Reversible secondary crystallization during cooling of polypropylene

P. D. Calvert and T. G. Ryan
School of Chemistry and Molecular Sciences, University of Sussex, Brighton, BN1 9QJ, UK, and Imperial Chemical Industries PLC, The Heath, Runcorn, Cheshire, UK
(Received 6 June 1983; revised 15 November 1983)

Ultra-violet microscopy has been used to follow the distribution of fluorescent additives during the isothermal crystallization and cooling of polypropylene. During cooling from the crystallization temperature there is a flow of additives away from the spherulite centres and into the spherulite boundaries. This demonstrates a marked densification at the centre of the spherulites with less within the bulk and only a small increase at the boundary. This change reverses when the sample is reheated to the crystallization temperature. Thus spherulites which appear to be quite uniform in crystallinity at high temperatures become non-uniform on cooling. The spherulites also become fibrous in appearance when cool. These effects are explained in terms of non-uniform concentrations of poorly crystallizable polymeric species which retard secondary crystallization.

(Keywords: polypropylene; spherulites; ultra-violet microscopy; additives; crystallization; fluorescers)

INTRODUCTION

Polypropylene contains a wide range of impurity species which may not be incorporated into the lamellar crystals during spherulite growth. This includes small mobile molecules such as dissolved gases, immobile particles of catalyst residue, a variety of atactic, stereoblock and low molecular weight polymeric species and stabilizing additives. In a previous paper[1] we described the use of ultra-violet and fluorescent microscopy to follow a number of additives, principally phenolic antioxidants and ultraviolet absorbers, during the crystallization of polypropylene. These large, partly aromatic molecules do not enter the crystals but diffuse into the interlamellar amorphous regions or ahead of the growing spherulite into the uncrystallized liquid and so tend to concentrate at the spherulite boundaries. These additive concentrations of 1 wt.% or less do not perceptibly alter the crystallization behaviour of the polymer.

In an extension of this technique[2] we found that prolonged annealing at the crystallization temperature did not lead to a disappearance of gradients in additive concentration within the sample although this would be expected to result from diffusion within the spherulite. Instead the additive concentration relaxed to a distribution which reflected the variations in the local amorphous content of the spherulite. Thus crystallinity variations within the spherulite could be measured.

Here we describe changes occurring when such annealed samples are cooled to room temperature. Largely as a result of constraints imposed by entanglements and chain folding, polymers rarely seem to approach an equilibrium state of crystallization. Instead, at temperatures above the glass transition, the morphology continually adjusts at a rate which depends on the temperature and the existing morphology[3,4]. For the purposes of this discussion we can identify the primary crystallization as the initial process occurring at the interface between the spherulite and the liquid. The main factors involved are the kinetics of addition of chains to suitable step sites on the lamellar surface which will determine growth rate, initial lamellar thickness and the pattern of folding of the chains. Concurrently with the growth of the spherulite, isothermal annealing will lead to an increasing crystallinity by lamellar thickening, crystal perfection and possibly the formation of new crystals in the interlamellar spaces[5,6]. The rate of annealing is much increased if the sample is heated above its original crystallization temperature[3].

Secondary crystallization occurs during cooling from the crystallization temperature. The effect has been studied by dilatometry[4] and small- and wide-angle X-ray diffraction[3,7]. Two processes may be involved, a reversible thickening of existing crystals due to changes in the fold surface layer[3] and growth of new crystals or extension of existing crystals into the interlamellar region[7]. This region will contain molecules rejected during the primary crystallization. The latter mechanism is supported in polyethylene by electron microscope observations showing regions of very small, thin crystals within a spherulite containing predominantly larger crystals[8,9]. Continuing slow secondary crystallization is probably the cause of the progressive mechanical property changes seen in crystalline polymers above their glass transition temperature[10-12].

Ultra-violet microscopy shows that secondary crystallization is not uniform within the spherulite but is strongly affected by the variations in the concentration of polymeric impurities rejected during the initial spherulite growth.

0032-3861/84/070921-06$03.00

EXPERIMENTAL

The methods of ultra-violet microscopy have been described in detail elsewhere[13,14]. The additive used in these experiments was Uvitex OB (2,5-di(5-t-butyl-2-benzoxazolyl thiophene) which absorbs strongly at around 320 nm and has a bright blue fluorescence. Observations were generally made both of fluorescence and of ultra-violet absorption in order to detect artefacts due to scattering within the sample. Uvitex concentrations in samples were measured either by micro-densitometry of micrographs or by direct analysis of a TV image using a waveform monitor[15]. Additive concentrations were normally 0.1% for fluorescence observations and 0.5% for absorption observation.

The polypropylene used was HF20 from Imperial Chemical Industries Ltd, Plastics Division. This was extracted with boiling heptane to remove low molecular weight and atactic material. The resulting polymer had molecular weights of M_n 89 500, M_w 666 000. It was stabilized by solvent blending with 0.1% Irganox 1010 (Ciba–Geigy Ltd), a phenolic antioxidant. The polymer was compression moulded into cylindrical discs at 200°C. For hot stage microscopy a 10 μm section was gently pressed between a carefully cleaned microscope slide and cover slip so that it wetted the surface. Samples were crystallized in a Mettler FP2 hot stage at between 100°C and 150°C under a flow of nitrogen.

RESULTS

Figure 1 shows spherulites of polypropylene containing Uvitex OB growing at 130°C, viewed by fluorescence. On quenching to room temperature the fluorescer becomes less uniformly distributed within the spherulites as shown in *Figure 2*.

Intensity traces across a fully equilibrated sample containing 0.5% Uvitex are shown in *Figure 3*. At the crystallization temperature of 135°C there is little variation in intensity (absorption) across the spherulite. On cooling to 25°C the 'wheatsheaf' morphology of the spherulite centre becomes marked by a lower Uvitex concentration. Traces are shown both across and parallel to the 'wheatsheaf'. The pattern is what would be expected for material rejected to either side and in front of this central structure as it forms. This change in appearance takes place on cooling through the range 100°C to 70°C. On reheating the sample the distribution slowly returns to the original as-crystallized one. This is shown in *Figure 4* where a sample crystallized at 125°C regains the original distribution on reheating to this temperature. Further heating leads to a more uniform additive concentration as shown. In a previous paper[2] it was shown that the additive distribution in a sample equilibrated at the crystallization temperature could be used to determine the local crystallinity. If the sample is held at constant

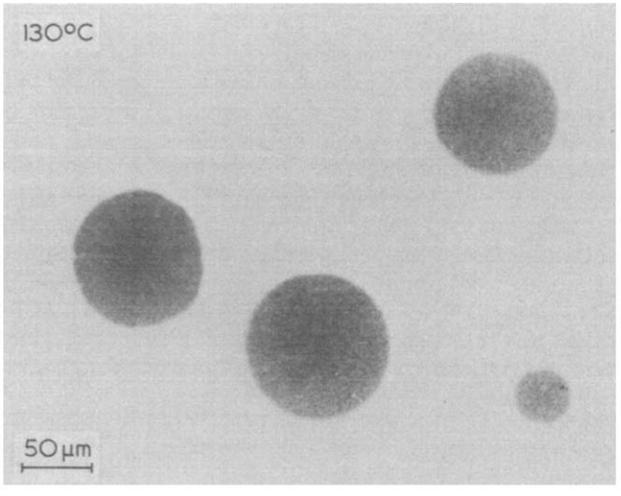

Figure 1 Spherulites of polypropylene containing 0.5% Uvitex OB crystallized and viewed at 130°C in fluorescence

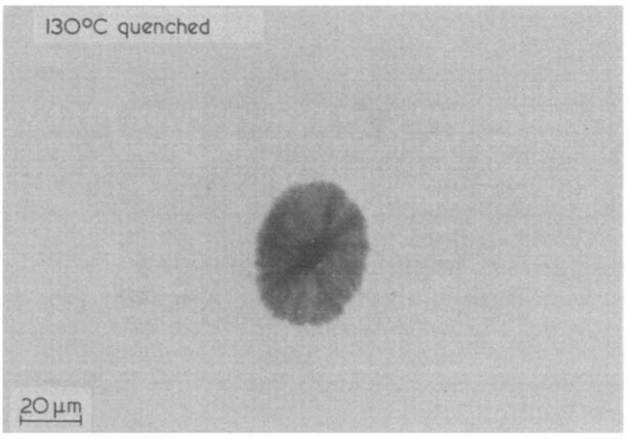

Figure 2 Spherulite of polypropylene as in *Figure 1*, at room temperature

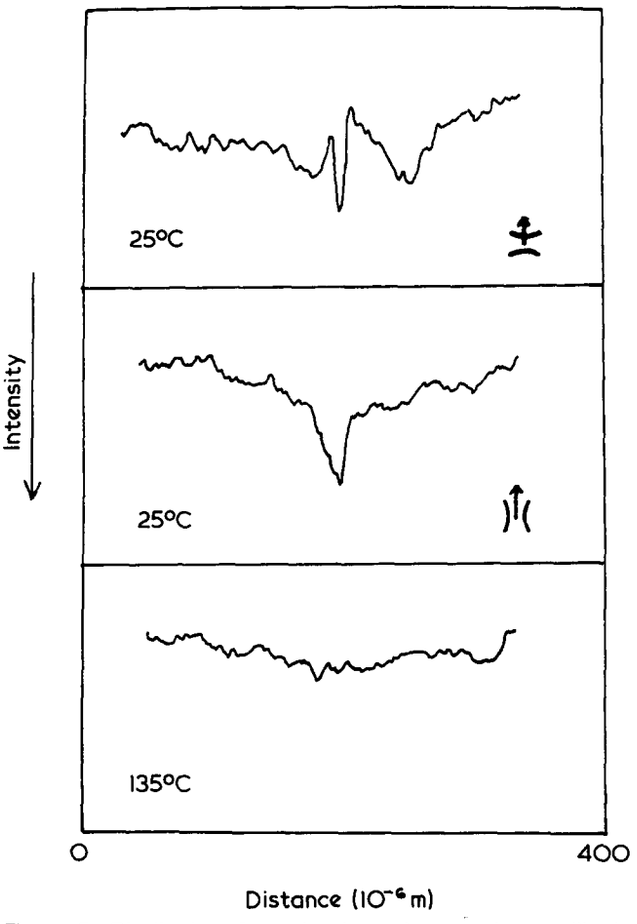

Figure 3 Distribution of u.v. absorbance in a sample crystallized at 135°C. Top: At 25°C, across central wheatsheaf. Middle: At 25°C along central wheatsheaf. Bottom: At 135°C

temperature for sufficiently long the additive will diffuse to become uniformly distributed throughout the amorphous phase. The perceived variations in concentrations of additive then arise from variations in crystallinity. If the average crystallinity of the spherulite is known the local crystallinity variations can then be determined. Applying this argument to samples at room temperature, *Table 1* shows the crystallinities of the centre, mid-radius and boundary of spherulites grown at different temperatures. Their average crystallinity was 55% by differential scanning calorimetry. The central crystallinity is very variable as it represents a small volume, about 0.1% of the total spherulite and the wheatsheaf may vary in orientation and position within the film. *Figure 5* shows the change of centre, mid-radius and boundary crystallinities with temperature for a sample crystallized at 125°C. It can be seen that the crystallinity variations disappear as the temperature increases. In *Figures 6, 7* and *8* are shown observed concentration distributions in

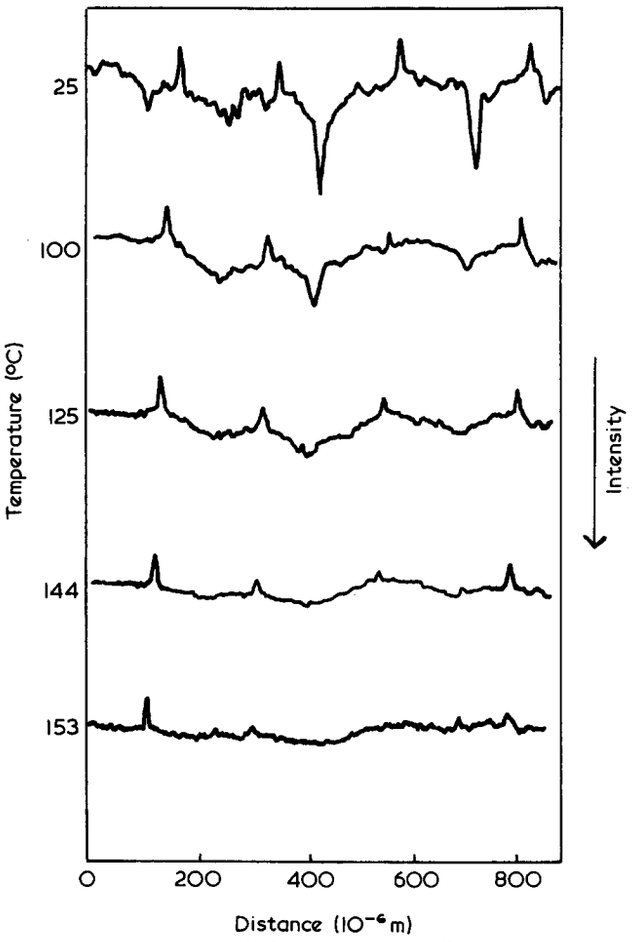

Figure 4 Changes in u.v. on slowly heating a sample of polypropylene containing 0.5% Uvitex OB

Table 1 Spherulite crystallinities

Local crystallinities (%)	Crystallization temp. before cooling, °C				
	115	120	137	140	147
Centre	76	85	83	79	76
Mid-spherulite	56	56	58	58	57
Boundary	54	52	49	50	50

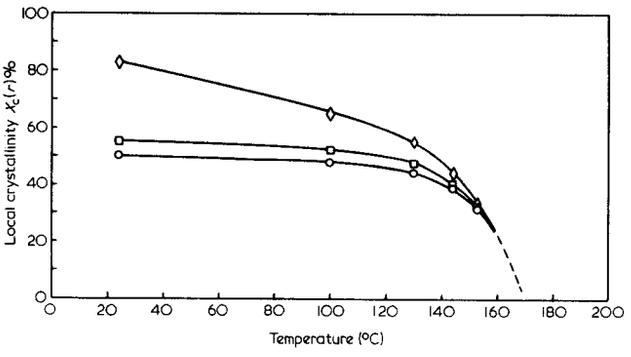

Figure 5 Local crystallinity changes on heating polypropylene crystallized at 125°C. (◇): centre. (□): mid-spherulite' (○): boundary

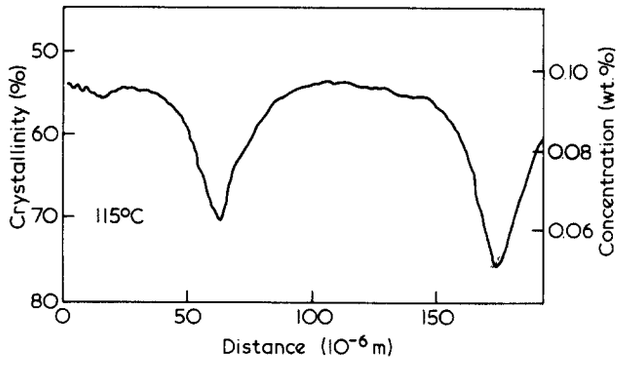

Figure 6 Distribution of u.v. absorption at room temperature in a sample crystallized at 115°C. Peaks are inter-spherulite boundaries, dips are spherulite centres

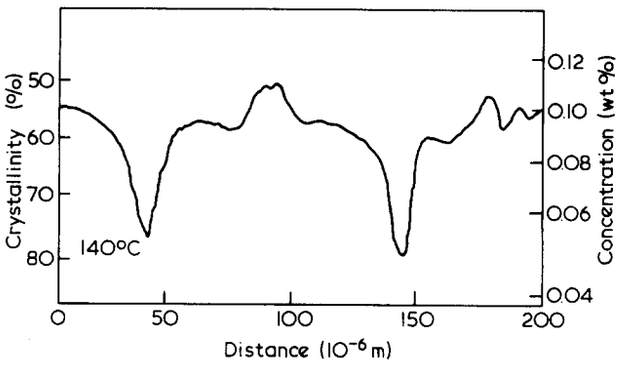

Figure 7 Distribution of u.v. absorption at room temperature in a sample crystallized at 140°C

samples crystallized at temperatures from 115°C to 147°C then cooled to room temperature. The central (dark) peaks get progressively narrower as the crystallization temperature increases. The shapes of these peaks reflect both the non-uniformities present at the crystallization temperatures and those which appear on cooling. It was shown in a previous paper[2] that markedly higher central crystallinities (lower additive concentrations) are found in samples crystallized at low temperatures while above 135°C the distribution is essentially flat when observed at the crystallization temperature. Thus the central peak in *Figure 8*, 147°C crystallization, forms on cooling while that in *Figure 6*, 115°C crystallization, largely forms at the crystallization temperature.

One possibility is that the Uvitex distribution observed at room temperature does not reflect crystallinity at all

but arises because secondary crystallization is initiated at the spherulite centres and progresses radially pushing the additive outwards to create a high boundary concentration. This process would be analogous in secondary crystallization to the original non-equilibrium distribution of the additive which is created during spherulite growth but which relaxes to a uniform concentration within the amorphous phase when the sample is annealed[2]. This is disproved by observations on samples in which Uvitex has been allowed to diffuse in after crystallization. The sample was soaked for two weeks in a solution of Uvitex in alcohol at 60°C then sectioned. As can be seen in *Figure 9* the additive distribution appears the same as for samples crystallized containing the additive.

A further difference between the sections at their crystallization temperature and after cooling is that the latter have a distinct substructure of radial fibres while the former are nearly uniform. This fibrosity apparently also reflects local crystallinity fluctuations within the sample and correlates with the fibrous structure seen in polarized light. *Figure 10* shows a spherulite viewed in fluorescence, cross polarized light and circularly polarized light. In cross polarized light the typical mixed birefringence of polypropylene can be seen superimposed on the normal spherulitic 'maltese cross' pattern. With the circular polars the sample birefringence is seen more directly. The dense dark radial lines in fluorescence correspond to dark lines with circular polars although the dark lines in fluorescence are narrower. During growth these

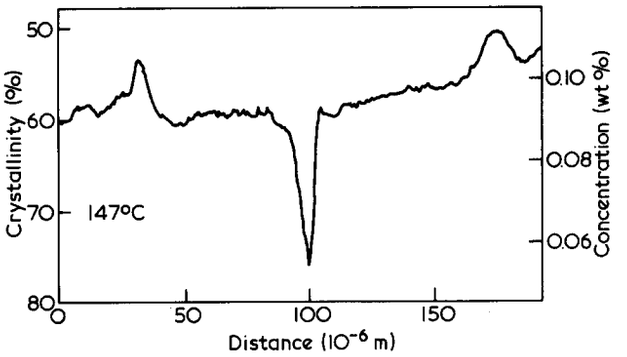

Figure 8 Distribution of u.v. absorption at room temperature in a sample crystallized at 147°C

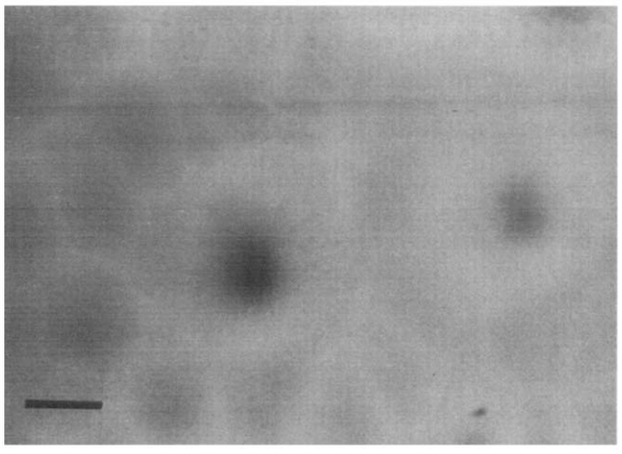

Figure 9 Sample crystallized at 130°C. Uvitex OB diffused in from alcohol solution at 60°C. Bar=50 μm

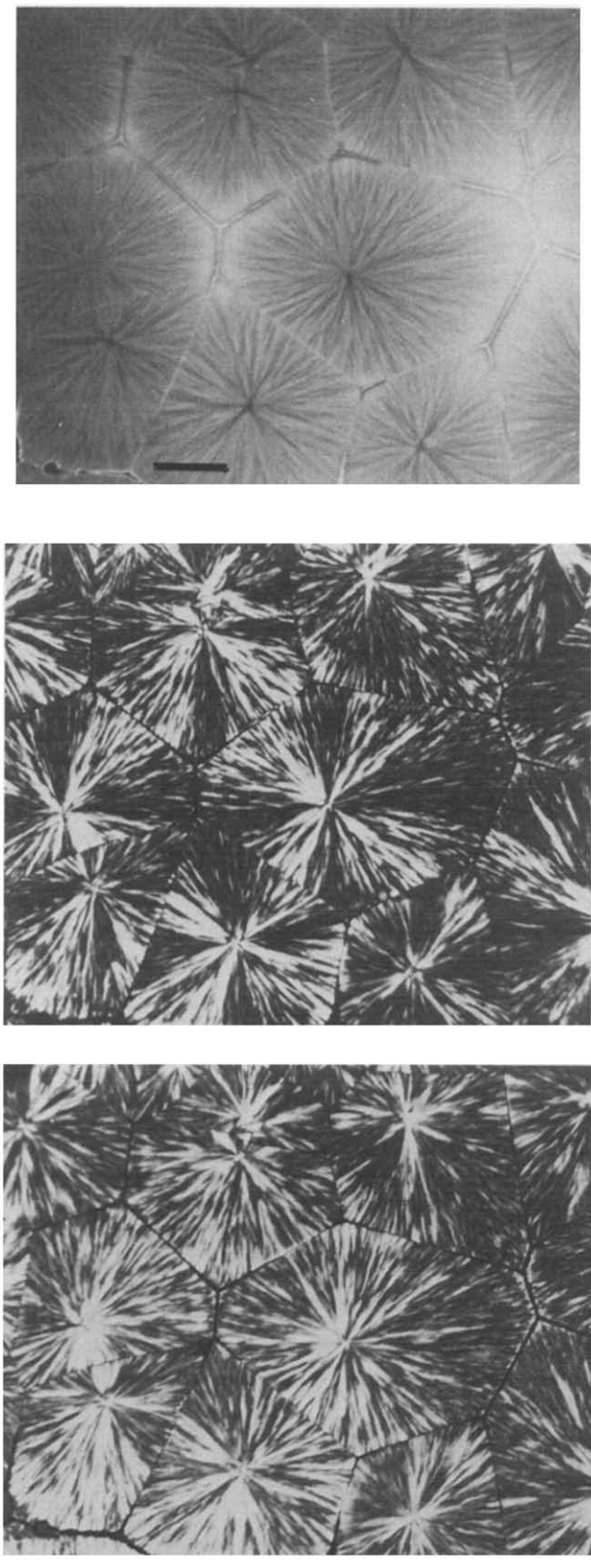

Figure 10 Sample crystallized at 135°C showing correspondence of fibrillar structure in polarized and fluorescent light. Top: fluorescence. Middle: crossed polars. Bottom: circular polars. Bar=50 μm

spherulites show a slightly irregular 'picket fence' interface. The dark lines correspond also to the leading points on the interface[22].

Beta form spherulites also occasionally occurred in these samples. They have a distinctly different distribution

of fluorescer as seen at room temperature (*Figure 11*). This is characterized by a sharper, larger boundary peak. The fibrosity of the two forms is similar for 115°C crystallization but much greater in alpha than in beta spherulites from 125°C upwards.

DISCUSSION

The changes in the distribution of Uvitex which occur on cooling spherulitic polypropylene require both structural changes within the sample and diffusion of the additive in such a way as to reflect this change. Thus a uniform increase in crystallinity within the spherulite would concentrate the additive into the remaining amorphous regions but give rise to no changes on a scale greater than that of the individual lamellae. Thus ultra-violet microscopy would show no change. In fact scanning calorimetry suggests that a 5% increase in crystallinity to 55% occurs on cooling in most of the samples studied here. However it must be remembered that reliable determination of this type of rather ill-defined interlamellar crystallinity is difficult.

There is no *a priori* reason for believing that, after cooling, the fluorescer is uniformly distributed throughout the amorphous regions. If secondary crystallization were to mimic primary crystallization by commencing at the spherulite centre and moving radially outwards, it would be possible to arrive at a non-equilibrium fluorescer distribution similar to that produced during primary crystallization[1]. Two arguments oppose this interpretation. Firstly samples can be crystallized with no fluorescer and the compound diffused in afterwards from solution. This distribution as shown in *Figure 9* is similar to the seen on cooling a sample containing Uvitex. Thus we can conclude that the distribution is close to diffusional equilibrium. Also we can estimate the equilibration time for an impurity diffusing into a polymer. This process was discussed in a previous paper[2]. For diffusion at 70°C with a coefficient of 0.1 $\mu m^2 s^{-1}$ [24] over a time of 10 min equilibrium would occur over a range of about 20 μm. Thus during slow cooling and slow melting, equilibrium should hold for this range at least. In fact the fibrillar structure appears and disappears reversibly for slowly cooled samples but does not reappear if the sample is rapidly quenched from 130°C.

Given that the fluorescer distribution seen at room temperature does represent the distribution of amorphous material within the spherulite, it seems reasonable that in these samples this variation arises from a non-uniform distribution of the low molecular weight and stereoblock impurities which are not capable of crystallization. This distribution arises from the rejection processes taking place during crystal growth.

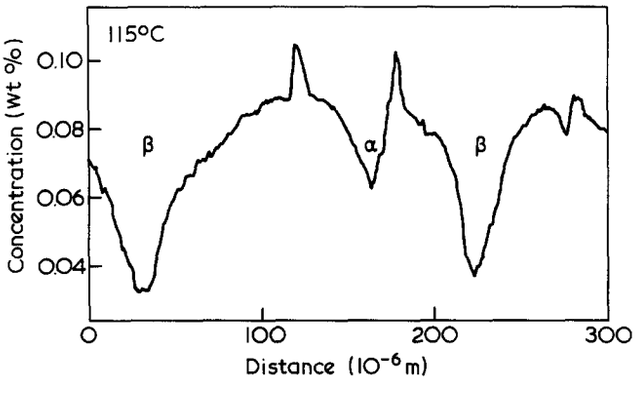

Figure 11 Sample crystallized at 115°C showing α and β spherulites

The effect of polymeric impurities on spherulite morphology has been described by Keith and Padden[16]. A more detailed treatment of the mathematics of the process has recently been given by Calvert[23]. Keith and Padden described the fibrillar morphology in terms of the coarseness, the fibril size and the compactness. Low growth temperatures gave rise to more compact and fine spherulites while coarse open structures characterized impure melts and high growth temperatures.

The partial exclusion of polymeric impurities from the fibrils is a consequence of the instability of the spherulite growth front[22,23]. A flat, growing crystal–liquid interface tends to set up an impurity rich layer ahead of the interface. Any perturbation on the interface which gets slightly ahead of the rest will then grow faster as it advances into purer liquid. As a result the interface breaks down into cells with retarded impurity-rich regions between. The fibrillar growth of polypropylene can be seen in this way except that classically the cell is a single crystal whereas here the fibril is a collection of lamellae. Simulations are being carried out to demonstrate fibril formation in a uniform lamellar spherulite.

As can be seen in *Figure 10* the elementary fibrils become visible in fluorescence at room temperature. The dense, dark regions in fluorescence correspond to dark lines seen with circular polars both at room temperature and at the crystallization temperature. At a crystallization temperature of 135°C and above the mixed birefringent spherulites become more negative as the crystallization temperature is raised. This effect appears to be due to the increased amount of high angle branching which forms tangentially oriented lamellae[17–19]. Thus the dark regions in fluorescence correspond to regions with more radial lamellar structure constituting the core of the fibril while the surrounding zones with more tangential lamellae are less dense and less pure. The additive distribution at room temperature does correspond to the expected distribution of low crystallinity impure regions.

What is surprising is the disappearance of the fibrosity and the dark centre when the polymer is reheated to 130°C. The crystallinity change measured by d.s.c. is quite minor over this range but the effect on the apparent crystallinity of the spherulite centre and fibrils is quite marked (see *Figure 5*). We must conclude that the additive is affected by ordering processes which do not show up as large crystallinity changes by d.s.c. or X-ray diffraction.

Warner *et al.*[20] and Yeh and Lambert[21] find that atactic polystyrene is similarly concentrated between the fibrils of isotactic polystyrene spherulites. A full analysis of the rejection pattern would need to take into account the lamellar branching behaviour of the polymer and the increasing fraction of non-crystallizable material at high crystallization temperatures. More information on this process can be obtained from the observation of rejection of fluorescently labelled atactic polymer[24].

CONCLUSIONS

The first paper of this series demonstrated that additives were rejected by growing spherulites according to a zone refining model[1]. The second paper[2] showed that, after

annealing at the crystallization temperature, the additives were distributed to reflect the local crystallinity of the spherulite. This crystallinity is somewhat lower than average at the boundaries and is more at the centre. It might be expected that this difference would remain on cooling to room temperature. However, fluorescence microscopy of polypropylene at room temperature shows marked density variations within the structure to a greater extent than is evident at the crystallization temperature. The structure becomes clearly fibrillar and the centres become much more crystalline than the bulk of the spherulite.

During crystallization, polymeric impurities are partly excluded from the fibrils and although they do not greatly affect the original crystallinity they subsequently inhibit secondary crystallization in the interfibrillar regions. Thus in polypropylene the amorphous phase is not homogeneous but ranges from relatively pure material between the lamellae which densifies on cooling to impure interfibrillar material into which the fluorescer diffuses on cooling.

ACKNOWLEDGEMENTS

We thank A. D. Curson of I.C.I. Plastics for his help and advice during this project. A. Uzuner (Sussex) prepared several of the samples shown.

REFERENCES

1 Calvert, P. D. and Ryan, T. G. *Polymer* 1978, **19**, 611
2 Ryan, T. G. and Calvert, P. D. *Polymer* 1982, **23**, 877
3 Kavesh, S. and Schultz, J. M. *J. Polym. Sci. A-2* 1971, **9**, 85
4 Schultz, J. M. and Scott, R. D. *J. Polym. Sci. A-2* 1969, **7**, 659
5 Hoffman, J. D. and Weeks, J. J. *J. Chem. Phys.* 1965, **42**, 4301
7 McCready, M. J., Schultz, J. M., Lin, J. S. and Hendricks, R. W. *J. Polym. Sci. Polym. Phys. Edn.* 1979, **17**, 725
8 Bassett, D. C. and Hodge, A. M. *Proc. Roy. Soc. A* 1978, **359**, 121
9 Schultz, J. M., Fischer, E. W., Schaumburg, O. and Zachmann, H. A. *J. Polym. Sci. Polym. Phys. Edn.* 1980, **18**, 239
10 Struik, L. C. 'Physical Aging in Amorphous Polymer and other materials' Elsevier, Amsterdam, 1978
11 Chai, C. K. and McCrum, N. G. *Polymer* 1980, **21**, 706
12 Zewi, I. G., Rudik, W. J., Cornelliussen, R. D. and Lind, E. V. *Polym. Eng. Sci.* 1980, **20**, 622
13 Billingham, N. C. and Calvert, P. D. *Dev. Pol. Characterisation* 1982, **3**, 229
14 Billingham, N. C., Calvert, P. D., Knight, J. B. and Ryan, T. G. *Br. Polym. J.* 1979 **11**, 155
15 Ryan, T. G. *D. Phil. Thesis*, University of Sussex, 1979
16 Keith, H. D. and Padden, F. J. Jr., *J. Appl. Phys.* 1964, **35**, 1270, 1286
17 Binsbergen, F. L. and DeLange, B. G. M. *Polymer* 1968, **9**, 23
18 Khoury, F. *J. Res. Nat. Bur. Stand.* 1966, **70A**, 29
19 Padden, F. J., Jr. and Keith, H. D. *J. Appl. Phys.* 1973, **44**, 1217
20 Warner, F. P., MacKnight, W. J. and Stein, R. S. *J. Polym. Sci. Polym. Phys. Edn.* 1977, **15**, 2113
21 Yeh, G. S. Y. and Lambert, S. L. *J. Polym. Sci. A-2* 1972, **10**, 1183
22 Kojima, M. *J. Polym. Sci. Polym. Lett. Edn.* 1979, **17**, 609
23 Calvert, P. D. *J. Polym. Sci. Polym. Lett. Edn.* 1983, **21**, 467
24 Uzuner, A. *D. Phil. Thesis*, University of Sussex, 1982