Spherulite formation in poly(ethylene oxide) mixtures

Stephen Z. D. Cheng, Jeffrey S. Barley and Paul A. Giusti
Institute and Department of Polymer Science, College of Polymer Science and Polymer Engineering, The University of Akron, Akron, Ohio 44325-3909, USA
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The morphologies of three-step crystallized poly(ethylene oxide) binary mixtures are studied. In the first step, the samples isothermally crystallize at high temperature to form precursors of the spherulites (or hedrites). The following quenching process of the samples to liquid nitrogen, as the second step, shows initial stages of the spherulitic (or hedritic) development. After quenching, the samples were brought back to room temperature, and further crystallized as the third step. Many different types of immature spherulites (or hedrites) are observed. This can be explained by anisotropic initial development of the spherulites. Two different morphological portions can be generally distinguished: the main framework portion grows first from its small single crystal precursors during the quenching, and the in-filling portion develops later in the third step. Microsectors and microfacets are found in the main framework portion of the spherulites.

(Keywords: crystal growth; hedrite; initial stage; in-filling and main framework portions; microfacet; microsector; morphology; poly(ethylene oxide); spherulite)

INTRODUCTION

Spherulitic crystalline texture is one of the most common morphologies in semicrystalline macromolecules. Over 50 polymers crystallized from the melt have shown this texture at relatively large supercoolings, as observed by optical or electron microscopy. The chemical structure, crystal lattice and symmetry, or flexibility of the chain molecules vary widely[1]. Typical observations are found in polyethylene (PE)[2–6], isotactic polypropylene (i-PP)[7–10], isotactic polystyrene (i-PS)[11–13] and poly(aryl-ether-ether-ketone) (PEEK)[14–16].

The spherulitic formation in macromolecules has been a focus of attention since the late 1950s. A common representation of the development of a spherulitic texture is shown in *Figure 1*. It is evident that generation of a spherulite starts from a precursor structure. Quite often, the precursor consists of single or twin crystal aggregates with polygonal shapes. Such spherulitic developments were detailed first by Popoff[17] and Morse and Donnay[18] in small molecules, and have been discussed in detail for application to polymer spherulites by Keller and Waring[19]. For macromolecules, the centre of the spherulite is not structurally homogeneous, but contains symmetrical double or leaf-shaped inhomogeneities (eye-structure). Many examples of such an initial stage of spherulite development (steps 2 and 3 in *Figure 1*) have been observed via electron microscopy and referred to in this paper as the main framework portion (sheaf-like structures).

Today it is quite certain that spherulitic developments involve three mechanisms: branching of folded chain lamellar crystals which comes about via spiral growth through screw dislocation along the chain direction in a crystal[20]; splitting, which is introduced by some kinds of defects on crystal growth surfaces which stop the lateral crystal growth[21,22]; and under certain crystallization and molecular mass distribution conditions, a morphological instability which is the result of gradients in the concentrations of segregated species[23]. However, the description of spherulitic formation as a whole remains open to development.

For the PEO binary mixtures (MW = 3468/105 000), it was found in our previous report[24] that the mixtures show three different texture levels: the spherulite as a whole; the crystal-growth unit comprised of a stack of lamellar crystals which apparently grow as one unit; and the individual lamellae. Each of these three texture levels change with supercooling. Furthermore, in the regime II growth of the high molecular mass component in the PEO mixtures[25], we have found a morphological instability of the crystals. The thickness of the stack of lamellar crystals is on the same order of magnitude as the characteristic length $\delta = D/v_c$ (ref. 24), where D is the diffusion coefficient of the low molecular mass component and v_c the linear crystal growth rate of the crystals, in the growth mechanism proposed by Keith and Padden[23].

In this paper, we will extend our study into a more general description of the spherulitic developments in PEO mixtures when a three-step crystallization procedure is applied. In the first step, the PEO mixtures isothermally crystallize at high temperature to form the precursors of the spherulites (or hedrites) (step 1 in *Figure 1*). This is then followed by quenching in liquid nitrogen as the second step. During the quenching, the main framework portion of the spherulites anisotropically forms from its precursor (steps 2 and 3 in *Figure 1*). After this quenching, the samples are brought back to room temperature, and the in-filling portion of the spherulites develops. Many apparently different types of observations in those spherulites can result from the examination of different cross-sections of the spherulites. Features that may be related to microfacets and microsectors in the spherulites are also discussed.

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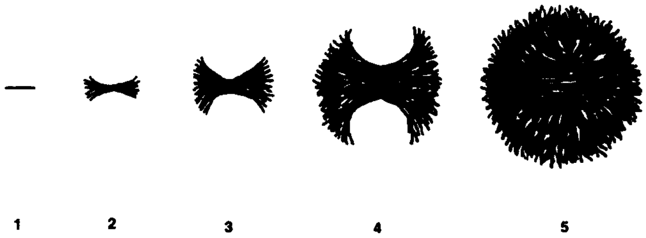

Figure 1 A schematic drawing of five stages of spherulitic development

EXPERIMENTAL

Materials and samples

The PEO fractions were purchased from Polyscience, Inc. and Polymer Laboratories, Ltd. The molecular mass distributions of the fractions are very narrow, typically with $\bar{M}_w/\bar{M}_n \leqslant 1.05$. Samples of the PEO mixtures were prepared by solution blending of a low molecular mass fraction (MW = 3468) with a high molecular mass fraction (MW = 105 000). The molar ratio of the low and high molecular mass components in the mixtures was 0.72/0.28.

The samples with free surfaces were prepared for transmission electron microscopy (TEM) on glass slides with a size of about 10 × 10 × 1 mm. The samples were held in the molten state on a hot stage (Mettler FP-52) for about 15 min under a dry nitrogen atmosphere. Crystallization was then carried out by quickly quenching the samples in a Neslab TMV-400D water bath to a prefixed temperature. The temperature of the water bath was controlled with an accuracy of ±0.1 K. After a certain predetermined crystallization time, the samples were quenched to liquid nitrogen.

Transmission electron microscopy

In order to study the internal crystalline texture of the PEO mixtures, a new etching method was developed[26]. It is especially useful for water-soluble polymers that cannot be treated by other traditional etching methods[27–30]. In comparison to replicas of the free surface, more detailed crystalline textures can be seen when such etching is utilized. Our optimal etching conditions were obtained using a 0.21 mass fraction of C_2H_5ONa in ethyl alcohol. The samples were etched at 298.2 K for 5 min with continuous agitation. Ethyl alcohol was then used to wash the samples at the same temperature for 10 min. After drying, the surfaces obtained were obliquely shadowed with Au/Pd (0.6/0.4) and then replicated with carbon. The replicas were floated off in water and picked up on copper grids from acetone (which helps in extending the replicas). The TEM was done at 100 kV (Jeol, JEM-120U transmission electron microscope).

RESULTS AND DISCUSSION

When one carries out crystallization of the PEO binary mixtures via a three-step procedure, it is possible to observe the initial stage of spherulitic development if the crystallization temperature, T_c, and time, t_c, are properly chosen. *Figures 2* and *3* show several examples after the mixture of 0.72/0.28 (MW: 3468/105 000) was crystallized at 331.2 K for 2 h before it was quenched in liquid nitrogen. The crystallization at the high temperature leads to a formation of the precursors which act as the primary nucleation of the spherulites (or hedrites). After bringing the quenched samples back to room temperature, two different portions can be distinguished in one spherulite. One portion is the main framework of the spherulites, and the other is an in-filling portion formed

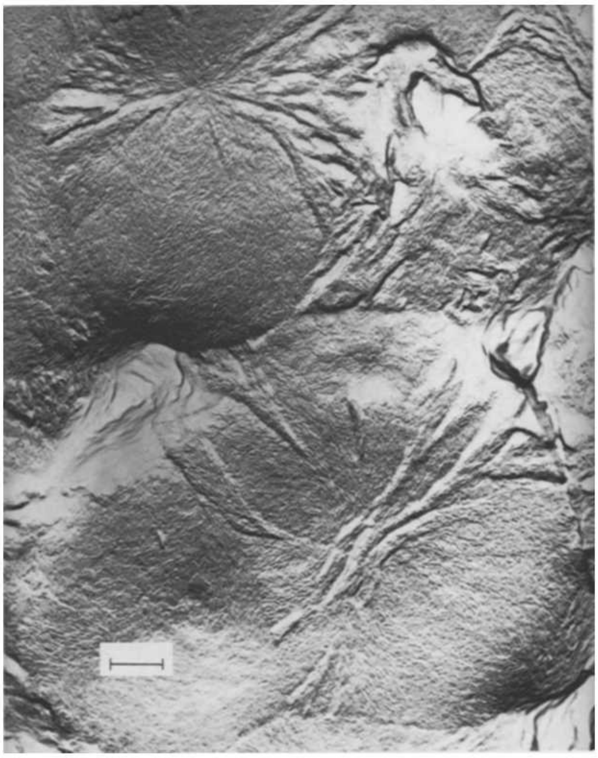

Figure 2 Spherulitic textures of the PEO mixture crystallized via a three-step procedure. The scale bar is 0.5 μm

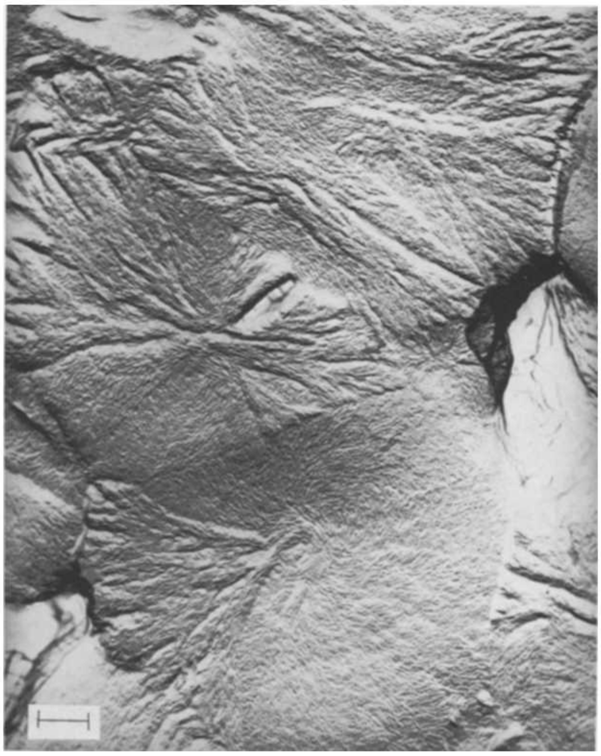

Figure 3 Spherulitic textures of the PEO mixture crystallized via the same three-step procedure used in *Figure 2*. The scale bar is 0.5 μm

laterally. A clear boundary can be observed between these two portions. Without this in-filling portion, the first portion can also be called a hedrite. It is quite clear that those main framework portions are predominantly two-dimensional and anisotropic, as shown in *Figure 1* (steps 2 and 3). They grow during the quenching to liquid nitrogen from their precursor aggregates. In contrast, the in-filling portion formed after the samples warmed to room temperature, but before etching. They can be recognized by different stacking and slightly but distinguishably different lamellar thicknesses in these two portions. More importantly, this judgment is based on the observations in *Figures 2* and *3* that the boundary between the two different portions in one spherulite is curved, and the tangential lines to this boundary are always on the side of the main framework portion, as shown in *Figure 4*. Furthermore, it appears that the main framework portions shown in *Figures 2* and *3* are not identical in pattern. The main framework portions in *Figure 2* seem more or less to fit the description diagrammed in *Figure 1*. However, in *Figure 3* (lower part), there is a fan-like texture only in one side of the spherulite. Even more differently, *Figure 5* shows spherulites which do not have any evident main framework portion. Additionally, *Figure 6* illustrates growth in which almost no in-filling portion is observed. From this figure, one can see that the crystalline texture keeps more or less the shape of a single polygonal crystal, and sometimes the shape of a twin crystal. We called the ledge boundaries of such a spherulite 'microfacets'. The line formed by microfacet intersection points and the point of the precursor is the boundary between two 'microsectors', as shown in *Figure 7*. These microsectors are formed due to different directions of crystal growth, but the linearity of the microsector boundaries indicates equal crystal growth rates for the microsectors.

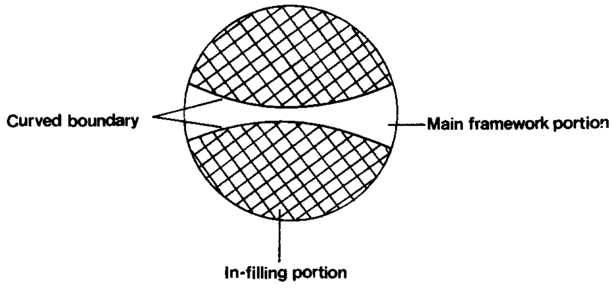

Figure 4 A schematic drawing of two different portions in one spherulite: the main framework and the in-filling portions

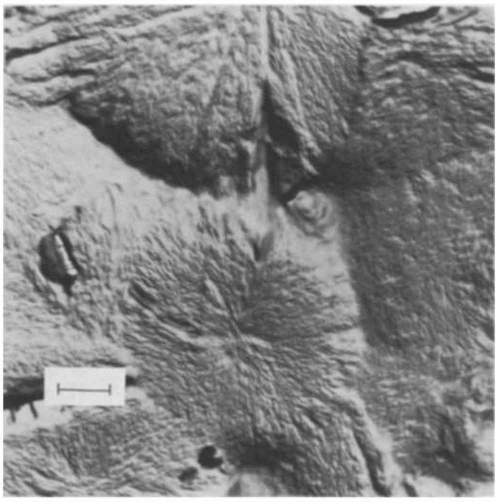

Figure 5 Spherulitic textures of the PEO mixture crystallized via the same three-step procedure used in *Figures 2* and *3*. The scale bar is 0.5 μm

Figure 6 Spherulitic textures of the PEO mixture crystallized via the same three-step procedure as used in *Figures 2*, *3* and *4*. The scale bar is 0.5 μm

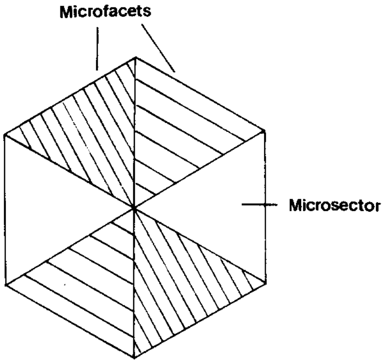

Figure 7 A schematic drawing of the microsector and the microfacet in the main framework portion of one spherulite

The apparently different types of spherulites observed in *Figures 2*, *3*, *5* and *6* can be explained as different cross sections of a given spherulite. The PEO samples are so thick that spherulites are nucleated at various depths below the surface, and with the main framework randomly oriented. Through the etching, the area of a given spherulite that intersects the surface is consequently also random. On our surface replicas, therefore, one may observe varying view directions and various levels of intersection of the spherulites as shown in *Figures 2*, *3*, *5* and *6*. Our detailed analyses are schematically drawn in *Figure 8*. The cutting planes, such as A–A, B–B, etc., are the planes which we observed via TEM after etching. The A–A cutting plane of *Figure 8* can thus be found in *Figure 6*; the B–B cutting plane, in *Figure 5*; the C–C

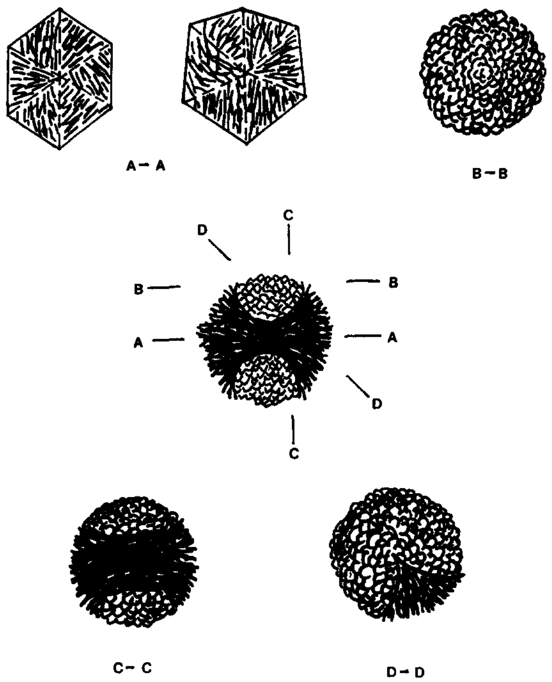

Figure 8 A schematic drawing of a spherulitic texture viewed from different directions

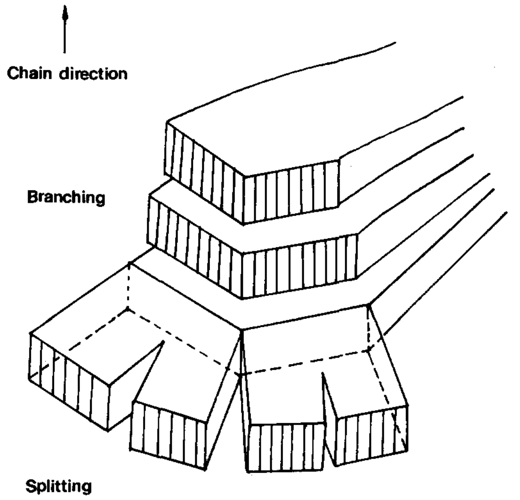

Figure 9 A perspective sketch of the branching and splitting of folded lamellar crystals during the crystal growth

cutting plane or the centre original, in *Figure 2* and upper part of *Figure 3*; and the D–D cutting plane, the lower part of *Figure 3*.

Of special interest is the formation mechanism of the microfacet and microsector. The microfacet is more or less a duplicate and enlargement of the shape of its precursor aggregate. However, in this case, we observe a polycrystal consisting of many lamellar crystals, instead of a single or twin crystal. It involves an important step of PEO spherulitic development, namely, the transition from a single crystal or a twin crystal of the precursor to lamellar crystals with elongated habits. This step is mainly caused by branching and splitting of the folded chain lamellae during the crystal growth. A perspective sketch is shown in *Figure 9*. Yet the detailed influences of branching and splitting in spherulitic development are not quantitatively clear.

On the other hand, the formation of microsectors is mainly caused by the different growth directions at different microfacets initially developed from its precursor. One may expect a limited translational symmetry along the growth direction during the development. However, this symmetry can be easily disturbed as shown in *Figure 6*. Such a change of the crystal growth direction between two different microsectors indicates that the growth of one microfacet from its precursor is more or less restricted to have the same growth direction, revealing their common origin; and screw and edge dislocations or other types of defects, such as internal stresses and microcracks, may be the cause of the change in crystal growth directions[31].

From our observations of the spherulitic development in PEO mixtures, we ask, how do precursors, which usually are regularly polygonal single or twin crystal aggregates, develop into a hedritic texture? If the crystal branching and splitting are the causes of the initial stage of spherulitic development, do they occur passively or actively? Namely, does each defect location function as an origin of branching or splitting? We know that morphological instability exists in PEO mixtures under certain crystallization conditions. What is its influence on the spherulitic development? These questions refer to many topics which are still in active debate. The relationships between the densities of branching, splitting and the thickness of the stack in lamellar crystals with respect to supercooling and concentration of PEO binary mixtures continue as topics of great interest in our research laboratory.

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