Diffusion and annealing in crystallizing polymers

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Ultraviolet and fluorescent microscopy of additives in crystallizing polypropylene can be used to study the development of crystallinity within growing spherulites. As the spherulite forms, impurity species including fluorescent additives are initially rejected then subsequently diffuse back in. Simultaneously the interior of the spherulite is increasing in crystallinity and tending to push the impurities back towards the outside.

The effect of these processes on the final distribution of impurities within the spherulite is calculated. These results suggest that non-uniformity in additive concentrations will have little impact on the stabilization of the polymer against photo-oxidation.

Keywords Crystallization; diffusion; spherulites; annealing; additives; impurities

INTRODUCTION

Crystalline polymers contain a variety of impurities which are partly or completely excluded from the crystals, being incompatible with the regular packing in the crystal phase. Included amongst these impurities are low molecular weight polymer, atactic or stereoblock polymer molecules, dissolved gases, partly degraded polymer, stabilizers and other additives. Price and coworkers[1] observed rejection of such impurities ahead of growing spherulites manifested as a slowing in the growth rate as spherulites approached one another. Moyer and Ochs[2] demonstrated that impurities are more concentrated at spherulite boundaries in the final solid and Keith and Padden[3] studied the effect of high impurity concentrations on spherulite growth kinetics and morphology. They also showed that rejection occurs into the interlamellar amorphous regions. Similarly Keller and coworkers[4] have shown that the spherulite structure of high density polyethylene, as revealed by hot solvent extraction, can be related to impurity segregation effects.

Recently we used ultraviolet microscopy to measure impurity distributions within growing spherulites and in the surrounding liquid polymer[5]. The impurities in this case were small concentrations ($<1\%$) of ultraviolet absorbing or fluorescing compounds. The measured concentrations were compared with those computed on the basis of a simple model in which all the impurity is excluded from the growing crystals at the spherulite boundary and diffuses into the surrounding liquid and the interlamellar amorphous regions. The impurity concentration profile at the spherulite boundary in samples which were partly crystallized and quenched, could be fitted to the computed profile by choice of a suitable diffusion coefficient for the additive in the liquid polymer. The diffusion coefficients so obtained were in general agreement with what would be expected from our knowledge of diffusion coefficients in solid polymers at similar temperatures. It was noted that the impurity distribution within the final spherulite after annealing and cooling to room temperature was not that expected from the impurity rejection process within a spherulite of uniform crystallinity but must reflect a decreasing crystallinity between the spherulite centre and the boundary. This is of interest as there is little understanding of the factors which control crystallinity within a spherulite.

In this paper we report on changes in the crystallinity and impurity distribution within polypropylene spherulites during and after crystallization. These measurements were made possible by an improved microscopy technique which allows direct recording of the concentrations at the crystallization temperature. We have observed impurity diffusion within the spherulite and the annealing of the crystal phase at the growth temperature. Knowing the additive diffusion coefficients both in the melt and within the spherulites it is possible to estimate the extent of non-uniformity in stabilizer distributions in moulded polymers. A subsequent paper will discuss the changes which occur in polypropylene spherulites on cooling to room temperature and on melting.

EXPERIMENTAL

The polypropylene used in this study was predominantly isotactic grade HF20 supplied to us in powder form by ICI Ltd, Plastics Division. It was extracted with boiling heptane to remove low molecular weight and atactic material. The resulting polymer had a number average molecular weight of 9×10^4 and weight average of 6.7×10^5. The additive used for ultraviolet microscopy was Uvitex OB (2,5 di(5-t-butyl, 2-benzoxazolyl)-thiophene), which absorbs at ~380 nm and has a strong blue fluorescence at 450 nm. This compound was incorporated into the polymer by thoroughly mixing a solution of the additive in dichloromethane with the

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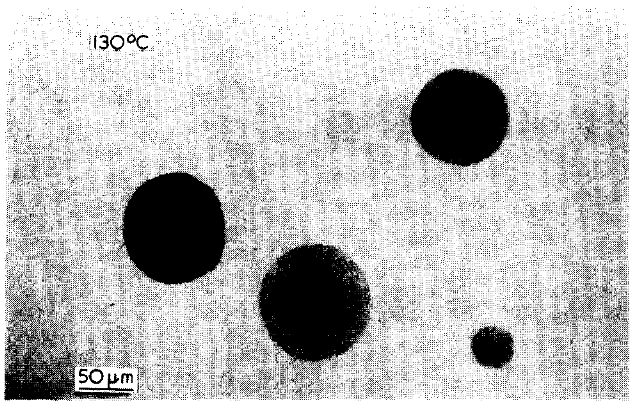

Figure 1 Polypropylene section containing 0.1% Uvitex OB crystallizing at 130°C. Viewed by fluorescence

polymer powder, allowing it to dry and then moulding the polymer. Irganox 1010 at 0.1% was also added as an antioxidant.

The ultraviolet microscope was a Carl Zeiss (Oberkochen) Universal microscope fitted with silica lenses and with front-surface mirrors rather than prisms as beam deflectors. Illumination is by a 150 W xenon arc with a 4 cm cell of distilled water as a heat filter and a combination of interference and dye filters for wavelength selection. The image was recorded on 35 mm Ilford FP4 film or viewed by a small Shibaden TV camera fitted with an EMI u.v. sensitive vidicon tube which displays the image on a TV monitor. To this we have coupled a waveform analyser (Textronix model 528) which shows the intensity distribution along any line of the TV image. With suitable calibration using standards of known, uniform concentration the impurity concentrations can be directly measured. At the sacrifice of some of the uniformity of intensity provided by Kohler illumination conditions it was possible to use a Mettler microscope hot stage such that changes in the impurity distribution could be seen during the growth and annealing of spherulites in thin films without the need for quenching.

Both fluorescence and u.v. absorption could be measured simply by changing filters although the fluorescence was not strong enough to be visible on the TV system. Full details of the experimental methods are given in ref 6.

Additive distributions around and within growing spherulites were computed using a model described previously[5,6]. It is assumed that the additive is completely excluded from the crystalline lamellae and that, at the growing interface there is no distinction between the interlamellar amorphous material and the liquid. The ratio of the additive diffusion coefficient to spherulite growth rate is a characteristic diffusion range which is 1–100 μm in this system. We assume that the lamellae are uniformly arranged at the spherulite surface with a spacing of ~10 nm and accordingly for the diffusional calculations we can treat the spherulite as a homogeneous solid. The additive rejection is described by a distribution coefficient defined as the ratio of the average additive concentration within the spherulite at the interface to that in the adjoining liquid. This is then equal to the interfacial amorphous content (1-crystallinity).

In the computation a grid of typically 100 points represents the spherulite radius from the centre to its final boundary with the neighbouring spherulites. The additive is initially uniformly distributed; then the interface steps along the grid from the centre with diffusion occurring throughout the system at each growth step. Reflective boundary conditions apply at either end of the grid. At the interface the additive concentration gradient within the liquid is defined by the rejection process; no diffusion is allowed across the interface. Separate liquid and solid ('back') diffusion coefficients apply on either side of the interface. The difference equations for diffusion in the spherically symmetric case are given by Crank[7]. Thin film crystallizations were modelled as a two-dimensional process.

The initial program was written in Fortran and run on a CDC 7600 computer. It employed the Crank–Nicholson implicit method[7] which involves a large matrix inversion. Subsequently to allow greater flexibility, the program was rewritten in Basic using the simpler and less accurate finite-difference (explicit) method but with finer growth steps. This was run on an 8 kbyte microcomputer with run times of several days. The results were checked for consistency by their insensitivity to changes in the size of the grid and by whether there was any change in the total additive in the system. A change of less than 10% of the total additive in the interfacial peak was taken as satisfactory.

Initial rejection of impurities

It was shown earlier[5] that the distribution of an impurity pushed ahead of the boundary of a growing spherulite, such as those shown in *Figure 1*, could be fitted by a simple model of total rejection from the crystalline phase and diffusion within the interlamellar amorphous and liquid regions.

Figure 2 illustrates the effect of spherulite growth rate on the additive distribution along lines crossing the centres of spherulites growing in the melt at 125°, 130° and 135°C and the equivalent computed distributions are shown in *Figure 3*. At 135°C there is a uniform additive concentration within and ahead of the growing spherulite. The concentration of additive within the spherulite is simply reduced in proportion to the crystal content. At 130° and 125°C the additive concentration increases from the spherulite centre to the boundary and decreases from the boundary into the melt. In the range 135° to 125°C the growth rate increases from 0.02 to 0.25 $\mu m\ s^{-1}$ such that at the higher growth rates the additive diffusion rate is insufficient to prevent accumulation at the growth front. Note that, according to our model[5] at the interface the concentration of additive in the melt is equal to that in the interlamellar regions. The ratio of additive concentration in the spherulite to that in the adjacent melt should thus be equal to the amorphous content (1-crystallinity) of the spherulite at the growth front. Using observed values for the growth rate and crystallinity at the interface we compute distributions which agree well with the data in the region of the interface with a diffusion coefficient of 8–12 $\mu m^2\ s^{-1}$, as shown in *Figure 3*.

The final distribution of impurities within the spherulite could in principle be calculated by continuing the computation until the spherulites meet and crystallization is complete. However the observed distribution will deviate from this for a number of reasons. Firstly the impurity continues to diffuse within the spherulite so that any gradients formed by the rejection process tend to disappear. Increases of crystallinity within the spherulite

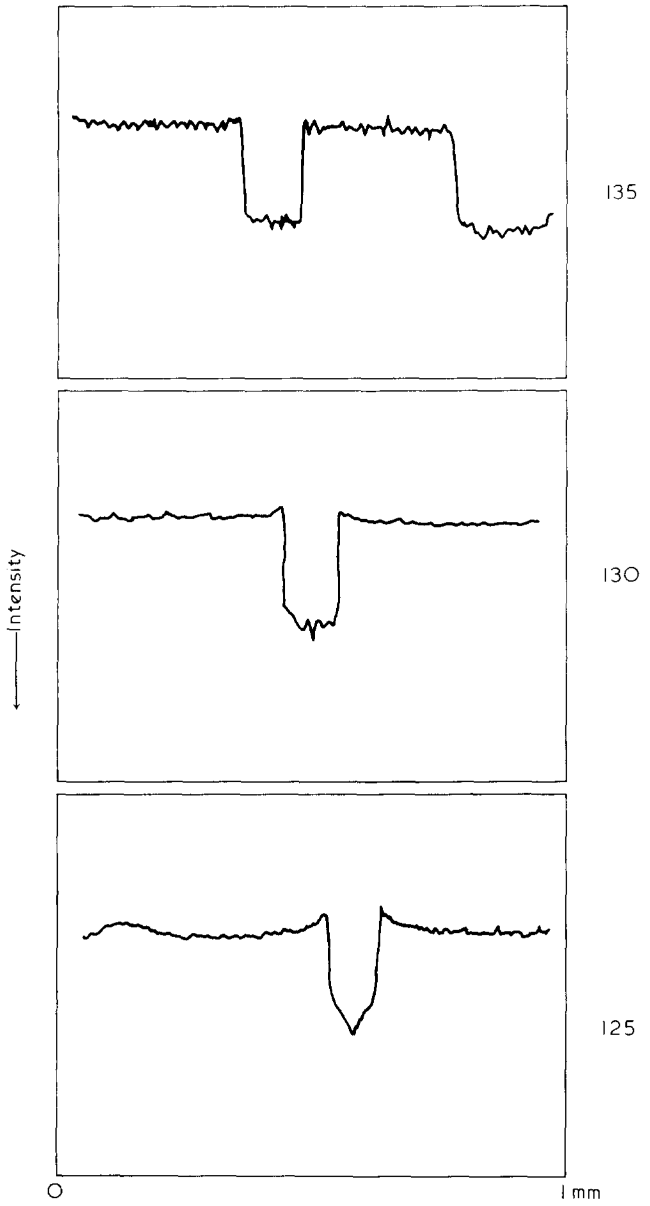

Figure 2 Distributions of Uvitex OB (0.5%) in samples crystallizing at 125°, 130° and 135°C. Intensity traces from TV image of u.v. transmission. Low intensity corresponds to high Uvitex OB concentration. Central high intensity regions are diametric traces across single spherulites

by annealing will also modify the distribution. The resulting crystallinity within the spherulite is not completely uniform, being somewhat higher in the small region around the spherulite centres. This zone is not large enough to modify the predicted distribution at the interface in a large spherulite but it does lower the observed final impurity level at the spherulite centre. We will consider these three processes in turn.

Back diffusion

The extent of diffusion within the spherulite has little effect on the predicted profile of impurity at the interface as is shown by *Figure 4*. Here the peak concentration of impurity at the interface is plotted as a function of the radius of a growing spherulite. This demonstrates the way in which the wave of rejected impurity develops as the spherulite grows. The computed peak heights are shown for a liquid diffusion coefficient of 8 μm^2 s^{-1} with a diffusion coefficient for impurity within the spherulite ('back diffusion') of 0 and 2.7 μm^2 s^{-1}. For comparison the peak heights due to a liquid diffusion coefficient of 10 μm^2 s^{-1} are also shown. It can be seen that a back diffusion coefficient of up to 33% of the forward (liquid) impurity diffusion coefficient has only the same effect as a modest increase in the forward coefficient. In this context it is worth noting that experimental difficulties with diffusion coefficient measurements are such that it is rare for independent workers to measure such coefficients to an agreement of better than a factor of two.

Whilst the back diffusion coefficient does not have much effect on the initial impurity segregation at the interface of a growing spherulite, it does not have a great effect on the final distribution. Any concentration

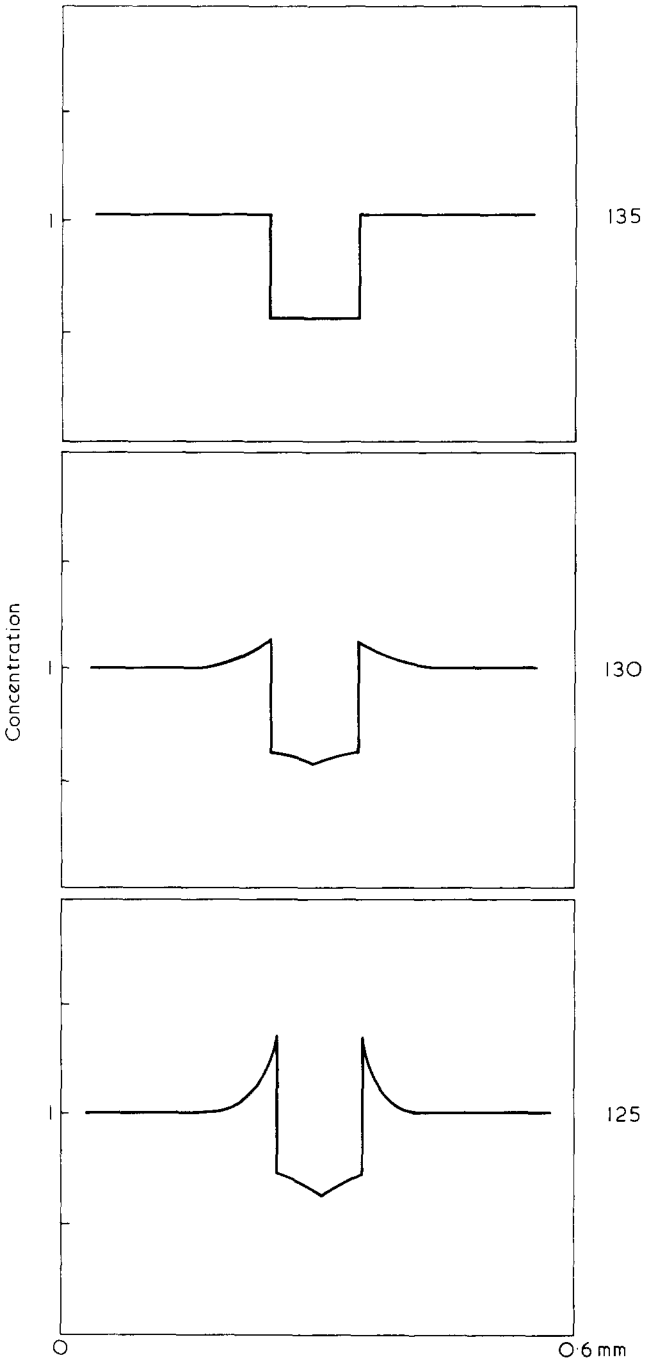

Figure 3 Computed distributions for Uvitex OB in single spherulites crystallizing under the conditions of *Figure 2*. Initial concentration is 1

gradients within the amorphous regions in the spherulite will tend to disappear. However radial variations in crystallinity will mean that in the u.v. microscope the final equilibrium distribution after long times at the crystallization temperature will not show a uniform impurity concentration but one which reflects the distribution of amorphous material. This process cannot be unambiguously studied in quenched samples because secondary crystallization during cooling gives rise to new concentration gradients. However direct observation of samples at the crystallization temperature shows that a considerable amount of back diffusion can occur as demonstrated in *Figure 5*. This shows the concentration gradients being formed as three spherulites grow and impinge and the subsequent levelling of these gradients by back diffusion. In principle it would be possible to determine the back diffusion coefficient from the rate of this levelling process but it is sufficient to note that the characteristic time for this process is of the order of 60 min. The back diffusion coefficient can be measured directly from the rate of penetration of Uvitex OB into a polypropylene sample from a non-swelling solvent. *Figure 6* shows the profiles for Uvitex OB diffusing into solid polypropylene at 130°C from solution in glycerol. These measurements were made on sections of rapidly cooled samples. The solid curves represent a diffusion coefficient of 0.6 $\mu m^2\ s^{-1}$ calculated according to the equation given by Crank[7]:

$$C/C_0 = 1 - \mathrm{erf}(x^2/4Dt)^{1/2}$$

where C_0 is the concentration in the polymer surface, D is the diffusion coefficient and erf is the error function. *Figure 7* shows the calculated relaxation by diffusion of the concentration gradients in a spherulite of radius 120 μm at 120°C. Within 60 min the initial concentration gradient has disappeared. Likewise in *Figure 5* the additive distribution has stabilized within 60 min and does not change markedly thereafter. Thus we conclude that back diffusion can be fully described using the

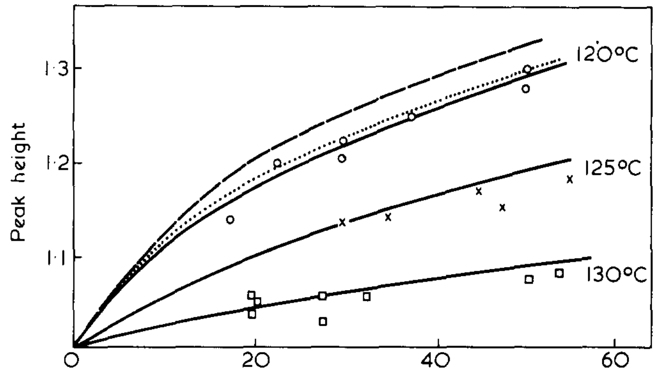

Figure 4 Peak additive concentration at boundary of growing spherulite as a ratio to the initial concentration. Computed values with various liquid and back diffusion coefficients compared with experimental values: (——) $D_{liq} = 10, D_{solid} = 0\ \mu m^2 s^{-1}$; (···) $D_{liq} = 8, D_{solid} = 2.66\ \mu m^2 s^{-1}$; (— — —) $D_{liq} = 8, D_{solid} = 0\ \mu m^2 s^{-1}$

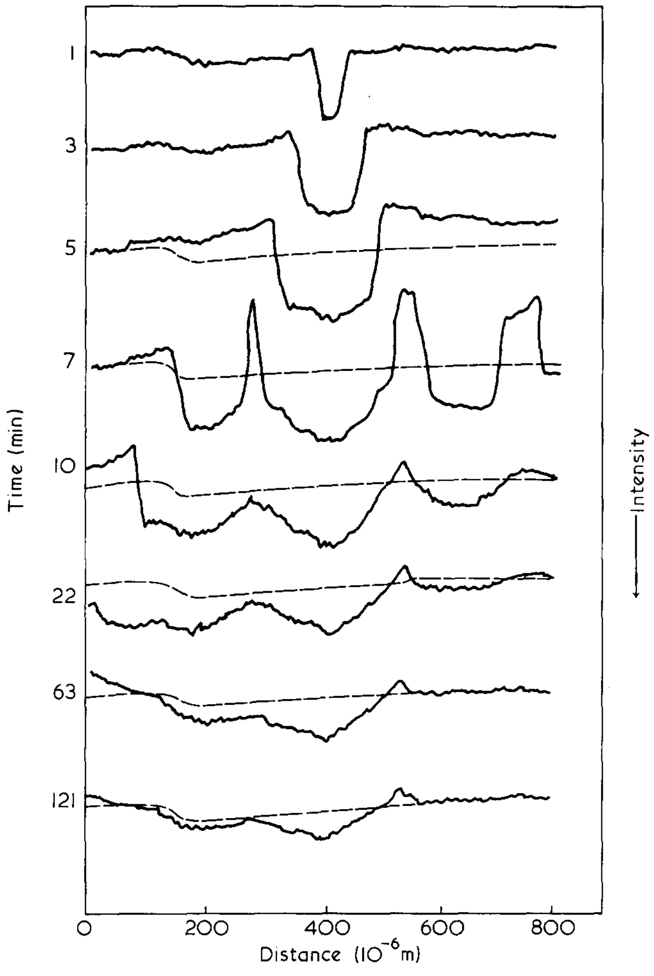

Figure 5 Observed distributions of Uvitex OB (0.5%) during growth, spherulite impingement and annealing at 125°C. Intensity traces from TV image of u.v. transmission. The central high intensity region is a diametric trace across a spherulite which grows until it meets its neighbours at 7–10 min. Their centres are not on the line of this trace. After this the additive diffuses back to equilibrium by 60 min. Broken line is trace in the original liquid state

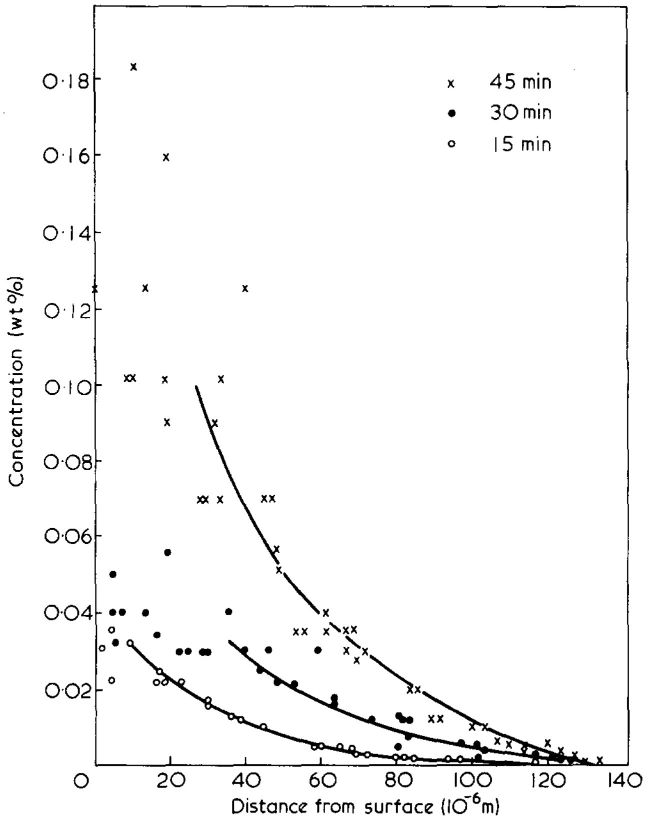

Figure 6 Concentration of Uvitex OB diffusing from solution into a solid polypropylene sample at 130°C, for three different diffusion times

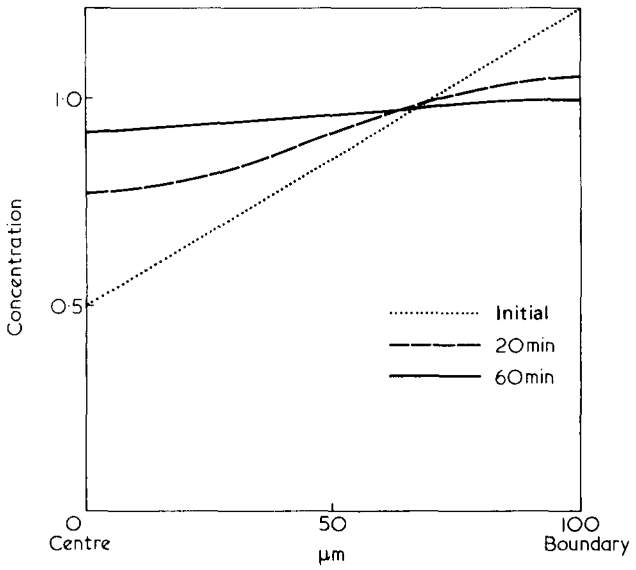

Figure 7 Computation of diffusion toward equilibrium of an initial concentration gradient along a spherulite radius under conditions equivalent to *Figure 5*. Back diffusion coefficient, D_{solid} = 0.6 $\mu m^2\ s^{-1}$

observed diffusion coefficient for Uvitex in solid polypropylene.

Measurements of diffusion coefficients of gases in rubbers[8] and of flexible molecules in polyethylene[9] suggest a solid state diffusion coefficient of about 1/3 that in the liquid. In contrast we observe a ratio of solid to liquid coefficients[5] for Uvitex OB equal to 1/12. Our previous data on diffusion coefficients of similarly rigid, bulky additives in liquid polypropylene can be compared with the measurements of other workers on diffusion in solid polypropylene quoted in ref 5. There is a 1:10 ratio of solid:liquid diffusion coefficients for compounds of similar molecular weight. However, unfortunately, for 2-hydroxy-4-octoxybenzophenone which is the only compound to be studied by two independent groups the measured diffusion coefficients disagree by an order of magnitude. We have noted elsewhere[10] the much slower diffusion of large rigid molecules in solid polymers when compared to flexible molecules of the same molecular weight.

Thus we conclude that Uvitex OB and similar compounds have a back diffusion coefficient which is about one tenth that of the liquid coefficient. This is sufficiently slow that its effect can be ignored in computing impurity profiles in the liquid around a growing spherulite.

Annealing

In addition to the primary rejection process and back diffusion the impurity distribution seen in the u.v. microscope may also be affected by annealing within the spherulite, causing local changes in the amorphous content. This will concentrate the impurities into a small volume so that a gradient is set up and they will diffuse to other parts of the spherulite where the increase in crystallinity is smaller. Thus for any annealing effect to be observed requires both nonuniform crystallinity changes and adequate time for diffusion.

The effect of annealing can be seen by observing the concentration of impurity at the spherulite centre. As can be seen from *Table 1* this decreases continuously as the spherulite grows at 120°C. Simultaneous back diffusion will tend to cause an increase in impurity concentration. Thus at this temperature there is a continuous increase in the crystallinity of the spherulite centre which is faster than that in the surrounding spherulite. The effect is much smaller in spherulites growing at 125°C and 130°C, presumably because annealing is slower and masked by back diffusion.

Table 1 also shows the interfacial partition coefficient, the ratio of impurity concentration in the spherulite at the interface to that in the immediately adjacent liquid. According to our model[5] this should be equal to the amorphous content (1-crystallinity) of the spherulite at the growth front. By extrapolation of calorimetric data[5] we had estimated this to be 0.54 (46% crystallinity). The observed partition coefficient was 0.58 at 120°C, 0.52 at 125°C and 0.53 at 130°C in good agreement with the model. No progressive change in the coefficient was observed at the growth temperature, showing that the spherulite grows with a constant interfacial crystallinity. This is reasonable in that it is well known that growth rate is not a function of spherulite radius.

In samples which have been extensively annealed at the crystallization temperature the low molecular weight impurities must diffuse until they are uniformly distributed throughout the amorphous regions. Any remaining inhomogeneities must reflect variations in the local amorphous content and also in the crystallinity. *Figure 8* shows traces of such annealed samples at 125°,

Table 1 Additive distribution in crystallizing polypropylene

Time (s)	Interfacial partition coefficient	Normalized centre concentration (Initial liquid = 1)	Radius (μm)
Temperature 120°C			
29	0.592	0.664	15
37	0.560	0.635	21
50	0.588	0.618	29
67	0.576	0.576	39
83	0.576	0.534	48
	Average 0.579 ± 0.014		
Temperature 125°C			
120	0.520	0.534	29
140	0.520	0.508	33
180	0.530	0.515	44
194	0.510	0.490	47
240	0.526	0.490	53
	Average 0.521 ± 0.007		
Temperature 130°C			
250	0.518	0.506	18
262	0.542	0.518	20
344	0.524	0.506	26
406	0.533	0.515	31
625	0.548	0.497	49
669	0.532	0.528	52
	Average 0.53 ± 0.011		

Expected value, (1-crystallinity), 0.54

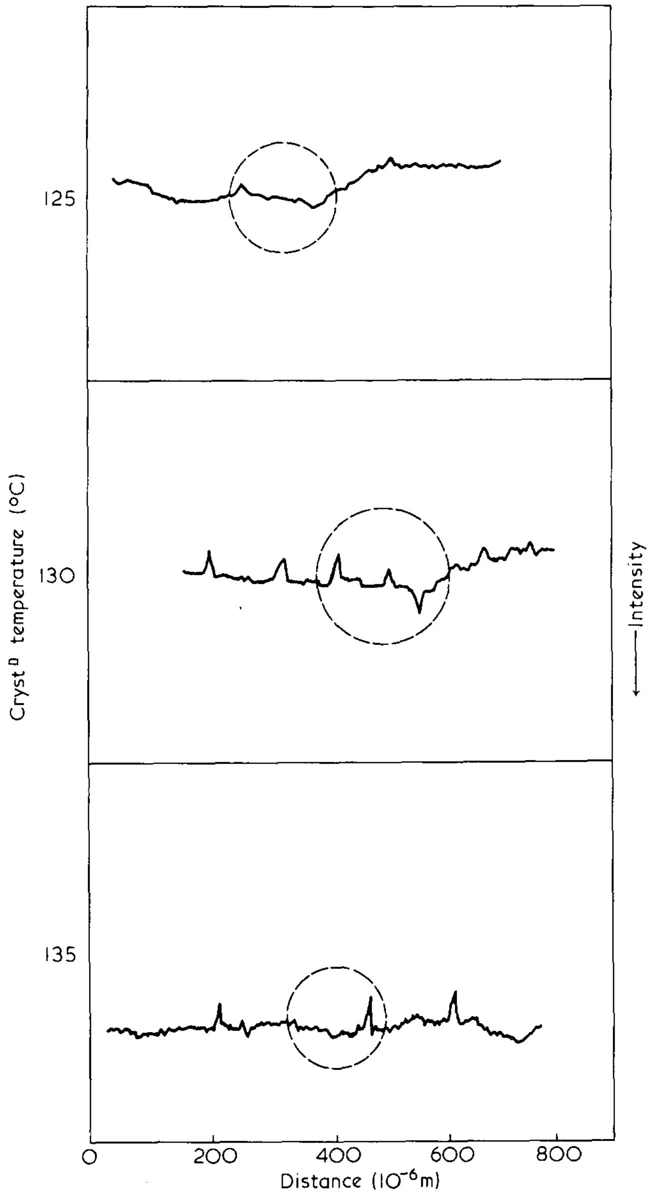

Figure 8 'Equilibrium' distributions of Uvitex OB (0.5%) in polypropylene at the crystallization temperature. Broken circles include a spherulite radius. Boundary is seen as a peak and at 125° and 130°C the centre is seen as a dip

130° and 135°C. The circled regions indicate where the trace passes through a spherulite centre. From the average crystallinity of such samples it is possible to calculate the local crystallinities using these data. *Table 2* presents measured crystallinities at the spherulite centre, at the boundaries and midway between. The variations are not great and at 125°C are consistent. At 130° and 135°C some spherulites had highly crystalline centres whilst in others the centre was close to the bulk material; we believe this reflects different orientations of the central 'wheatsheaf' structure. The effect is clearly seen in cooled samples and will be discussed in more detail in a subsequent paper. This central region constitutes only 0.01% of the spherulite volume so this region has little effect on the total crystallinity. The boundary crystallinity values are subject to error because shrinkage can give rise to local thickness changes and diffraction effects from the curved film surfaces in samples crystallized as thin films. However, the specific boundaries measured appeared unaffected by this.

These results show that either at the time of growth or in subsequent annealing, spherulite centres become more crystalline than the surrounding spherulite and the boundaries less crystalline. This effect is probably due to the rejection of uncrystallizable and partly crystallizable polymeric impurities which occurs during growth simultaneously with the rejection of small amounts of our fluorescent additive. Even when heptane extracted, polypropylene comprises a broad range of molecular weights and tacticities[11] and some fraction of these could modify the initial crystallinity or subsequent annealing of the polymer.

Figure 9 summarizes the effects of back diffusion and annealing on additive concentrations. The computed curve shows the expected additive concentration at the centre of a spherulite during growth and annealing at 125°C. The experimental points lie consistently below the computed curve, the difference being attributable to annealing. This difference increases roughly linearly with log (time), then levels off. Lamellar thickness is known similarly to increase linearly with log (time) during annealing.

DISCUSSION

One original aim of this study was to determine the extent of non-uniformity in the distribution of stabilizers within crystalline polymers. If large concentration

Table 2 Local crystallinity in annealed spherulites at crystallization temperature

	Temperature (°C)		
	125	130	135
Centre	56	55–68	52–70
Mid-radius	50	55	52
Boundary	44	40	42

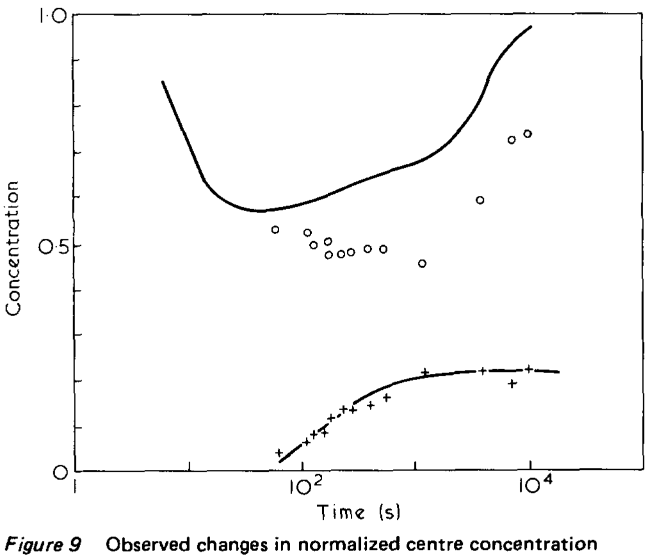

Figure 9 Observed changes in normalized centre concentration with time in spherulites crystallized at 125°C (○) compared with changes computed for back diffusion alone at 125°C (———). Difference, due to annealing (—+—)

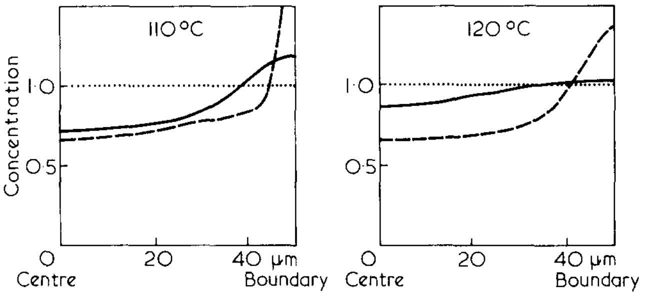

Figure 10 Computed stabilizer distributions along a spherulite radius in polypropylene crystallized at (a) 110°C and (b) 120°C. Diffusion coefficients as for Uvitex OB. (i) (— — — —) as crystallized. (ii) (———) after an additional time at the crystallization temperature equal to the crystallization time. (iii) (· · · ·) after 1 week at room temperature

differences are set up within the structure during crystallization and these remain in the cooled material, it should be possible to choose additives and moulding cycles which would optimize these distributions to give the polymer greater stability.

Given that the additives are all within the amorphous regions and that only the amorphous material is subject to oxidation, we wish to know whether the stabilizer distribution is uniform within the amorphous material. Thus the variations in crystallinity on annealing are of secondary importance compared to the initial rejection and subsequent back diffusion of the stabilizers. *Figure 10* shows calculated stabilizer distributions for the u.v. stabilizer UV531 in polypropylene crystallized to completion at 110° and 120°C. Also shown are distributions after holding the sample for an additional period equal to the crystallization time and after holding the sample for 1 week at room temperature. It can be seen that the final distributions expected in practice will not show significant gradients in stabilizer concentration. *Figure 11* shows the effect of reducing the stabilizer diffusion rate by a factor of 10.

CONCLUSIONS

We have shown that ultraviolet microscopy can be used to observe impurities in polymers during crystallization. These studies confirm our earlier observations on impurity rejection by growing spherulites which were made on quenched samples.

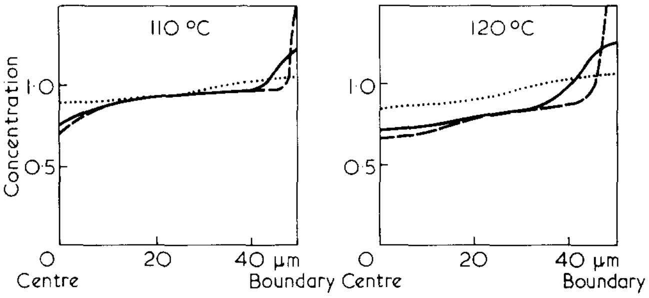

Figure 11 As *Figure 10* but with the additive diffusion 10x slower

The diffusion of additives within spherulites can be observed in this way. We conclude that gradients in stabilizer concentration within spherulites will not play a major role in governing the stability of polypropylene. We show that this technique can also be used to measure local crystallinity within spherulites and to follow the annealing process. Polypropylene spherulites form with a constant crystallinity at the surface of the growing spherulite. Subsequent annealing is more marked at the spherulite centre so that the final structure has a high crystallinity centre and low crystallinity boundary. This is believed to be due to the effect of rejected polymeric impurities.

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