RuO₄ Staining and Lamellar Structure of α - and β -PP

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Received 16 April 1998; accepted 10 November 1998

ABSTRACT: Monoclinic (α) and hexagonal (β) polypropylene (α - and β -PP) were stained in the vapor of a ruthenium tetroxide solution prepared *in situ*. The effect of staining on the fusion behavior was investigated using a DSC. A staining duration between 10 and 24 h was found suitable for obtaining a good electron contrast between the crystalline and amorphous regions for TEM examination without causing severe damage to the crystals. The spherulites of the water-quenched α -PP were found to be composed of very fine cross-hatched lamellae whose long period was about 10 nm. In comparison, the β -PP spherulites crystallized isothermally at 130°C had a category 2 morphology and the lamellae have a long period of 20 nm. The morphology of the spherulite boundary varied depending on the contact angle between the lamellae of the neighboring spherulites. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1529–1538, 1999

Key words: ruthenium tetroxide staining; α -PP; β -PP; lamellar structure

INTRODUCTION

As a relatively new staining agent for semicrystalline polymers, ruthenium tetroxide (RuO₄) has stimulated much work on polymer morphology.¹⁻⁶ In organic synthesis, RuO₄ is usually prepared by oxidation of ruthenium compounds at lower oxidation states, usually ruthenium trichloride or ruthenium dioxide. It has been suggested that the most convenient method to generate RuO_4 is by reacting hydrated ruthenium dioxide with an aqueous solution of periodate followed by extraction of the tetroxide with carbon tetrachloride.⁷ In a previous study,⁸ we developed a technique for preparing RuO_4 solution in situ by oxidation of ruthenium compounds at lower oxidation states with an excess of sodium periodate. The solution contained a high concentration of RuO_4 and was able to stain polyoxymethylene (POM) in the vapor phase.

Sano et al.⁴ showed that the efficiency of RuO_4 staining depends on the molecular mobil-

ity in the amorphous region and staining should be carried out above the T_g of the polymer. Another factor which likely affects the staining result is the presence of function groups to react with the tetroxide. Isotactic polypropylene (iPP) is a relatively inert polymer compared with POM; nevertheless, it has a trace of unsaturated bonds or active hydrogen atoms. There are three known possible polymorphic phases in iPP, namely, monoclinic (α), hexagonal (β), and triclinic (γ) . The lamellar structure of the α -phase has been studied quite extensively^{4,9-} 12; however, the work on the other two phases is relatively little.¹³ One possible explanation is their scarce occurrence under normal processing conditions. Recently, we developed a pimelic acid-based nucleating agent for the β -phase.¹⁴ In this study, both α - and β -polypropylene (PP) would be produced and stained in the vapor of the RuO₄ solution prepared *in situ*. The effect of staining time on the fusion behaviors of the two polymer phases was analyzed using a DSC. The lamellar structures of the α - and β -spherulites were examined under a transmission electron microscope.

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Journal of Applied Polymer Science, Vol. 72, 1529–1538 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/121529-10

EXPERIMENTAL

Polymer Material and Processing

The iPP resin used was Himont 6501 in powder form. The α -phase was prepared by melting the resin at 200°C in a 2-mm-thick compression mold and then quenching it in water at room temperature. In the preparation of a mixture β - and α -phases, the resin was first doped with 0.6% of pimelic acid/calcium stearate. The β -nucleating agent was prepared by mixing a 1% ethanol solution of pimelic acid with a 2% suspension of calcium stearate in ethanol and the mixture had a pimelic acid/calcium stearate composition ratio of 1/1.5. The resin was added to the mixture, stirred, and then dried in an oven at 100°C. The resin did not dissolve in the ethanol solution. The doped resin was melted in the compression mold at 200°C. Then, it was quickly moved to another press and crystallized isothermally at 130°C for 30 min.

RuO₄ Staining

The preparation of the RuO₄ solution for staining was reported in a previous article.⁸ Thin strips of iPP samples, with a cross section of 0.2×0.3 mm, were cut from the molded plates. They were first blackened in the vapor of the RuO_4 solution and then embedded in epoxy resin to cure at 40°C for 48 h. The embedded specimens were trimmed first with a razor blade and then with an ultracut microtome equipped with a glass knife. An extremely smooth trapezoidal top was obtained with the cross section of the polymer strip on the top surface. For staining, the trimmed specimens were exposed to the vapor of the ruthenium tetroxide solution in a sealed test tube for 24 h. After staining, the specimens were washed in a 3% aqueous solution of sodium periodate and then in distilled water and finally dried in a desiccator.

Ultramicrotomy and TEM Examination

The ultramicrotomy was performed at room temperature in a Reichert-Jung Ultracut E microtome. The top layer, about 1 μ m, was first removed from the stained specimen using a glass knife (45°). Then, ultrathin sections of about 50 nm were cut using a Diatome diamond knife (35°). The cutting speeds were 1.5 mm/s for the glass knife and 1.0 mm/s for the diamond knife. The ultrathin sections were supported on 200-mesh copper grids and dried in a desiccator. Finally,

they were examined under a JEOL JEM-100SX transmission electron microscope (TEM) with an accelerating voltage of 80 kV.

Thermal Analysis

Some 40-µm-thick films were cut from the molded iPP plates and stained for various lengths of time to investigate the effect of staining on the α - and β -crystals. The thermal analysis was performed in a DuPont 9900 differential scanning calorimeter (DSC) at a scan rate of 10°C/min in nitrogen. One layer of the stained films, about 3 mg, was tightly sealed in the aluminum DSC sample pan to ensure good contact with the heat source so that the error due to poor conduction of heat could be minimized. The temperature at which the DSC thermograph diverged from the horizontal baseline by more than 0.05 W/g was taken as the incipient fusion temperature of the polymer crystals. The value of 0.05 W/g was chosen with consideration that the noise level of the equipment is about 0.02 W/g.

RESULTS AND DISCUSSION

Effect of Staining on Crystallinity and Fusion Behavior of iPP

Figure 1 shows the fusion behaviors of some α -PP samples stained for various lengths of time. Their incipient fusion temperatures, melting temperatures, and degrees of crystallinity are listed in Table I. In the calculation of the degrees of crystallinity, the heats of fusion of the α - and β -crystals were taken as 178 and 170 J/g, respectively.¹⁵ The effect of staining on the fusion behavior was negligible within the first 10 h. As the staining was prolonged to 24 and 48 h, however, there was a slight upward shift of the fusion curves at high temperature. One possible explanation is that the heat capacity of the samples has changed, thus resulting in a shift of the baseline. Alternatively, the shift may be caused by an exotherm associated with reactions between the staining agent and the polymer. It was shown that RuO₄ would convert to RuO₂ during staining of polyolefins and crosslinking would occur, particularly in the amorphous region of the polymer sample.⁴ To approximate the crystallinity of the heavily stained samples, the baseline was assumed to be a straight line between the incipient fusion temperature and a point at the end of the fusion process



Figure 1 DSC thermographs of water-quenched α -PP samples: (A) unstained and stained in RuO₄ vapor for (B) 10 h, (C) 24 h, and (D) 48 h; scan rate: 5°C/min.

where the curve was approximately horizontal. The area enclosed by the baseline and the fusion peak was taken as the fusion heat of the sample. It should be pointed out that the crystallinity determined by this method might not be the true value; nevertheless, the results should roughly reflect the effect of RuO_4 staining.

The results of the DSC analysis suggest that the staining had little effect on the α -crystals and RuO₄ mainly affected the amorphous region within the first 10 h. This is conceivable as the amorphous material has a lower density which facilitates the diffusion of RuO₄. In addition, the

Table IEffect of Staining Time on FusionBehavior of α -PP

		St	Staining Time (h)			
Fusion Behavior		0	10	24	48	
Incipient fusion temperature	(°C)	108	109	114	123	
Melting point	(°C)	165	165	164	164	
Specific fusion heat	(J/g)	103	103	100	81	
Crystallinity	(%)	58	58	56	46	

polymer molecules there are more mobile to react with the tetroxide. Major reactions between RuO_4 and the crystals are believed to take place when the amorphous material becomes more or less saturated with the staining agent and the number of active polymer groups is low. The excessive amount of the staining agent will then infiltrate into the less perfect regions of the crystals.

Figure 2 shows some DSC thermographs of the doped sample after staining for various lengths of time. Normally, the doped resin will give a mixture of α - and β -PP crystals. The α - and β -fusion peaks are located near 168 and 152°C, respectively. The thermal analysis results are summarized in Table II. It was noted that the melting point of the α -crystals in the doped sample was slightly higher than that of the undoped sample in Table I. This was probably because the doped sample was isothermally crystallized at 130°C while the undoped sample was produced by quenching the melt into water at room temperature. In general, the effect of staining on the fusion behavior of the β -phase is less apparent than that on the α -phase. The β -fusion peak of the sample stained for 24 h, curve C, was almost overlapped on that of the unstained sample, curve



Figure 2 DSC thermographs of doped iPP samples crystallized isothermally at 130°C: (A) unstained and stained in RuO_4 vapor for (B) 10 h, (C) 24 h, and (D) 48 h; scan rate: 10°C/min.

A. The crystallinity of the β -phase after staining for 48 h dropped by 11% (compared with the crystallinity of the unstained sample), while the α -phase within the same sample suffered a 21% loss. Furthermore, the incipient fusion temperature of the β -phase increased by only 1°C, which is insignificant compared with an increase of 15°C for the α -phase.

Table IIEffect of Staining Time on FusionBehavior of Doped iPP

Fusion Behavior		Staining Time (h)			
	0	10	24	48	
Incipient fusion temperature (°C)	111	112	112	112	
Melting point of β -PP (°C)	153	153	153	153	
Melting point of α -PP (°C)	168	168	168	168	
Crystallinity of <i>β</i> -PP (%)	52.6	51.4	48.4	46.8	
Crystallinity of α-PP (%)	11.9	11.8	11.0	9.4	

In conclusion, the effect of the RuO_4 staining on the β -phase is less severe than that on the α -phase. The phenomenon may be explained as follows: A high content of β -PP can only be obtained within a limited range of crystallization temperature and the most favorable temperature for β -growth is near 130°C.^{16–19} There are lower and upper temperature limits beyond which the β -growth will convert to the α -growth. The lower critical temperature is about 105°C, while the upper critical temperature is 140°C.²⁰⁻²² Pure β -PP was observed in the crystallizing polymer between the upper and lower critical temperatures.^{20,21} However, when the sample was cooled below the lower critical temperature, some α -crystals were formed due to conversion of the growth pattern from β to α .^{20,22} In this study, the β -phase was isothermally crystallized at 130°C. The slow crystallization process at such a high temperature would produce crystals with fewer defects. On the other hand, the α -phase crystals in the doped sample were mostly formed below the lower critical temperature during the subsequent cooling process. In other words, most of the crystallizable polymer material had been consumed in the formation of the β -phase during the isothermal crystallization process and the α -crystals were formed under the constraint of the already crystallized β -phase; therefore, the resultant α -crystals were expected to be less perfect than the β -phase. As a result, the α -crystals were more easily affected by the staining agent.

In addition, the α -phase has a unique crosshatched lamellar structure in which the tangential daughter lamella grows epitaxially on the radial mother lamella with the respective *c*-axis parallel to the *a*-axis, making an angle of about 80° between the two lamellae.²³ There is a slight mismatch between the unit cell constant c of the daughter lamellae and constant a of the mother lamellae at the epitaxial nucleation sites. After exposing in the vapor of the RuO_4 solution for 24 h, many of the epitaxial nucleation sites appear blurry (Figs. 3-6). This is a sign of staining and believed to be partly responsible for the drop of the crystallinity. The elimination of some less perfect parts of the crystals is also a possible explanation for the increase in the incipient fusion temperature of the samples after staining. Unlike the cross-hatched structure of the α -phase, the β -phase lamellae are generally packed in parallel within the spherulite. This will likely reduce the number of sites for reaction between the staining agent and the β -crystals.

The purpose of RuO_4 staining is to increase the electron contrast between the crystalline and the amorphous phases of a semicrystalline polymer. Ideally, it is best to stain the amorphous regions alone while leaving the crystals intact so that a strong contrast can be obtained for TEM observation. It can be seen from Table II that there is a significant drop of 8% in the crystallinities of the α - and β -phases (relative to the unstained sam-



Figure 3 TEM micrograph of an α -PP ultrathin section; sample exposed in RuO₄ vapor for 24 h before microtomy.



Figure 4 Arrangement of lamellae near the center of an α -PP spherulite.

ple) after 24 h. This suggests that a proper staining duration for iPP should be less than 24 h. In fact, the iPP samples hardened slightly after being exposed to the vapor of the RuO_4 solution for 24 h and they could be microtomed into ultrathin sections thinner than 50 nm. The ultrathin sections possessed a proper electron contrast between the crystalline and the amorphous phases and were reasonably stable under the electron beam for high-resolution TEM examination.

Lamellar Structure of α -PP Spherulite

Figure 3 shows the lamellar structure of the central region of an α -PP spherulite. It should be mentioned that the possibility of obtaining a properly stained ultrathin section of the central region is rather low because it is small compared with the overall dimension of the spherulites. Only a few spherulites in several hundreds were found to be sectioned through the central region (let alone the actual center of the spherulite). To locate the central region of the spherulite, one should first look at the right-hand side of the micrograph where a few long radial lamellae are clearly visible and their growth directions are denoted by arrows pointing away from the central region. Figure 4 shows an enlarged view of the central region. The long period of the lamellae is about 10 nm and they appear to interweave together to form small trellises similar to the quadrites reported by Olley and Bassett.¹¹ In fact,



Figure 5 Arrangement of lamellae away from the center of an α -PP spherulite; sample stained in RuO₄ for 24 h.

the cross-hatched structure is a result of epitaxial growth of some daughter lamellae on the parent ones. According to a number of studies, 9,10,12 the angle between the daughter and parent lamellae is about 80°. However, there is a slight deviation from the angle in some regions of Figure 4. Such a phenomenon is likely caused by the fact that the sectioning plane is not exactly perpendicular to the line of contact between the daughter and parent lamellae and that the water-quenched crystals are substantially distorted under the rapid cooling condition.

Figure 5 shows the arrangement of the lamellae roughly halfway between the center and the periphery of an α -PP spherulite. The spherulite center is located below the bottom-right corner of the micrograph. Some long radial lamellae become apparent as they grow from the spherulite center toward the upper-left corner. They appear to grow in bundles rather than as individuals. The regions between the long radial lamellae are filled with numerous short tangential lamellae and amorphous material. As the radial lamella bundles grow, their width continuously increases through fanning and branching. As a result, different lamella bundles may cross at a small angle and, consequently, some are overgrown by others. Furthermore, some radial lamellae are interrupted by short tangential lamellae, forming small distinctive trellises similar to those at the spherulite center. Beyond the trellises, however, some long radial lamellae will emerge again.

Figure 6 shows the arrangement of lamellae at the boundary of two α -PP spherulites. The boundary runs from the bottom-right to the top-left corner of the micrograph. Near the bottom-right corner, the radial lamellae of the two spherulites grow approximately in opposite directions, leaving the tangential lamellae of the two spherulites being approximately parallel. As the tangential lamellae come near the boundary, they gradually adjust their orientation so that they become parallel with the spherulite boundary. Consequently, a thick band of parallel lamellae is formed between the spherulites. In contrast, the tangential lamellae of the two spherulites are at a relatively large angle near the top-left corner of the micrograph. When the spherulites come into contact, the lamellae from both sides appear to make no adjustment in their orientations but cross each other bluntly, resulting in a thin and distinctive boundary.

Lamellar Structure of β -PP Spherulite

Although the crystallization conditions and crystal structure of β -PP are quite well known,^{23,24} information about the lamellar structure of the β -PP spherulite is surprisingly scarce. Figure 7 shows an SEM micrograph of a β -PP sample after etching in permanganic acid for 60 min. The etch-



Figure 6 Boundary between two α -PP spherulites.



Figure 7 Morphology of a β -PP spherulite revealed by permanganic etching for 60 min; sample doped with 0.6% pimelic acid/calcium stearate.



Figure 9 Morphology of β -PP spherulites etched in permanganic acid for 30 min.

ing process was similar to that as described by Norton and Keller.¹² The spherulite in the middle of the micrograph exhibits a typical category 2 morphology with two characteristic eyes symmetrical about the center of the spherulite. Somehow, the lamellae in the micrograph appeared rather coarse. In fact, the sample was etched for too long and the fine details of the lamellae were blemished.

Figure 8 shows another β -PP sample after etching for a shorter period of 45 min. Compared with Figure 7, this micrograph gives a clearer view of the lamellae. The left side shows part of a spherulite with an edge-on view of the lamellae, that is, the viewing angle is approximately parallel with their a-b planes. In contrast, the spherulite on the right gives a flat-on view of the lamellae. Layers of the lamellae are piled up with their



Figure 8 Morphology of β -PP spherulites etched in permanganic acid for 45 min.

a-b planes parallel with the plane of the micrograph, giving a viewing direction along the *c*-axis or molecular chains of the lamellae. It can be seen that the width of the lamellae is much greater than their thickness. Furthermore, it is interesting to see how the lamellae rotate to give a flat-on view inside an eye of the spherulite on the left.

Figure 9 shows another β -PP sample after etching for an even shorter period of 30 min. The etching result has improved significantly and the lamellar structure is clearly visible. The spherulite on the left develops essentially through unidirectional growth; however, it has not fully developed and no eyes can be observed. The nucleating agent induced a large number of β -spherulites and they came into contact before growing to maturity. Nevertheless, the sheaflike lamellae and the fanning of the lamellae can be easily seen. In contrast, the spherulite on the right appears more like a category 1 spherulite with a central nucleating entity from which some thick lamellae grow radially to the periphery. In fact, it is also a category 2 spherulite, but the sectioning plane happens to lie roughly parallel with the initial lamellae. As a result, one eve has been removed while the other is below the plane of the micrograph; thus, no eyes can be seen. The hole at the spherulite center was possibly left by the nucleating agent which dissolved during etching.

Figure 10 shows the boundary areas between three β -PP spherulites which have grown from the right, left, and bottom of the micrograph. Within the spherulites, the a-b planes of the lamellae are generally oriented perpendicular to the plane of the micrograph, hence, giving an



Figure 10 Arrangement of lamellae at boundaries of β -PP spherulites; sample etched in permanganic acid for 20 min.

edge-on view of the lamellae. However, the slender edge-on view gradually gives way to the thick flat-on view as the lamellae come near the boundary (A). This is due to twisting of the lamellae and the phenomenon may have been brought about by interactions between the molecules in the neighboring spherulites. The lamellae from different spherulites may meet at different angles depending on their growth directions. If the lamellae of the neighboring spherulites meet perpendicularly (B), the boundary can be easily located. On the other hand, when the lamellae of the neighboring spherulites are growing in opposite directions (C), they may infiltrate into each other and the boundary becomes difficult to identify.

The TEM micrograph in Figure 11 shows a RuO_4 -stained β -PP ultrathin section. It was no-



Figure 11 Lamellar structure of β -PP spherulites; sample stained in ruthenium tetroxide vapor for 24 h; section thickness 50 nm.

ticed that only the edge-on view of the lamellae could be examined under the TEM. When the lamellae lay flat in the ultrathin section or inclined at a small angle, they could not be imaged clearly due to poor electron contrast along the viewing direction. The most apparent spherulite is located at the center of the micrograph while parts of two other spherulites are at the top-left and bottom-right corners. Within the central spherulite, the growth direction of the initial lamellae is approximately parallel with the diagonal joining the top-right and bottom-left corners. The long period of the lamellae is about 20 nm. Unlike the α -phase spherulite, there is no crosshatching in the β -phase and the neighboring lamellae are packed in parallel. It is observed that some lamellae at the spherulite center have grown beyond the limit of the micrograph. It is generally believed that a category 2 spherulite develops from one single crystal through essentially unidirectional growth.¹² Later, new crystals are formed in parallel with the initial lamella, causing thickening of the core region. As the growth continues, further nucleations occur between the growing lamellae. This will lead to the phenomenon of fanning and finally to the formation of the characteristic eyes. Due to the high nucleation density, however, the growth of the central spherulite was halted by the adjacent ones before the eyes were fully developed.

Figure 12 shows another TEM micrograph taken halfway between the center and the periphery of a β -PP spherulite. It can be seen that different lamella bundles are well developed. When



Figure 12 Lamellar structure of a β -PP spherulite halfway between the center and periphery.



Figure 13 TEM micrograph showing disrupted lamellar structure of a β -PP spherulite.

they cross each other, some may be overgrown. Under certain circumstances, a growing lamella may bend over and disrupt the growth of other lamellae (Fig. 13).

It is shown in Figure 10 that the morphology of the boundary between two β -spherulites may appear rather different depending on the contact angle of the lamellae. The detailed morphology of the spherulite boundary can be clearly observed after the RuO₄ staining. Figure 14 shows a boundary where the lamellae of the neighboring spherulites are growing in opposite directions. The lamellae from one spherulite



Figure 15 Structure of β -PP spherulite boundary; lamellae of the neighboring spherulites are perpendicular.

tend to grow into the neighboring spherulite and it is difficult to define the boundary between them. Figure 15 shows another TEM micrograph in which the neighboring sets of lamellae meet almost perpendicularly. A well-defined and relatively straight boundary is formed. It can also be seen that some of the lamellae from the bottom spherulite infiltrate into the top spherulite, forming a short-range interwoven structure. Finally, Figure 16 shows a boundary where the two sets of lamellae meet at an oblique angle. In this case, a zigzag boundary appears.



Figure 14 Structure of β -PP spherulite boundary; lamellae of the neighboring spherulites are growing in opposite directions.



Figure 16 Structure of β -PP spherulite boundary; lamellae of the neighboring spherulites are inclined.

CONCLUSIONS

The ruthenium tetroxide solution prepared *in situ* by oxidation of ruthenium dioxide with an excess of sodium periodate was able to stain both α - and β -PP in the vapor phase. During the early stage of the staining process, the tetroxide reacted preferentially with the amorphous material. Prolonged staining would cause the crystals to degrade; hence, the crystallinity would drop. A vapor-phase staining process between 10 and 24 h at room temperature was suitable for obtaining an appropriate electron contrast between the lamel-lae and amorphous regions within the α - and β -PP spherulites.

The spherulites of the water-quenched α -PP were composed of very fine lamellae whose long period was about 10 nm. The spherulite center had a similar structure to the quadrites reported by Olley and Bassett,¹¹ within which the cross-hatched lamellae interwove together to form small trellises. Away from the spherulite center, long radial lamellae began to develop and grow in bundles. Different bundles tended to cross each other as a result of fanning and branching within the bundles. Areas between the radial lamellae were filled with short tangential lamellae which were cross-hatched on the radial lamellae.

The β -PP spherulites had a category 2 morphology of 20-nm-thick lamellae. The width of the lamellae was much greater than their thickness. It is believed that the initial lamellae at the spherulite center primarily adopt a unidirectional growth. As the growth continues, fanning occurs due to insertion of new lamellae, thus resulting in the formation of the characteristic eyes. The morphology of the boundary between two β -PP spherulites varied depending on the contact angle between the lamellae of the neighboring spherulites. No clear boundary could be identified when the two sets of lamellae were growing in opposite directions. A sharp boundary was formed if they met perpendicularly. When they came across each other at an oblique angle, a zigzag boundary would appear.

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