

SALS AND MORPHOLOGY OF POLYPROPYLENE SPHERULITES

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ABSTRACT

Spherulites of different morphological features have been obtained by varying the cooling rate of polypropylene melts through the crystallization temperature range from 120°C to 90°C. It was found that SALS is very sensitive to the changes of internal structure of the spherulites, and information about their morphological difference can be obtained according to the model theories and statistical theories of SALS.

INTRODUCTION

Small angle light scattering is a very useful technique in studying the superstructure of crystalline polymers. It gives us information about the shape and size of the superstructures and the crystalline packing within them. Spherulites usually show the well-known four-leaf clover H_V scattering patterns which are resulted from the spherical symmetry of the orientation of the refractive index ellipsoid axes of the volume unit with respect to the center of the spherulite^[1]. These scattering patterns may be extended in directions of different azimuthal angles and this has been attributed to the difference in orientation of crystallites or molecules with respect to the radius of the spherulite^[2]. For spherulites of most polymers the H_V patterns are extended in directions of 45° to the polarization direction of polarizer and analyzer (the $\times$ type). Only in few cases^[3-5], as for polyethylene terephthalate, polybutylene terephthalate (PBT) and PBT segments of block copolymers H_V scattering patterns extended in the polarization directions of the polarizer and analyzer (the $+$ type) have also been detected at appropriate conditions of crystallization in addition to the usual $\times$ type patterns. It is interesting to study the SALS patterns and morphology of polymers with different chemical structure, with the purpose of finding out the main factors affecting the molecule and crystallite packing within the spherulites. In this paper various types of scattering patterns for isotactic polypropylene spherulites are reported.

EXPERIMENTAL

An isotactic polypropylene sample J300 of the Xiangyang Chemical Engineering Factory was used. Its melting index at 230°C was 1g/10min under the shear stress of 2×10^5 dyne/cm. The polypropylene films between two pieces of microscope cover glass were at first melted at 230°C for 2–3 min on a Mettler FP2 hot stage, then cooled down to a set temperature followed by a quenching treatment. The thickness of the films was about 50 micron.

SALS experiments were performed with a Spectra-Physics model-145 He-Ne gas laser ($\lambda = 6328\text{\AA}$). Scattering patterns were recorded on Polaroid Film type 52. A Wild Heerbrugg polarizing microscope and a Siemens D-500 X-ray diffractometer were also used in this work.

RESULTS

Three types of scattering patterns have been observed for polypropylene films by changing the cooling conditions, which are listed in Table 1 and are principally distinct from each other

Table 1 Thermal history of samples of different types

Type	Cooling conditions from 230°C				Cooling rate through 120°C—90°C
	Cooling		Quenching		
	Rate(°C/min)	$T^*(^{\circ}\text{C})$	Type	$T^*(^{\circ}\text{C})$	
A	10	140—230	Metal block	25	3000°C/min
B	10	120—230	Air	25	200°C/min
C	0.2, 10	90	Air	25	0.2, 10°C/min

T^* : End temperature of cooling or quenching process.

in magnitude in their cooling rate through the temperature range of 120°–90°C. The cooling rate for type A and type B has been measured by molding a thermocouple within the film sample. In the case of rapid cooling (type A) typical $\times$ type spherulitic H_V scattering patterns were obtained (Fig. 1a) as in the literature. Decrease of the cooling rate (type B) results in scattering patterns of quite different characteristics. The H_V patterns are extended at the azimuthal angles of 0° and 90° (the + type) and the V_V patterns have the $\times$ type (Fig. 1b). The scattering intensity does not show a maximum with increasing the scattering angle. Further decrease of the cooling rate through the temperature range of 120°–90°C (type C) results in a very strong but circular symmetric scattering pattern for both H_V and V_V conditions (Fig. 1c).

The polarizing micrographs of polypropylene of the three types are given in Fig. 2. The spherulites of type A have the spherical shape and the clear Meltase cross. Their size is about 15 μm . The micrographs of samples of type C show very large spherulites of dimensions around 75 μm , and clear truncation boundaries between them. Stripes developed radially from the center of the spherulite were observed, but there was not any clear Meltase cross. In the case of type B the morphological features are rather diffuse. One can still find some crystalline

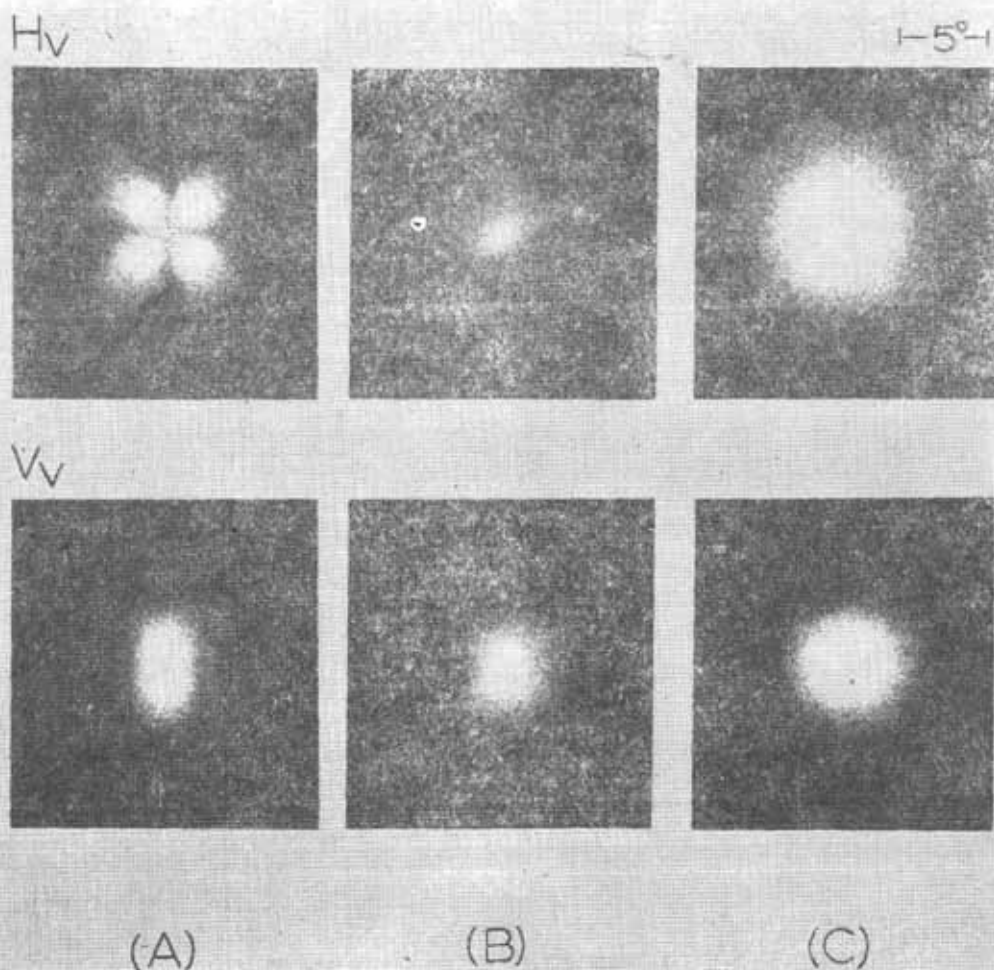


Fig. 1 SALS patterns for polypropylene samples of different types

superstructures with stripes radially extended from their center but their boundary is usually not clear and no Meltase cross was observed.

WAXS studies indicate the usual monoclinic crystallographic structure for all the samples. Fig. 3 is a result for sample of type A. Observation of SALS patterns during heating process shows that the $+$ type H_V scattering for samples of type B does not disappear until the temperature reaches the melting range.

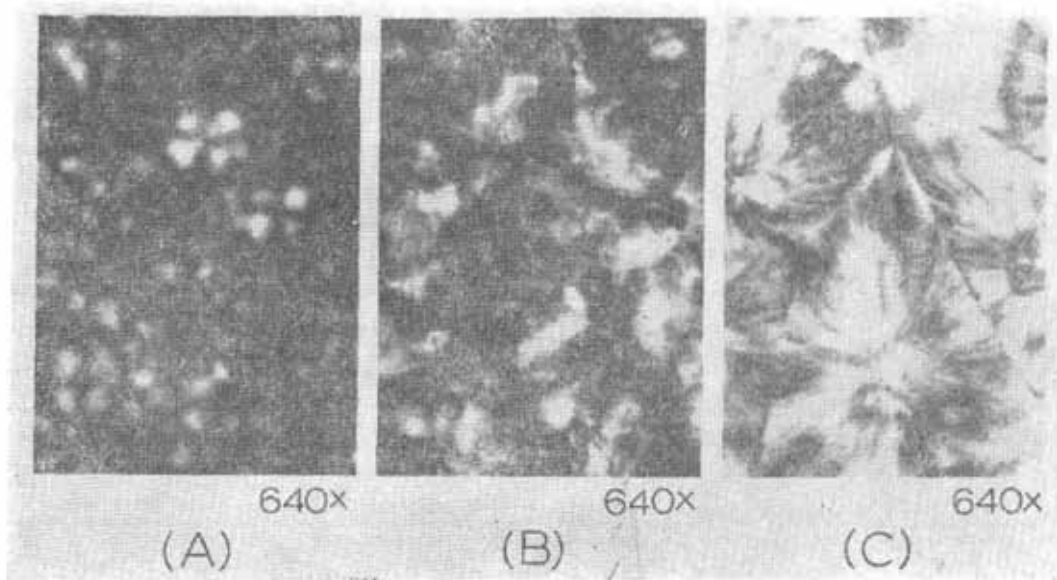


Fig. 2 Polarizing micrographs for samples of different types

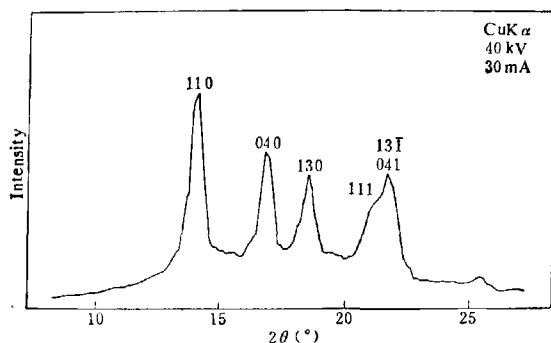


Fig. 3 WAXS results for samples of type A

DISCUSSION

The results show that the morphology and the scattering patterns of polypropylene samples can be evidently changed by varying the crystallization conditions. Although the superstructures in samples of type B and type C are not the typical spherulites as in the case of type A, but we can still find crystalline stripe-like structures extended outward radially from a common center within these superstructures. In this sense these samples of different types can still be considered as polypropylene containing spherulites of different features. Padden and Keith^[6] have described five different types of spherulites for polypropylene samples crystallized at different temperature ranges, but they did not give the scattering patterns of their

samples. Spherulites of type A and type B are corresponding to their type III and the mixed type respectively, but no evidence of polymorphism is found for type A as in the case of their type III. Spherulites of type C should be similar to their type II according to some morphological features and crystallization conditions. As the crystallization conditions of our samples and those of Padden and Keith's are different, so a complete identification of the different types of morphology reported in the two papers is not supposed to be expected.

The difference in scattering patterns of polypropylene spherulites means that polyterephthalates are not the only polymers which may have different crystallite packing within their spherulites and give different scattering patterns. It seems that the crystallization conditions, but not the chemical structure of the molecules, should be the decisive factor in controlling the internal structure of the spherulites.

In the case of polyterephthalates different types of scattering patterns can be explained on the basis of the same model—the model of anisotropic sphere^[1,2], while for the polypropylene samples the scattering patterns are so different that they should be explained by using different SALS models. The model^[1] with spherical symmetry of the optical properties of the volume unit with respect to its center can describe the scattering patterns of spherulites of type A. According to the SALS theories the four-leaf clover H_V pattern without intensity maximum for type B implies the existence of anisotropic rod-like scattering entities within these samples^[2,7], and the circular symmetry of the H_V scattering pattern of type C should be attributed to the situation of random correlation of orientation fluctuation in these samples^[8]. It is obvious from these results that the internal structure of spherulites for a given polymer can be quite different and light scattering is very sensitive to these variations.

The scattering patterns of anisotropic rod-like scatters have been observed for many polymers^[9-13], and the H_V patterns can also be extended in different directions as in the case of anisotropic spheres. It has been considered to be related to the crystallite packing within the rods and the orientational correlation between the rods^[14]. To our knowledge no polymer having rod-like scatterings of different extensions even at different conditions has been reported before. As the $\times$ type scattering patterns without intensity maximum have been obtained for polypropylene blended with SBS block copolymers^[13], so polypropylene may be one of the examples that shows both $\times$ type and $+$ type rod-like scattering patterns.

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