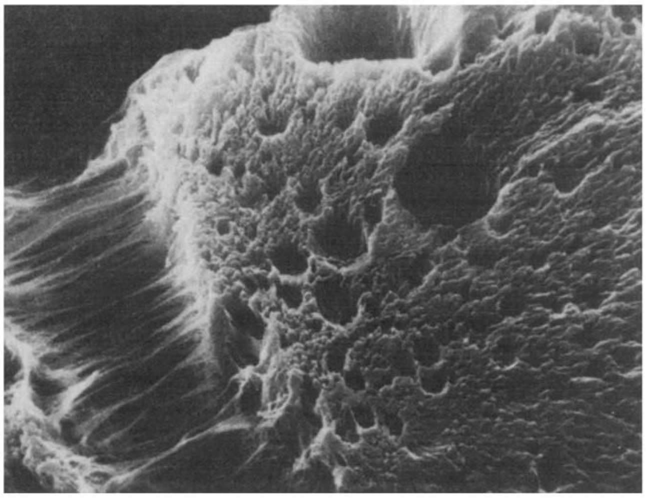

Figure 10 PP powder (x3000)

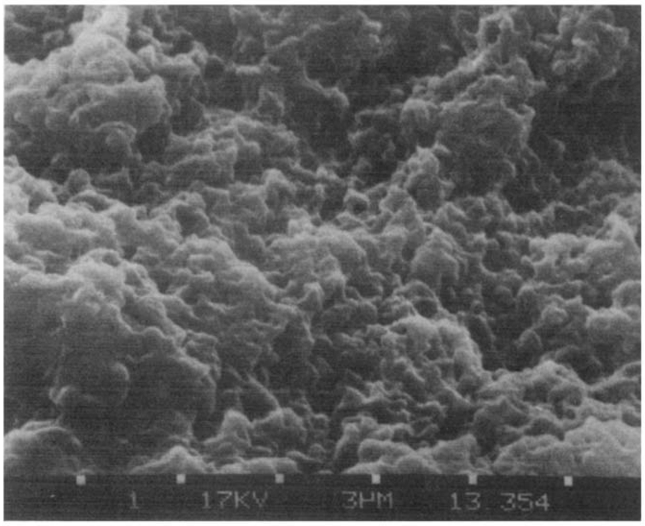

Figure 9 PP film exposed 100°C, 10 s (x5200)

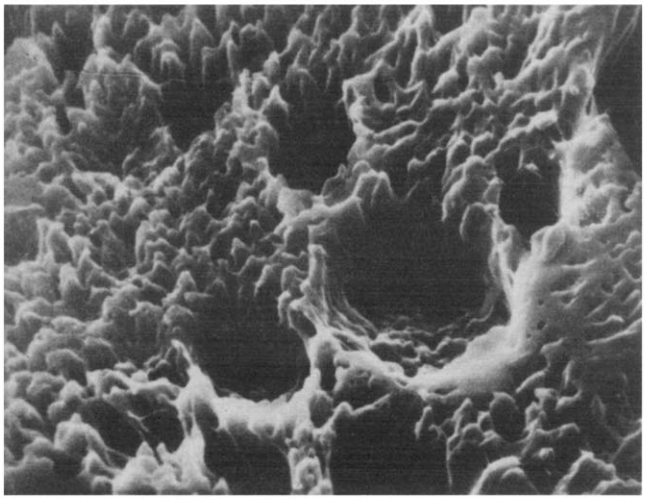

Figure 11 PP powder (x10000)

polydispersity indices fall drastically, indicating dissolution of amorphous components of the polymer. After 10 s exposure, however, the molecular weight averages begin to decrease as higher molecular weight chains are dissolved.

The electron micrographs obtained for the exposed film samples are included as *Figures 8* and *9*. These micrographs were obtained to show polypropylene film in mid-dissolution. However, it is more likely that they show polypropylene crystallized from a concentrated solution formed on the film surface on exposure to the solvent. Indeed they show some similarity to micrographs of the surface of polypropylene powder precipitated from a concentrated solution (10%w/w) of the polymer in tetrachloroethylene and included here as *Figures 10* and *11*.

CONCLUSIONS

The results for polypropylene film exposed to tetrachloroethylene solvent at 95° and 100°C show the differential solubility of a semicrystalline polymer, where some regions of the polymer are more soluble than others under given conditions.

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