

THE SPHERULITE-LIKE STRUCTURE OF MAIN CHAIN THERMOTROPIC AROMATIC COPOLYESTERS*

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Abstract A new spherulite-like structure of main chain thermotropic aromatic copolyesters formed in solution cast specimens was observed and was studied by means of polarizing microscopy, X-ray diffraction, SEM and IR spectrometry. Results indicate that the spherulite-like structure of main chain thermotropic aromatic copolyesters formed from the casting solution (phenol/ $\text{Cl}_2\text{CH}_2\text{CH}_2\text{Cl}_2$) is not a real crystal but only a high oriented arrangement of the macromolecular chains as a spherulite. This resulted from the interaction between the needle-like crystal of phenol and the rigid mesomorphic groups of molecular chain. The parallel packing of extended copolyester molecules along the needle-like crystal of phenol leads to the formation of the spherulite-like structure.

Keywords Spherulite-like structure, Thermotropic aromatic copolymer, PET/PHB

INTRODUCTION

In the last decade, the study of main chain liquid crystalline polymers (LCPs) has been an active area of scientific and practical interests. Recently, attention has been paid to the study of the crystalline morphology of LCPs. It has been found that large spherulites of lyotropic aromatic polyamides can be formed from their anisotropic solutions^[1-4], but the morphological structures of thermotropic aromatic copolyesters (TACPs) are not well understood^[5, 6]. TACP is a kind of rigid polymer containing mesogenic units which has been postulated as a having rigid backbone to form liquid crystalline melts. Because of the rigidity of the molecular chains, the aromatic copolyester has very special characters of the crystalline morphological structure^[7, 8]. In a previous paper, we discussed the crystalline morphology of thermotropic aromatic copolyesters with flexible spacers of different lengths^[9]. It was found that the crystalline morphology is dependent on the rigidities of the macromolecular chains. In the present paper, we report a large and highly oriented new structure of rigid aromatic copolyesters. This was formed during the evaporation of the solution of the aromatic copolyesters. So far as we are aware, this is the first time that this kind of large size spherulite-like structure of thermotropic aromatic copolyesters can be formed during solvent evaporation. The morphological structure of this large spherulite has been investigated by means of polarizing optical microscopy (POM), wide angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) and IR spectrometry.

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EXPERIMENTAL

Materials and Sample Preparation

The main chain thermotropic aromatic copolyesters used in this work were copoly(ethylene terephthalate-*p*-oxybenzoate)(PET/PHB) with different ratio of components and copoly(*p*-oxybenzoate-6-oxy-2-naphthoate)(PHB/HNA). PET/PHB was supplied by the Beijing Chemical Industry Research Institute. PHB/HNA was synthesized at our institute. The intrinsic viscosities of these aromatic copolyesters were measured at 30°C, using the mixed solvent of phenol and 1, 1, 2, 2-tetrachloroethane (weight ratio: 1:1), which are listed in Table 1.

Table 1. The intrinsic viscosity of materials

Samples	PET/PHB				PHB/HNA	PET
	50/50	40/60	30/70	20/80	50/50	
$[\eta]$ (dL/g)	0.661	0.783	0.942	0.967	0.637	0.670

The polymers were dissolved in the mixed solvent of phenol and 1, 1, 2, 2-tetrachloroethane (1:1) to form an isotropic solution. Drops of this solution were dripped on clean and dry glass slides. The drops were spread out evenly on the slides, and then the slides were put into culture dishes. We placed the culture dishes into a desiccator and kept it at a cool and dark place for slow evaporation of the solvent. Finally, the large spherulites formed under these conditions were put into a vacuum oven at 50°C for 24 h to remove the remaining solvent, especially phenol.

The specimens for SEM observation were made by peeling off the polymer films from the glass slides, then coating a layer of gold on the surface of the films before observation.

Instruments

The microscopes used in this work were the Olympus Model BH-2 polarizing microscope and the Hitachi Model S-350 scanning electron microscope. The IR spectra and dichroism analysis were measured by using the Bruker IFS-113V Fourier transform infrared spectrometer, and X-ray diffraction patterns were recorded by using a Siemens Model D-500 X-ray generator, with Fe $K\alpha$ radiation operated at 25 mA and 50 KV.

RESULTS AND DISCUSSION

Spherulite-like Structure

When drops of the isotropic solution of PET/PHB in the mixed solvent of phenol and 1, 1, 2, 2-tetrachloroethane (1:1) were dripped on the glass slides, a special structure, just like a large spherulite, was formed after the evaporation of the solvent (Fig. 1). Its diameter is about several centimeters, so the structure can be seen clearly by naked eyes. The size of this structure depends on the area covered by the solution drop on the glass slide. It can be seen from Fig. 1 that numerous concentric circles form round the nucleus separated by a space of several millimeters. In most cases, only one nucleus is found in the sample, but sometimes, more than one nucleus appears on the same specimen. Between the nuclei, non-circular bounds can be seen. Under POM of crossed polarizers the spherulite-like structure shows a clear Maltese cross extinction pattern (Fig. 2). When a red compensator is inserted into the optical path of the microscope, the interference color in the first and third quadrants of the spherulite is blue, and the color in the second and fourth ones is orange. This phenomenon indicates that this spherulite-like structure has positive birefringence. Figure 1 also shows that the extinction of the spherulites under POM of crossed polarizers is a superposition of a Maltese cross and uniformly distributed dark concentric rings. The radial distance between neighboring rings is about 0.3 mm. Similar morphology of ringed spherulites has been reported^[8] for flexible chain polymers crystallized at proper conditions and was explained as being composed of radially packed lamellae in which the crystallographic

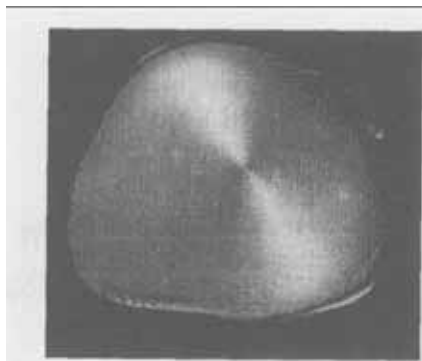


Fig. 1 Photo of the spherulite-like structure of PET/PHB (50/50) formed from casting solution

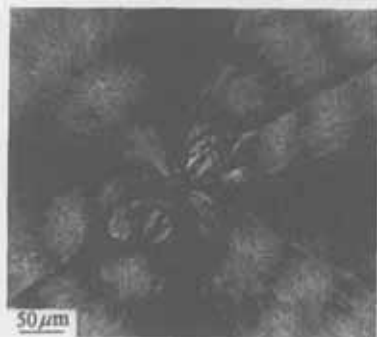


Fig. 2 POM micrograph of the spherulite-like structure of the same PET/PHB (50/50) used in Fig. 1 under crossed polarizers

orientation twists regularly. The samples used in this work are noncrystalline copolyesters. The formation of concentric circles cannot be explained by the regular twist of crystallographic orientation.

The formation of the spherulite-like structure is similar to that of common spherulites of polymers. The observation of the formation course shows that the structure grows from one nucleus, developing radially and simultaneously in different directions at the same speed. When there are several nuclei, the developing structures will meet each other, so non-circular bounds are formed. The two symmetric holes in the nucleus (Fig. 2) reveal that the formation mechanism of the spherulite-like structure is similar to the sheaf-like unidirectional growth mechanism of spherulites^[10]. After the nucleus forms, the fibrils grow radially to form a sheaf, the sheaf grows continuously and the two ends of the fibrils wind constantly until the two ends contact and penetrate each other to form a whole spherulite-like structure. Figure 3 is the POM micrograph of the spherulite-like structure of PET/PHB (40/60) copolyester formed under the same conditions. It can be seen that the morphology of this large spherulite-like structure is similar to that of Fig. 2. This large spherulite-like structure can also form in all copolyester samples of different composition under a proper condition.

To confirm the noncrystallinity of the spherulite-like structure, the samples were characterized by using WAXD analysis. The results indicate that although spherulite-like structure can be observed in most of the samples, their X-ray diffraction pattern did not show any peaks of crystals except a diffusion peak (Fig. 4). Figure 5 shows the SEM micrograph of the surface of the spherulite-like structure. The twisted lamellar sheaves in conventional spherulites were not observed, but concentric circles composed of holes can clearly be seen. These holes are arranged regularly radially in the spherulite and may result in the concentric circles under POM. All of these results proved that the spherulite-like structure is not a real spherulite, but only a highly oriented structure of the macromolecular chains.

In order to prove whether the large spherulite-like structure belongs to the copolymer or to the phenol, the samples were characterized by POM equipped with hot-stage. When the sample was heated to a temperature above the melting point of phenol and maintained there for a long time, the spherulite-like structure does not change. When it was heated to a temperature above the liquid crystal transition temperature of the PET/PHB copolyesters, the dark cross pattern can be maintained for some time, after which it changes into a nematic melt exhibiting schlieren texture (Fig. 6). This phenomenon indicates that the spherulite-like structure is formed by the polymer itself, and not by the phenol crystals.

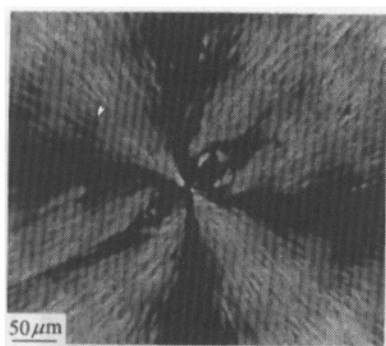


Fig. 3 POM micrograph of the spherulite-like structure of PET/PHB (40/60) under crossed polarizers

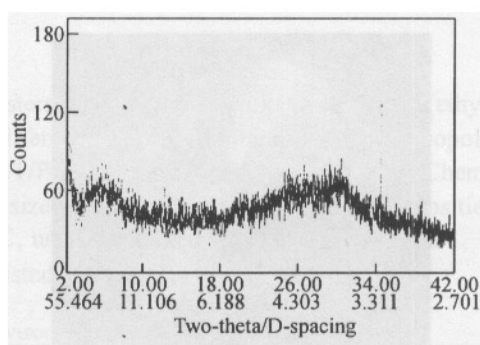


Fig. 4 WAXD pattern of the spherulite-like structure of PET/PHB (50/50)

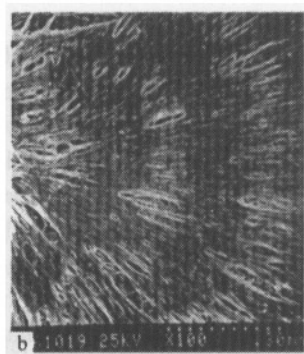
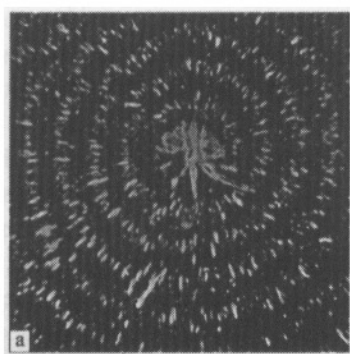


Fig. 5 SEM micrograph of the surface of the spherulite-like structure of PET/PHB (a); local magnification (b)

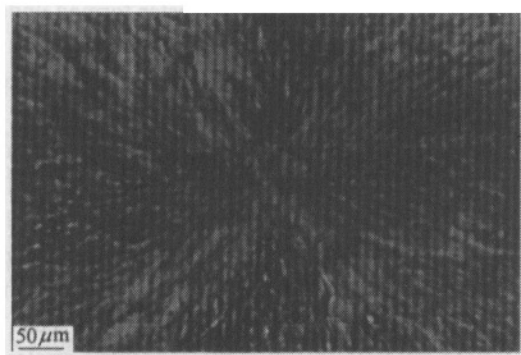


Fig. 6 POM micrograph of the spherulite-like structure of PET/PHB (50/50) heated to 220°C, under crossed

The Arrangement of Molecular Chains in the Spherulite-Like Structure

Polarized infrared spectroscopy is an effective method for characterizing the orientation of macromolecular chains. Figure 7 is the polarized infrared spectrum of the spherulite-like structure of PET/PHB copolyester. The absorption bands at 1261, 1204, 1163, 1099 and 1063 cm^{-1} belong to the C—O stretching vibration mode; the band at 1015 cm^{-1} is the bending vibration of C—H on the benzene ring; the absorption at 1601 cm^{-1} corresponds to the stretching vibration of the benzene ring. The transition moments of these vibration modes are along the directions of the bonds. The intensity of these bands for vibrations in the radial direction is much higher than that for vibrations

in the tangential direction. Defining the radial direction as the specified direction, we obtained the dichroic ratio $R > 1$, so the above bands are parallel bands. The band at 1720 cm^{-1} is the stretching mode of $\text{C}=\text{O}$, and the band at 727 cm^{-1} represents the bending vibration of the benzene ring. Their transition moments are vertical to the axial direction of the bonds. These two bands are perpendicular bands, because $R < 1$ was observed. These data indicate that the benzene rings and the $\text{C}-\text{O}$ bonds that extend along the molecular chain are put in order along the radial direction, but the $\text{C}=\text{O}$ bonds that are vertical to the molecular chain are arranged perpendicular to the radial direction. This means that the molecular chains of PET/PHB are extending along the radial direction.

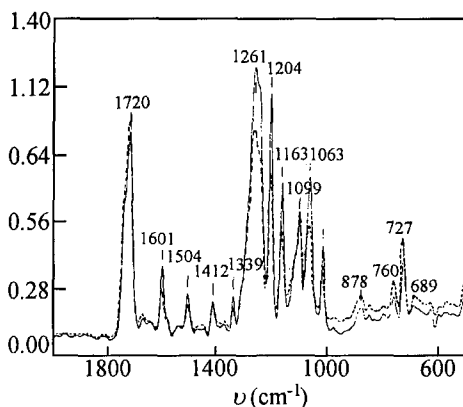


Fig. 7 The IR dichroism spectra of the spherulite-like structure of PET/PHB (—) parallel to direction; (-----) perpendicular to direction

The Influence of Phenol on the Formation of the Spherulite-Like Structure

When the spherulite-like structure forms from the solution, the crystals of phenol always form simultaneously, and the needle-like crystals of phenol cover the surface of the spherulite-like structure of the polymer. As the crystals of phenol are sublimating, the spherulite-like structure of the polymers gradually becomes visible. The needle-like crystals of the phenol are also orderly arranged along the radial direction. We found that the distance between the concentric circles in the spherulite of the polymer depends on the size of the needle-like crystallites in the phenol spherulite and increases with increasing size of the needle crystallites.

In order to reveal the influence of phenol on the formation of the spherulite-like structure of the polymers, the temperature of the system was controlled to prevent the separation of the phenol crystals from the polymer. As a result, the spherulite-like structure of the polymer cannot be formed. If the temperature of the system is decreased the phenol crystals separate out quickly, then the spherulite-like structure of the polymers can be formed from the solution at the same time. For a comparative test, a solvent mixed from *p*-chlorophenic acid and 1, 1, 2, 2-tetrachloroethane was used. We found that in this case the spherulite-like structure cannot be formed, when the solvent was evaporated. These phenomena indicate clearly that the crystallization of phenol plays a very important role for the formation of the spherulite-like structure of the aromatic copolyesters.

The Function of the Rigid Mesogenic Groups in the Formation of the Spherulite-Like Structure

In order to reveal the relationship between the rigidity of the molecular chain and the formation of the spherulite-like structure, another thermotropic aromatic copolyester PHB/HNA and pure PET without mesogenic groups were used for comparison. The same spherulite-like structure was formed for the specimens of PHB/HNA as shown in Fig. 8. The Maltese cross extinction pattern and the concentric circles can be seen clearly. The change of interference color verifies the

existence of positive birefringence. Figure 9 is a POM micrograph of the structure of pure PET crystallized from the mixed solvent of phenol and 1, 1, 2, 2-tetrachloroethane (1:1) after the sublimation of phenol crystals. Obviously, this structure is different from the spherulite-like structure observed above. The crystallites of PET only precipitated randomly along the extending direction of the phenol crystals. It implies that the formation of spherulite-like structure is an intrinsic behavior of the thermotropic aromatic copolyesters with rigid mesogenic groups.

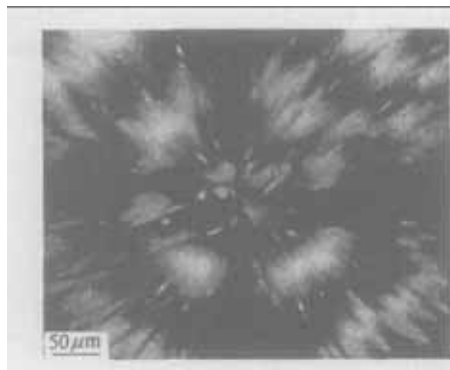


Fig. 8 POM micrograph of the spherulite-like structure of PHB/HNA, under crossed polarizers

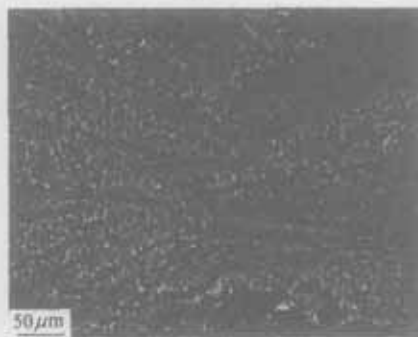


Fig. 9 POM micrograph of the crystallites of pure PET precipitated out after the sublimation of phenol crystal

The Formation Mechanism of the Spherulite-Like Structure

The spherulite-like structure of main chain thermotropic aromatic copolyesters formed from solutions is a result of the anisotropic interaction between the needle-like crystals of phenol and the mesogenic groups of copolyester molecules. It is a reflection of the “self-assembly” property of the liquid crystalline molecules. As is well known, PET/PHB and PHB/HNA are two thermotropic aromatic copolyesters, their molecular chains are composed of rigid mesogenic groups which contain several benzene rings. Because of the high polarizability of the π electron cloud of the benzene ring, the intermolecular interaction between the benzene rings is very strong. The planes of the benzene rings attract each other so that the mesogenic groups are arranged orderly. When the phenol crystals were crystallized from the solution, the extension of its needle-like crystals causes an inducing force to make the mesogenic groups of PET/PHB and PHB/HNA oriented along the direction of the force on the base of the phenol crystals. This orientational self-assembly mechanism for rigid macromolecular chains is similar to that of the orientational arrangement of small molecule liquid crystals on a rubbed substrate. At the same time, the interaction between the benzene rings of the mesogenic groups impels the molecular chains of the copolyesters to arrange themselves closely and parallel with each other. When the molecular chains extend to the ends of the needle-crystallites of phenol, the chains become disordered and form the holes due to the intersection of the crystals, therefore, concentric circles are formed. From the above mentioned results, it is concluded that the spherulite-like structure of TACPs formed in the solution cast specimens is resulted from the parallel packing of extended copolyester molecules along the needle-crystallites of phenol before its evaporation.

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