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Morphology of Poly(tetramethylene succinate) Spherulites

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Some of the aliphatic polyesters have been reported to be decomposed relatively easily under natural environmental circumstances,[1-3] while many synthetic polymers create pollution problems because of difficulty in decomposition.[4-7] Poly(tetramethylene succinate) (PTMS) is a prominent one in the aliphatic biodegradable polyesters, but few reports about it's morphological features are available.

In our previous work,[8] PTMS were synthesized and electron micrographs of the single crystals were presented with the lattice parameters which were determined from electron diffraction pattern of the stretched films.

Lots of studies have been performed to investigate the structure of spherulites by the optical and electron microscopy. In 1950s Keller reported excellent studies on the structures of polymer spherulites. In the series of his works,[9-11] the morphological feature of spherulites of poly (ethyleneterephthalate) (PET), polyethylene and polyamides were presented. The major characteristic of PET spherulites between cross polars was the extinction cross pattern which referred as Maltese cross.

In the case of polyethylene, both of the Maltese cross and the closely spaced dark ring system are observed. As the crystallization temperature increase, Maltese cross becomes irregular and bushy like in appearance. All these extinction effects are understood on an optical level. And it is generally observed in ring structured spherulties that the ring spacing increase with crystallization temperature and may disappear altogether for crystallization at low supercoolings.

There are several arguments about the mechanisms of ring formation. Many people agree with Keller's idea[9] that the ring pattern under polarized light may originate from diffraction by phase grating in helicoidal structure. However Bassett[12] thought that the lamellae themselves form the ring structure, although he had not found any morphological evidence of twisted lamellar growth.

The concentric double ring structure in polymer spherulites is not a very common phenomenon, although the concentric double ring has been reported by other scientists. For example, Polyhexamethylene sebacamide[9] and polytrimethylene glutarate spherulites show the double rings between cross polars.[13] For the mechanism of this concentric double ring formation, either two theory which were mentioned above could be correct. But in general, it has been known that, in helicoidal structure model, double concentric rings may originate from the rotating of biaxial ellipsoid forming a helicoidal arrangement along the radius.

In this paper, the morphological changes of PTMS spherulites associated with the crystallization temperature were studied by Polarizing Optical Microscopy and Transmission Electron Microscope.

Experimentals

PTMS were fused between cover glasses on a hot plate for 5 minutes at 150 °C and subsequently immersed in a silicone oil-bath preheated to the crystallization temperature. The morphological features of PTMS spherulites were observed between crossed polars in optical microscope, OPTIPHOT-POL, Nikon.

In the above case, the material was crystallized between coverglasses. If the film crystallized with free surface, essentially similar spherulites were obtained. The surface morphology of that was investigated by Transmission Electron Microscope, JEOL-2000EX(II), using the replica method. And also the surface of samples grown between coverglasses was observed in the same way to compare with free standing one.

Results and Discussion

Straight Maltese cross is shown along the vibration directions of polarizer and analyzer in Figure 1. This spherulites was crystallized at 80 °C. The Maltese cross could be observed in the spherulites crystallized at the temperatures low-

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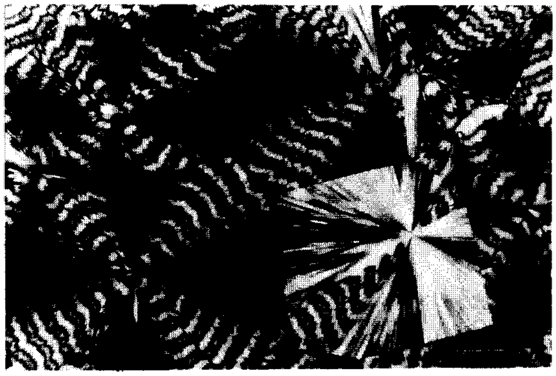

Figure 1. A polarizing optical micrograph (43 μm scale bar) of PTMS spherulites grown at 80 °C.

er than 80 °C. The picture also shows dark concentric rings in addition to the Maltese cross. The double ringed pattern was observed in the spherulites crystallized at above 60 °C, and it is more apparent with increase in temperature. It is known that the double ring pattern attributes to the biaxial optical property of the spherulites. We could know with the careful inspection of Figure 1 that the brightness of the alternating spaces between dark rings are different. That is to say, the gray band and the white band are shown in turns. This means that the birefringence of the bright bands are different in sign or magnitude if we accept the concept that the dark concentric ring arise from the twisted lamellar growth. By the insertion of red plate between crossed polars, it was found that signs of birefringence of the gray and white bands are different. The details are followed this.

First, in order to investigate the relationship between the direction of molecular chain orientation and that of the high refractive index, wide angle X-ray diffraction measurement was performed. And it was confirmed that drawn fibers of PTMS showed the chain orientation aligned along the draw direction. When this drawn fiber was placed parallel to the higher refractive index of the first-order red plate, the color changed to higher order, that is to say, they are in addition position in the cross polars. This means that the refractive index corresponded to the drawing direction of fiber is higher than that to the normal direction.

In the case of PTMS spherulites, it was observed by using the compensator that the color of white bands moved to higher order and that of gray bands moved to lower order within the quadrants perpendicular to the higher refractive index direction of the compensator. From these results, we can understand that the gray bands and the white bands correspond to positive and negative birefringence, respectively, and the chain was along the tangential dirction of spherulites.

The double ringed pattern of the spherulites was changed to the single ringed pattern when the crystallization temperature was lower than 60 °C. The spherulite grown in this temperature exhibited negative birefringence. At the temperature higher than 60 °C, the ring spacing consisted of gray and white band becomes wide with increasing temperature. The change of ring spacing against the crystallizing temperatures was plotted in Figure 2. The width of a gray band and a white band were almost the same over

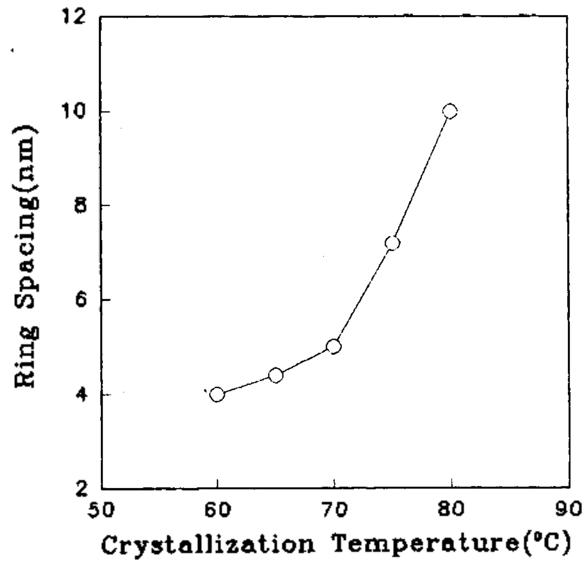

Figure 2. Changes of ring spacing consisted of gray and white band as a function of crystallization temperature.

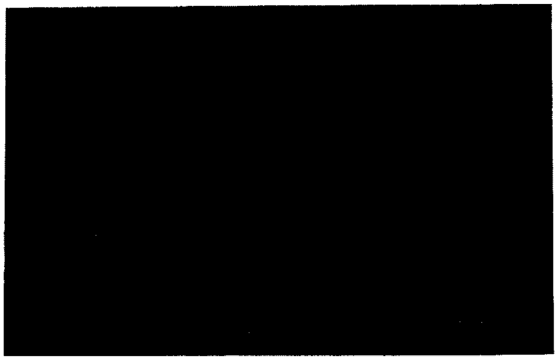

Figure 3. A transmission electron micrograph (1.43 μm scale bar) from the free surface of PTMS film crystallized at 80 °C for 20 minutes.

the whole crystallization temperature range at which the double ringed patterns are observed. From this result we knew that the value of optic angle was to be about 45° ± 5°. Figure 3 is the morphology of surface of spherulites crystallized at 80 °C which presented concentric double ring structure in Figure 1. However we could not find the morphological trends corresponded to concentric double ring. The dominant lamellae are the multilayer crystals which was formed with its edge-on stand. The edge-on growth was due to the volumetric restriction in thickness direction of samples. Besides the growth direction of axialites, in other quadrants direction in spherulites, lamellae lying flat on the basal plans of specimens, and they shows the growth manner of screw-dislocation.

The spherulites crystallized at temperature below 80 °C shows ringed patterns predominantly. A spherulite of radiating fibrillar growth as shown in Figure 1 is rare in the morphological feature of spherulites crystallized at below 80 °C.

The concentric double rings as shown in Figure 1 became irregular with increasing temperature and disappear at around 85 °C. Finally Maltese crosses could not be dis-

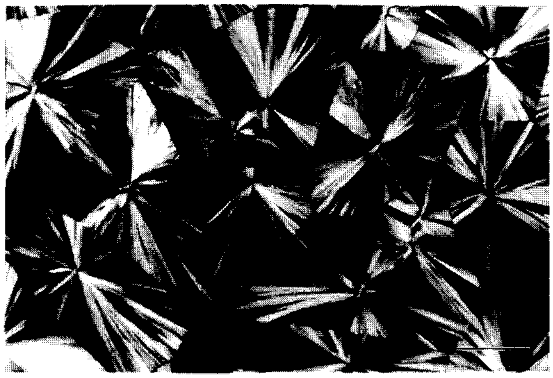

Figure 4. A polarizing optical micrograph (43 μm scale bar) of PTMS spherulites grown at 90 °C.

Figure 5. A transmission electron micrograph (1.6 μm scale bar) from the free surface of PTMS film crystallized at 90 °C for 30 minutes.

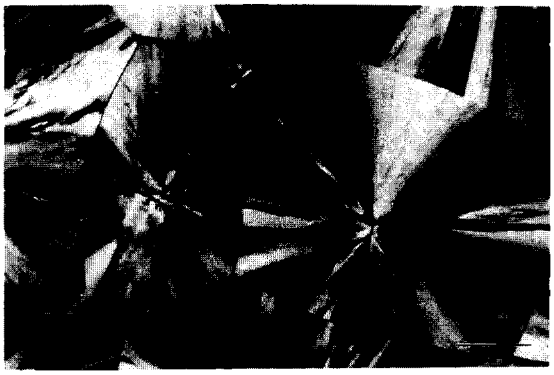

Figure 6. A polarizing optical micrograph (43 μm scale bar) of PTMS spherulites grown at 100 °C.

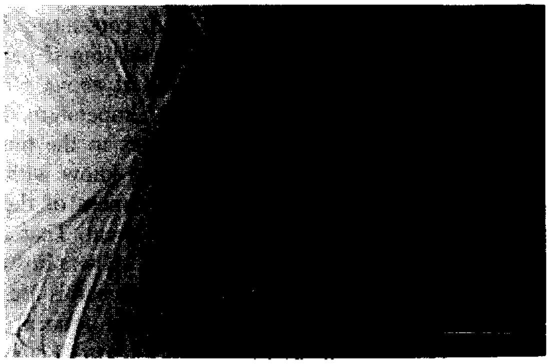

Figure 7. An optical micrograph (30 μm scale bar) of PTMS spherulites grown at 90 °C. This micrograph was taken by half-insertion of a black filter in order to increase the contrast.

tinguished above 85 °C (see Figure 4). The disappearance of Maltese crosses might result from the thickening of samples. In fact, when the fibrous structure is located in the middle of ring patterns (Figure 1), we could see the trace of Maltese crosses. And the irregularity and disappearing of dark concentric rings might comes from the irregularity of helicoidal structure.

The morphology composed of fibrillar growth and coarse structures propagating toward the radial direction were obtained at the temperature above 90 °C as shown in Figure 4. The similar structure were observed in the other polymers such as polypropylene, etc.

Figure 5 shows the surface morphology of spherulites crystallized at 90 °C. The dominant lamellae is the edge-on axialite propagating from center to outside. And between them, in the area marked by arrow, the lamellae were laid down flat on the basal plane of samples. We also observe the subsidiary lamellar branch which originated from the dominant lamella in the center of picture.

In Figure 6, the spherulites crystallized above 100 °C exhibit coarse surface which is similar to the arrowed region in Figure 4. The black lines on the surface of spherulites and black boundaries between the spherulites can be seen. Sometimes these black lines and boundaries, altogether were regarded as cracks in the case of spherulites crystallized at high temperature.[15] In the case of PTMS spherulites, the black lines on the surface and the boundaries revealed different structure. This different manner was checked by a simple test with half-insertion of a black filter between the specimen and eye-piece in the optical microscope in order to increase the contrast in unpolarized light. In Figure 7, it was proved that the boundaries of spherulites which were appeared black lines between the crossed polars were formed by grooves, however the black lines on the spherulites surface is caused by the protrusion of the fibrous structure on the surface of spherulites. When the spherulites were grown at high temperature, the grooves of spherulite boundary became more pronounced and individual spherulites were separated with each other easily.

Conclusively, it was found that the PTMS spherulites show different morphologies according to the crystallization temperature. One of the important finding is that the PTMS showed double ringed pattern. The origin of the concentric double rings could be interpreted on the basis of twisted biaxial ellipsoid model. Interestingly, double ringed spherulites were observed only in the aliphatic polyester samples among synthetic polymers. This might be related to the strong reflective power of ester groups which aligned nearly normal to the chain direction, while strong reflective power locates along the chain direction.

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