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# Characterization of spherulite boundaries and general observations of solvent action on crystallized polypropylene and polybutene

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As part of a general study of the electrical properties of thin polymer films swollen by dielectric liquids, the crystallization dynamics, final morphology and the intermediate stages of spherulitic growth in polypropylene and polybutene have been studied, along with the optical effects of solvent action. These studies have helped to clarify the action of an impregnant on a polymer film and to visualize which regions are dissolved by the solvent and hence where it resides after impregnation is completed.

## 1. Introduction

It is well known that when semi-crystalline polymer films are immersed in solvents, having similar solubility parameters, a large part of the non-crystalline low molecular weight material is dissolved [1]. If the sample is left immersed in the solvent this material will diffuse out of the main body of the sample. The film will also become swollen to greater or lesser degrees depending on the liquid temperature, the time of immersion and, naturally, the type of polymer used.

Although studies have been carried out on the swelling and dissolution (partial and complete) caused by such immersion [1, 2] and although much work has covered the crystallization habit and dynamics of the system [3], very little work has been done to actually visualize where the liquid resides inside the impregnated film.

To this end, a microscopic study of the spherulitic crystallization habit was undertaken and this, linked with other work carried out by us as part of a more general study of the electrical properties of thin polymer films swollen by dielectric liquids [4], has greatly helped in the visualization of the processes involved and the behaviour of the polymer–impregnant systems under electric fields.

The production of spherulites of very large diameters in thin films provided an essentially two-dimensional structure which greatly aided interpretation of our results.

## 2. Materials

Our aim was to study the general morphological characteristics of thin polymer films as used in applications requiring electrical insulation and to this end two main polymers were used; polypropylene (PP) and poly-l-butene (PB) having degrees of crystallinity of respectively 65% and 45%. The samples used were unstretched extruded polypropylene films, of thickness 350 μm, supplied by Bolloré Industries, Paris, France [5], and blown polybutene films, of thickness 40 μm, kindly supplied by the Laboratoire de Chimie Macromoléculaire, University of Villeurbanne, France, who produced the samples for their own experiments, the characteristics of which are well documented [6].

Although the objective was to study PP, it was decided in some cases to use PB, because of the difficulties involved with observations of the small spherulites produced by PP. The electrical and mechanical properties of the two polymers have been shown to be similar [6], and our studies show similar behaviour under solvent action.

## 3. Experimental details

### 3.1. Sample preparation

All the samples were crystallized in a vacuum, either on glass microscope slides, or on thin teflon films on a heated oven plate. The large samples, i.e. 6 cm × 6 cm, were electrostatically charged to produce close contact between sample and

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substrate, improving thermal contact and hence the uniformity of the crystallization.

## 4. Results and discussion

Both untreated PP and PB show bi-refringence under the microscope and small-angle light scattering showed this to be due to non-spherulitic structure uniformly distributed over the surfaces. These samples were re-crystallized in order to produce readily visible spherulitic structures.

By choice of the crystallization temperature, it was possible to vary the average spherulite diameters from a few micrometers up to several millimeters, this being necessary for the electrical part of the study. The maximum spherulite diameters used were 450 $\mu$m for the PP samples and 5 mm for the PB samples.

The values given above for PB indicate that the resultant form is far from spherulitic, having a thickness-to-diameter ratio of 1:125. The end product is thus essentially a disc-like structure. We will, however, continue to term these structures spherulites for the sake of convenience.

When PB was used the normal geometrical arrangement (Fig. 1) was invariably noted, caused by multiple nucleation points and subsequent growth until inter-spherolite contact and/or consumption of all crystallizable matter was achieved. It was often noted that regions of small spherulites, formed during cooling, existed. It was thought that these regions contained matter resistant to crystallization, such as syndiotactic and atactic chains or impurities. After solvent extraction and drying the samples were remelted and recrystallized. The resulting samples showed few if any regions of small spherulites as previously noted (using identical conditions), which seems to confirm our initial idea.

The boundary regions seem at first sight, to form perfect butt joints but, as a better understanding of these areas was needed to assist the interpretation of the electrical measurements, it was decided to take a closer look. The boundaries are generally accepted [7] to contain a large percentage of the non-crystallized materials making them particularly susceptible to solvent attack. From time to time spherulite boundary regions were found in which little or no polymer existed due either to shrinkage or to absorption of material into the growing spherolites [3], as shown in Fig. 2. After treatment with hot solvents, these boundary regions became darkened and seemed to widen when observed with crossed polarizers, but if phase contrast microscopy was used little or no difference was observed. Fig. 2

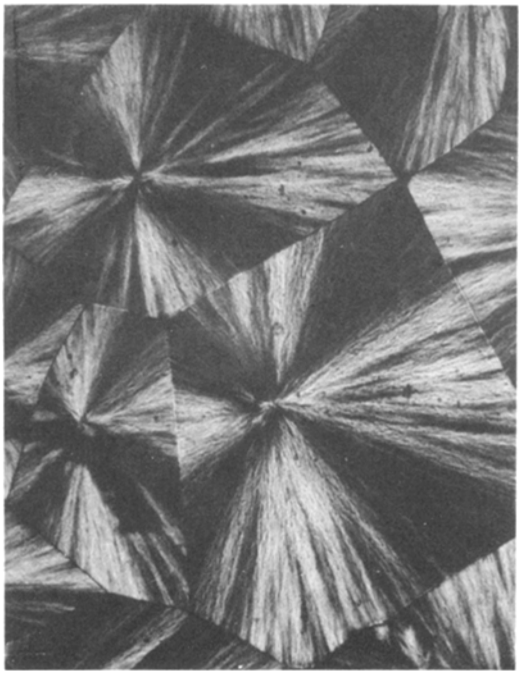


*Figure 1* Normal geometrical pattern of spherulites in PB, $T_c = 120°$ C (transmission micrograph with crossed polarizers) (X 30).

*Figure 2* Imperfect joint between three spherulites in PB, $T_c = 125°$ C (reflection micrograph) (X 60).

also presents an absolute proof of the existence of "grain boundaries" between spherolites in PB. The idea of grain boundaries is regarded as an unrealistic representation of interspherulite joints and this point of view is more or less bourne out, in the case of small spherolites in PP, by Fig. 3, but is shown to be in error when large spherulites are considered. In fact, a darkening of the boundaries implies increased light scattering in these regions. This could be due either to surface or volumic voiding or pitting induced by the solvent. Reintroducing the solvent at low temperature removes, to a certain extent, the darkening and hence reinforces our initial suggestion. Solvent-attacked boundary regions have been investigated in polyethylene (PE) and polyethylene terephthalate by other workers [1, 8] using electron microscopy, and it has been clearly shown that voids are formed due to material extraction. Weight and volume measurements carried out by us indicate that the voids formed occupy about 3 to 5% of the volume for the samples used. These data have been linked with electrical measurements to produce an electrical equivalent circuit of the impregnated films [9].

After treatment, at both 100° C and 60° C, two further effects were invariably seen following solvent removal: firstly, the whole film became opaque, much of the surface detail also being lost; secondly, irregularly-spaced dark and light rings, around the spherolite centres, became visible (Fig. 4).

The whitening was thought to be due to the large-scale production of voids, within the film, caused by extraction of non-crystalline material. These voids, which will scatter light passing through the film, have already been proposed as an explanation of spherulite boundary darkening after solvent action in PE [8]. Reintroducing the solvent gives the film back its transparency, reinforcing the idea of light scattering by voids.

The reason for the appearance of the annular rings is much less evident. Generally, such rings are due to regular twisting of the crystalline axis as radial growth continues. In Fig. 1, however, no such detail was noticed and such rings only appeared after solvent action. It was decided to investigate the role of temperature in the ring formation, and to this end, we focused a light beam into the sample just long enough to cause partial remelting. After the treatment irregular ringing was once again observed: it has been suggested that the rings are most likely to have

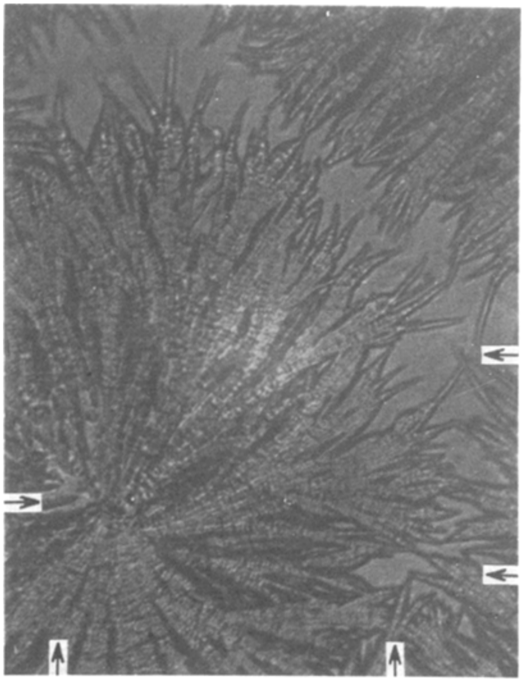
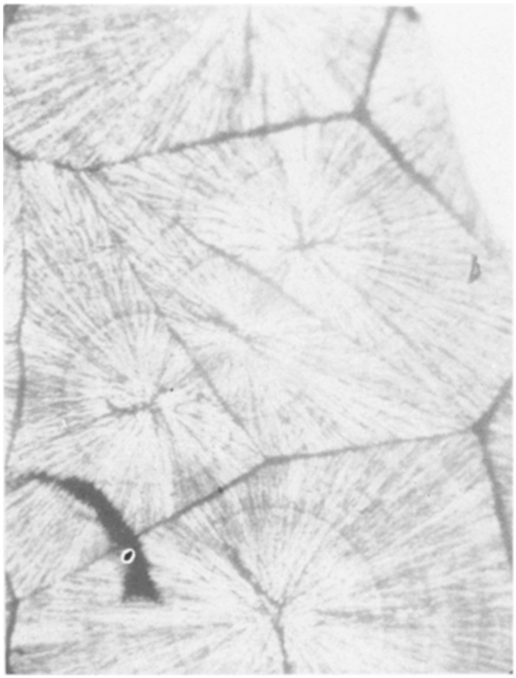


*Figure 3* Impinging spherulites in PP, $T_c = 125°$ C. Arrows indicate, trapped, non-bulk crystallized, regions (reflection micrograph) (× 185).



annular ringings, appearing after impregnation/extraction for crystallized PB. The impregnant used is benzylneocaprate (reflection micrograph) (× 30).

been formed either by a form of stop–go recrystallization* in the presence of the solvent or by a structural reorganization aided by the large glass transition temperature depression, $\Delta T_g$, during impregnation (in this case $\Delta T_g \approx 70^\circ$ C).

During the above experiments regions which were partially melted showed that the original outline of size, $d \geqslant 2$ mm, of the spherulites remained, but that small-angle light scattering [10] indicated the presence of small spherulites, of size $d \leqslant 10\,\mu$m, in the boundary regions. The probable cause for the remaining outlines is that these regions contain large quantities of non-crystallized impurities, as has been already suggested, and that large-scale nucleation has taken place along these impurity-rich lines.

During the optical investigations in PP and PB the well-documented double-leaf structure has been observed for sizes up to 300 $\mu$m radial diameter and the uniformly distinguishing regions, as described by Magill [11] in Nylon 56 and 96.

As already noted it was sometimes observed that the impinging spherulites do not seem to come into perfect contact as shown in Fig. 2, but it must be admitted that this arrangement is an exception rather than the rule. When investigating PP, the situation shown by Fig. 3 is found which clearly shows the fibre-like growth and radial branching from the central nucleation point. The frond-like nature of the individual branches is clearly visible and several different levels of growth can be seen in the sample thickness.

Fig. 3 suggests that the final joint will be a highly inter-locked one due to the crossing over of many branches. Close observation shows that once the "fingers" come into contact with others either extending from other spherulites or from the parent one, their growth stops due to lack of crystallizable material available in their direction of growth.

The final joint will be highly inter-locked and it is likely that regions will exist at the interfaces and inside the spherulites which are left uncrystallized until the sample is cooled, as indicated at the point of intersection of the arrows on Fig. 3. Subsequently crystallized or not, on cooling, these regions will be suceptible to solvent attack and it is thought that these are the regions responsible for the voiding observed under solvent action.

The presence of many cross-linking chains, in the inter-spherulite regions has also been evidenced by the results of mechanical fracture tests.

Films which have been treated with hot solvents, which were then extracted using methanol, and have lost up to 10% of their original material, *never* fracture along the spherulite boundaries; they fracture either cross-diametrically or execute semi-circles about the spherolite centres.

A link between the ringing found and the fracture paths has been sought but no conclusive evidence has yet been found.

## 5. Conclusion

Our studies show that the boundary regions between the spherolites are not perfect "butt" joints, but are highly interlocked and must contain a large number of non-crystalline or small-scale crystallized regions. Along with the similar regions inside the spherulites formed by branch splaying and enclosure by impinging branches, these regions will be particularly susceptible to solvent attack. It is probable that there is as much "voiding" inside the spherulites as there is at the boundaries.

Further work is being carried out to investigate the effect of an applied electric field on the crystallization process and this work is linked with solvent impregnation studies conducted in the presence of an applied field. Studies are also underway to determine the effects of varying degrees of crystallinity on the electrical and impregnation properties of thin polymer films such as those used as industrial insulators.

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