

Lamellar Structure of POM Spherulites Imaged by a Two-Stage RuO₄ Staining Technique

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SYNOPSIS

Ruthenium tetroxide solution was prepared *in situ* by oxidation of ruthenium compounds at lower oxidation states with an excess of sodium periodate. The solution was able to stain saturated polymer POM in the vapor phase and it remained effective for up to 2 weeks. The melting behavior of POM samples stained for different lengths of time was studied with DSC and the staining process was analyzed. The results indicated that ruthenium tetroxide affected both the amorphous region and the crystals. During the early stage of the staining process, the tetroxide reacted preferentially with the amorphous material near the specimen surface. Much of this affected material was washed away after the rinsing process, thus resulting in an apparent increase in crystallinity. Prolonged staining would cause more crystals to degrade; hence, the crystallinity would drop. A two-step vapor staining technique was developed to improve the contrast between the amorphous and crystalline regions of ultrathin POM sections. The lamellar structure of POM spherulites was revealed and examined under TEM. The results showed that POM spherulites possess a category 2 structure and the thickness of the lamellae is about 7 nm. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Transmission electron microscope (TEM) is a very useful instrument for revealing the microstructure of heterogeneous materials at a high level of resolution. For polymer materials, however, it is important to obtain sufficient mass contrast among the phases in the specimen to make it possible to image the phase structure under TEM. The most common approach to enhance the mass contrast in polymer samples is the adoption of a staining agent.¹ Osmium tetroxide has been used successfully as a staining agent for unsaturated polymers.¹⁻³ In the case of saturated polymers, Kanig⁴ first used chlorosulfonic acid and uranyl acetate for staining bulk crystallized polyethylene. But Kanig's technique appears to have no application beyond polyethylene.⁴⁻⁷ It requires the polymer samples to be soaked in the acid for hours or even days. When polypropylene (PP) samples were soaked in the acid, dissolution was found to occur before the samples could be properly

stained.⁸ The situation was improved by Trent et al.^{9,10} who successfully stained a number of unsaturated and saturated polymers by exposing them to the vapor of a 0.5 wt % aqueous solution of ruthenium tetroxide. However, there are problems associated with this new staining technique, which are related to the instability and toxicity of purified ruthenium tetroxide, and the commercial source of the tetroxide is rather rare.

Montezinos et al.¹¹ and Janik et al.¹² tried to avoid the above problems by an alternative method in which a ruthenium tetroxide solution was prepared *in situ* by oxidation of ruthenium trichloride with an aqueous solution of sodium hypochlorite or ruthenium dioxide with sodium periodate. These solutions appeared either dark red or olive green, while the 0.5% aqueous solution of ruthenium tetroxide used by Trent et al.¹⁰ was golden yellow in color. This seems to indicate that the concentration of ruthenium tetroxide in the solutions prepared in the alternative method was low, and so was the partial pressure of ruthenium tetroxide vapor in the container. This will inevitably reduce the effect of vapor staining. In the alternative methods, the bulk polymer samples were immersed in the solution for

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staining. This will lead to the same problem of dissociation when polymers of poor chemical resistance are immersed in the solution for a long time.

Polyoxymethylene (POM) has outstanding mechanical properties and is one of the widely used engineering plastics. Surprisingly, very few studies on the lamellar structure of bulk POM have been reported. The chemical resistance of POM is poor and chalking will occur in the presence of 5% sodium hypochlorite, 10% aqueous ammonia, or oxidizing acids.^{13,14} Obviously, this mitigates against the staining of POM in the liquid phase. Furthermore, the backbone of the POM molecule is a flexible chain which consists of C—O bonds and is completely linear without branching. It exhibits very high crystallinity, up to 85%. Since diffusion of a staining agent is more difficult in highly crystalline materials, therefore, to effectively stain and image the lamellar structure of POM, different procedures from those reported earlier may be required. This study is concerned with modifying the formula of preparing ruthenium tetroxide solution *in situ* and improving the staining technique for POM.

EXPERIMENTAL

Polymer Material and Processing

The POM investigated in this study was DuPont Delrin 500. It has a melt flow index of about 5 g/10 min and is supplied in granule form. The POM resin was placed in a steel mold and melted in a press at 200°C for 5 min. Then, it was quickly moved to another press, molded into a 2.5 mm-thick plate, and crystallized isothermally at 130°C under pressure for 60 min. The degree of crystallinity of the POM samples, determined by a differential scanning calorimeter (DSC), was 81% when the value of 250 J/g was adopted as the specific fusion heat of 100% crystalline POM.¹⁵

Preparation of Ruthenium Tetroxide Solution

The starting materials for the staining agent were sodium periodate (NaIO₄, 99.8%), hydrated ruthenium dioxide (RuO₂·2H₂O), hydrated ruthenium trichloride (RuCl₃·H₂O, 99.9%), and potassium perruthenate (KRuO₄) supplied by Johnson Matthey in powder form. The ruthenium tetroxide was prepared by oxidation of the ruthenium compounds in a saturated sodium periodate aqueous solution in the presence of undissolved sodium periodate. Typically, 20 mg of ruthenium dioxide and

10 mg of sodium periodate were put into a test tube; then, 3 mL of saturated sodium periodate aqueous solution was added. The test tube was sealed and shaken. The ruthenium dioxide dissolved quickly and a clear golden yellow solution of ruthenium tetroxide was formed. The solution was used for vapor staining without further treatment.

Staining and Ultramicrotomy

Thin strips of POM specimens, with cross section of 200 × 300 μm, were cut from the compression-molded POM plates using a microtome. They were first exposed to the vapor of the ruthenium tetroxide solution to blacken and then embedded in epoxy resin. 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 in parallel with the top surface. For the first-stage staining, the trimmed specimens were exposed to the vapor of the ruthenium tetroxide solution in a sealed test tube for up to 24 h. After staining, the specimens were washed in a 3% solution of sodium periodate and distilled water and then dried in a desiccator.

A Reichert-Jung Ultracut E microtome was used for the ultramicrotomy. The top layer, about 1 μm, 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 was performed at room temperature and the cutting speed was 1.0 mm/s. The ultrathin sections were supported on 200 mesh copper grids and dried in a desiccator. In the second-stage staining, the ultrathin sections were further exposed to ruthenium tetroxide vapor for up to 30 min in a 58 × 15 mm culture dish which contained 10 mL of the ruthenium tetroxide solution. This complementary staining process was designed to improve the contrast among the crystalline and amorphous regions of the POM samples. Finally, the samples were examined under a JEOL JEM-100SX transmission electron microscope (TEM) with an accelerating voltage of 80 kV.

Thermal Analysis

Thermal analysis of some stained POM samples was performed with a DuPont 910 differential scanning calorimeter (DSC) at a heating rate of 10°C per min in a nitrogen atmosphere. POM films of uniform thickness, 40 μm, were cut from the compression-molded plates with a Leitz 1400 microtome and were

exposed to ruthenium tetroxide vapor for various lengths of time. For each test, only one layer of the stained film, about 3.5 mg, was put into an aluminum sample pan. The sample pan was covered with an aluminum lid and pressed tightly together to ensure good contact between the specimen and the aluminum pan. Good contact between the sample and the pan will minimize the error due to a poor conduction of heat. The temperature at which the DSC thermograph diverged from the horizontal base line by more than 0.05 W/g was taken as the incipient fusion temperature of the POM 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. The peak temperature was taken as the melting point of the polymer.

RESULTS AND DISCUSSION

Staining Agent and Process

In the study of organic synthesis, ruthenium tetroxide is usually generated *in situ* by shaking an aqueous solution of periodate with a carbon tetrachloride solution containing ruthenium compounds of lower oxidation states and an organic compound.^{16,17} In this study, it was noticed that when a saturated aqueous solution of sodium periodate with a ruthenium compound, such as potassium perruthenate, ruthenium dioxide, or ruthenium trichloride, was shaken, a clear golden yellow solution would form at once. The solution is believed to contain a high concentration of ruthenium tetroxide. When it was stored in a sealed glass container, the solution remained golden yellow in color for more than 2 weeks at room temperature and was effective for staining PP¹⁸ and POM in the vapor phase. If a POM sample was present above the solution in a sealed container, the color of the solution would fade gradually until all the ruthenium tetroxide had vaporized and been absorbed by the polymer sample. The solution would become colorless and transparent, while the polymer sample became dark due to reduction of ruthenium tetroxide to ruthenium dioxide, which is a dark compound.

The color of the ruthenium tetroxide solution prepared in this study was similar to that by Trent et al.¹⁰ using purified ruthenium tetroxide, but different from those by Montezinos et al.¹¹ and Janik et al.¹² In Montezinos et al.'s study, the fresh mixture was dark red in color and should be used immediately inasmuch as it would deteriorate within a few hours. In Janik et al.'s work, the solution was olive green,

and if the container was quickly sealed, the solution could stay green for up to 72 h at room temperature. In comparison, the ruthenium tetroxide solution prepared in this study had a much longer life. This was due to the fact that the excessive amount of sodium periodate was able to oxidize ruthenium compounds, which might have deteriorated from ruthenium tetroxide, into ruthenium tetroxide continually until all the ruthenium was consumed. The three ruthenium compounds investigated in this study, i.e., potassium perruthenate, ruthenium dioxide, and ruthenium trichloride, could all be used to prepare the ruthenium tetroxide solution. Considering the toxicity and efficiency, it is believed that ruthenium dioxide is the best starting material for *in situ* preparation of ruthenium tetroxide.

The staining process of polymer samples with ruthenium tetroxide is a complicated solid-state reaction. The main factors that would affect the results include diffusion of the tetroxide in different phases of the polymer sample and possible reactions between polymer molecules and the tetroxide. Based on the ability of ruthenium tetroxide vapor to blacken polyoxyethylene (POE), Trent et al.¹⁰ predicted that the tetroxide would be able to stain the polymer. Since POM has the same ether functional group as has POE, ruthenium tetroxide should also be a suitable staining agent for POM. While POM molecules are highly active to ruthenium tetroxide,^{13,14} it is also highly crystalline. The former factor would facilitate absorption of the tetroxide by POM, while the latter might retard penetration of the staining agent deeply into the samples.

It was noticed that the samples hardened significantly after vapor staining. A similar phenomenon was also observed on polyethylene by Sano et al.¹⁹ The top layer of our stained POM samples had to be removed before ultrathin sections could be cut. For specimens stained for less than 24 h, the ultrathin sections normally had too low a contrast for good imaging results under TEM. Also, the ultrathin films were destroyed rapidly by the electron beam. On the other hand, specimens stained for more than 24 h were hard enough to blunt the glass knife in just one or two cuttings, and several glass knives were needed just to remove the too heavily stained surface layers. Also, it was difficult to obtain an ultrathin film having the proper amount of staining.

Cryogenic sectioning at subzero temperatures is often adopted to prepare good-quality ultrathin sections of ductile polymer samples for vapor staining. Since POM is one of the hardest engineering thermoplastics, it was thought that ultramicrotomy might be carried out at room temperature. However,

this procedure was not successful in obtaining ultrathin sections of less than 100 nm from the unstained samples. In this study, attempts were also made to stain POM by immersing the samples in the ruthenium tetroxide solution. Chalking was found to occur on the specimen surface and ultramicrotomy was not successful.

To solve the above problems, a two-stage staining procedure was adopted. First, the embedded specimens were stained for 8 h and then ultrathin sections of about 50 nm thick were prepared. Second, the ultrathin sections were further exposed to the vapor of the ruthenium tetroxide solution for up to 30 min as described earlier. The first-stage staining was designed to facilitate the ultramicrotomy process. The specimens hardened slightly after 8 h of staining and were easier to cut. The complementary staining in the second stage would give the proper amount of staining for good imaging results. Also, it would make the ultrathin samples more stable under the electron beam.

Effect of Staining on Sample Weight, Crystallinity, and Melting Behavior

Figure 1 shows the melting behavior of four POM samples which were exposed to ruthenium tetroxide vapor for various lengths of time. The incipient fusion temperature, melting point, specific fusion heat, and degree of crystallinity of the samples were obtained from the thermographs and are summarized in Table I. For the unstained sample (A), the DSC thermograph begins to diverge from the base line by more than 0.05 W/g at 139.4°C, which is taken as incipient fusion temperature of POM crystals. The melting point is 176.7°C. In general, the fusion peak is quite sharp. This suggests that the sample pos-

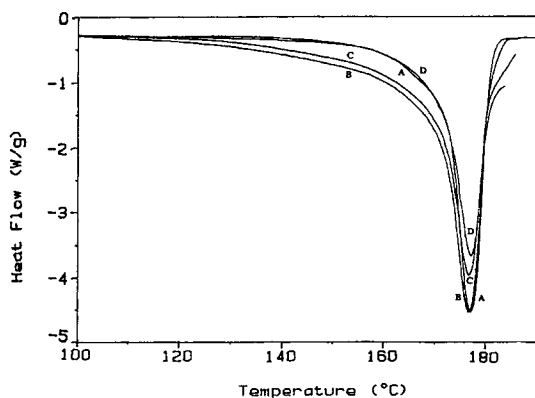


Figure 1 DSC thermograph of POM stained for various lengths of time: (A) unstained; (B) 2.5 h; (C) 8 h; (D) 12 h.

Table I Effect of Staining Time on Fusion Behavior of POM

	Staining Time (h)				
	0	2.5	8	12	24
Incipient fusion temperature (°C)	139.4	102.0	119.3	138.5	
Melting point (°C)	176.7	176.7	176.7	177.1	177.3
Specific fusion heat (J/g)	202.6	215.6	201.0	180.6	173.4
Crystallinity (%)	81	86	80	72	69

sessed very few imperfect crystals and the fusion process took place within a narrow temperature range. In fact, POM has outstanding mechanical properties, which accounts for its attractiveness as an engineering plastic. From the area of the fusion peak, the degree of crystallinity of the unstained POM was determined to be 81%.

Once the POM samples had been exposed to the vapor of ruthenium tetroxide for 2–3 h, its incipient fusion temperature was reduced markedly and its fusion peak broadened. Curve B shows the melting behavior of the sample stained for 2.5 h. It can be seen that the thermograph diverged from the horizontal base line much earlier, giving an incipient fusion temperature of 102°C. Also, the fusion peak became wider and the specific fusion heat was 215.6 J/g, about 6% higher than that of the unstained sample. However, the peak temperature remained almost unchanged. As the staining time was further increased, the incipient fusion temperature rose again and the fusion peak became narrower. The incipient fusion temperature of sample C (stained for 8 h) and sample D (stained for 12 h) were 119.3 and 138.5°C, respectively. The latter is almost the same as that of the unstained sample. After staining for 12 h, the specific fusion heat dropped to 180.6 J/g, about 11% lower than that of the unstained POM. Furthermore, prolonged staining caused a very slight increase in the melting point.

It was also observed that the weight of the POM samples had changed after the staining and washing procedures. The results are listed in Table II. It can be seen that the weight increased after the staining process due to absorption of ruthenium tetroxide. After washing and drying, however, the weight might increase or decrease depending on the length of staining time. For the samples which were stained

Table II Average Weight Variation of POM After Staining and Washing

	Staining Time (h)				
	0	2.5	5	8	16
Weight of unstained sample (mg)	8.35	9.95	9.7	9.25	8.75
Weight after staining (mg)		10.25	10.2	9.55	9.2
Weight after washing and drying (mg)	8.35	9.7	9.6	9.25	8.85
Average weight variation (%)	0	-2.5	-1.1	0	+1.1

for 2.5 h, there was an average weight loss of 2.5%. As the staining time was increased to 5 and 8 h, the average weight loss became smaller and further increase in staining time to 16 h resulted in a net weight gain of 1.1%.

From the results of the thermal analysis and weight measurement, the following points about the staining process can be deduced: At the early stage of the staining process, ruthenium tetroxide reacts rapidly with POM molecules near the specimen surface, especially in the amorphous region. The reaction is likely to take place at the hydrogen atoms of the POM molecules because they are highly reactive with ruthenium tetroxide.¹⁰ For specimens stained for 2.5 h, much of the amorphous material near the specimen surface was washed away after the rinsing process, thus resulting in a weight loss of 2.5%. Also, the loss of amorphous material would cause an apparent increase in the degree of crystallinity from 81 to 86%, as shown in Table I.

In fact, ruthenium tetroxide also attacks the polymer crystals and causes them to degrade. However, it is more difficult for the tetroxide to infiltrate into the lamellae than for the amorphous material because of the more close-packed arrangement and lower mobility of the chain segments in the crystals. The amount of crystals is not expected to reduce significantly after a short staining time, say 2.5 h. However, the crystals will become less perfect. This is shown in the thermograph, curve B of Figure 1, which has a broader fusion peak toward the low-temperature range and a lower incipient fusion temperature than has curve A of the unstained sample. The less perfect crystals tend to melt at a lower temperature than do the perfect ones. It should be pointed out that the degree of crystallinity is measured based on the specific fusion heat of the sample. Therefore, changes in sample weight due to absorp-

tion of ruthenium tetroxide during staining will drag down the degree of crystallinity. In contrast, loss of amorphous material after rinsing tends to raise it. Curve B shows the combined effect of crystal degradation due to reaction with ruthenium tetroxide and of weight changes as mentioned above.

As the staining time was increased, more ruthenium tetroxide infiltrated deeply into the specimens, mainly through the amorphous regions, and resulted in a net weight gain despite the fact that some polymer material was washed away from the specimen surface. After staining for 8 h, the degree of crystallinity dropped below that of the unstained samples and continued to drop for further increase in staining time. Furthermore, the fusion peak became narrow again and the melting point increased slightly, curves C and D. This suggests that the less perfect parts of the crystals have largely been eliminated; thus, the fusion peak moves slightly to the high-temperature range.

In summary, the changes in sample weight, crystallinity, and melting behavior suggest the following: For short staining time, the tetroxide affects mainly the amorphous material and causes some crystals to become less perfect. The removal of amorphous polymer material after rinsing appears to be the main factor responsible for the weight loss and increase in crystallinity. For a longer staining time, the situation of weight loss in the rinsing process seems to stabilize. On the other hand, continuous absorption of ruthenium tetroxide becomes the determining factor responsible for the weight gain and elimination of the less perfect crystals.

Lamellar Architecture of POM Spherulites

Figure 2 shows a TEM micrograph taken between the center and perimeter of a POM spherulite. The most common view of the lamellar structure observed in this study is as shown on the lower half of the micrograph. The dark areas are the amorphous regions infiltrated with ruthenium tetroxide, while the bright regions are the lamellae relatively unaffected by the staining agent. The lamellae grow from the top-left to the bottom-right corner. On the bottom center of the micrograph, the lamellae appear very fine. It is believed that the section plane is approximately perpendicular to the *a*-*b* plane of the lamellae, and, hence, the width of the crystals here reflects more or less the true thickness of the lamellae. The average long period here and at similar locations in other micrographs was measured to be about 7 nm. It is similar to those reported by Makajima and Hamada.²⁰ They found, using small-an-

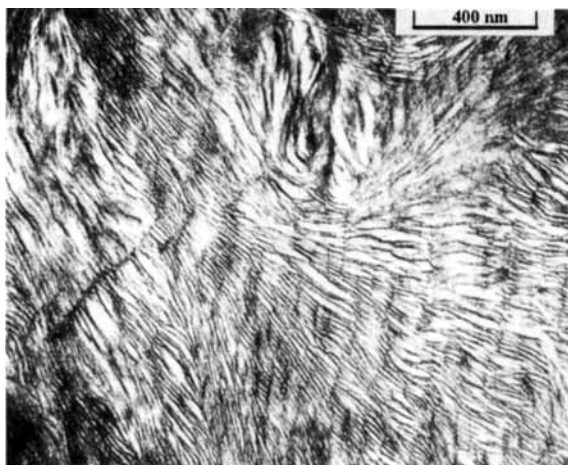


Figure 2 TEM micrograph of POM lamellae, growing from top-left to bottom-right corner, the top center region showing a swirl due to excessive fanning and twisting of the lamellae.

gle X-ray diffraction, that the long period of solution-grown POM crystals varied between 6 and 10 nm as the crystallization temperature was changed from 60 to 140°C. In contrast, some crystals on both the right and left of Figure 2 appear much thicker. This is probably due to a slight twisting of the lamellae so that the viewing direction becomes more inclined to the “c” axis of the crystal lattice. When twisting becomes severe, a swirl may form as shown at the top center of the figure. However, such a phenomenon does not occur frequently.

Furthermore, the lamellae are packed in bundles. As the bundles grow, their widths continuously increase through branching. Different lamellar bundles grow in slightly different directions, and as a result, they may cross each other. It can be seen from the left of Figure 2 that two bundles cross each other at about 20° and the bundle on the left is overgrown by the one on the right.

Figure 3 shows another general view of the lamellar structure away from the spherulite center. The distribution of the relatively large white patches indicates the tendency of the lamellae to twist. It should also be noticed, near the bottom-right corner, that two lamellar bundles cross each other almost perpendicularly, leaving a straight boundary between them. Such phenomenon often occurs at spherulite boundaries.

Figure 4 shows an area where the lamellae have been sectioned approximately parallel with the *a*-*b* plane, i.e., the viewing direction is along the “c” axis. The width of the crystals varies between 50 and 300

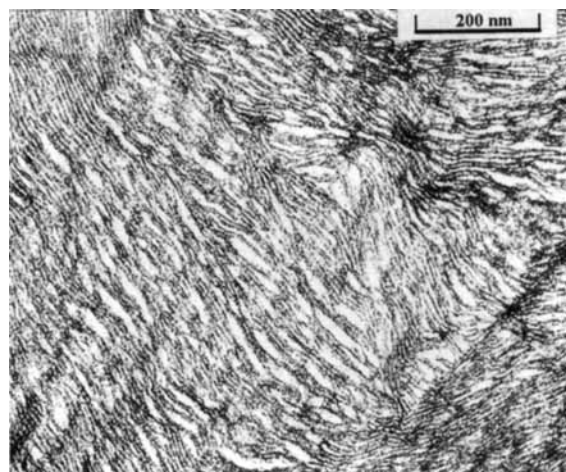


Figure 3 TEM micrograph of POM lamellae; the relatively large white patches are due to twisting of the lamellae.

nm, which is an indication of the width of the lamellae.

It is generally accepted that spherulites in crystalline polymers can be classified into two main categories.^{20,21} In category 1, the growth starts from a central nucleating entity and the lamellae radiate in all directions. In category 2, the spherulite develops from one single crystal through essentially unidirectional growth. The spherical shape is attained through continuous branching and fanning via an intermediate stage of sheaves. Figure 5 shows a spherulite which was sectioned approximately through the center. The characteristic “eye” (marked by letter E) of a category 2 spherulite can be identified. The initial crystal probably grows

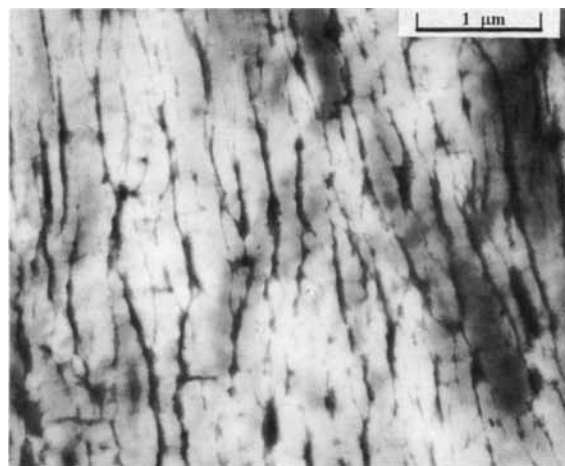


Figure 4 TEM micrograph of POM lamellae; viewing direction inclined to the “c” axis.

along the lamellar bundle marked by letter M. The phenomena of branching and fanning of lamellae are apparent as they grow from top to bottom of the micrograph. It is also noticed that branching is often associated with the twisting of lamellae (see region marked by letter B).

Figure 6 shows the center of another POM spherulite. Branching and fanning of lamellae are particularly clear around the "eye" in the middle. It is also noticed that the region between the "eyes" does not exhibit the expected unidirectional growth but, rather, different lamellar bundles crossing each other almost perpendicularly. One possible explanation to the phenomenon is as follows: During the early stage of spherulite growth, the initial lamella will trigger crystallization of other lamellae which tend to grow in plane with the initial lamella. Later, branching and fanning occur and the "eyes" begin to form. At this stage, the spherical shape is not yet attained and the lamellae are packed more or less in plane. As the growth continues, the lamellae become much longer and twisting will occur. This will change the growth pattern from coplanar to three-dimensional and the spherulite starts to take shape. Most lamellae will grow outward away from the spherulite center, due to slight branching, fanning, and twisting. However, lamellae which undergo excessive branching, fanning, and twisting will change the growth direction drastically toward the spherulite center. Inward growth is possible as the polymer material on both sides of the plane of the initial lamellar bundle may still be molten. The inward growing lamellae tend to cross the initial lamellae at large angles. If the section plane of the ultrathin sample is inclined to the initial growth plane, then

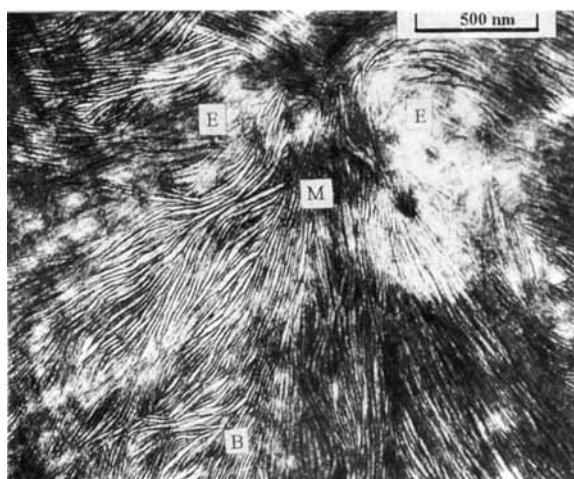


Figure 5 TEM micrograph of the center region of a POM spherulite, the letter E denoting the "eyes."

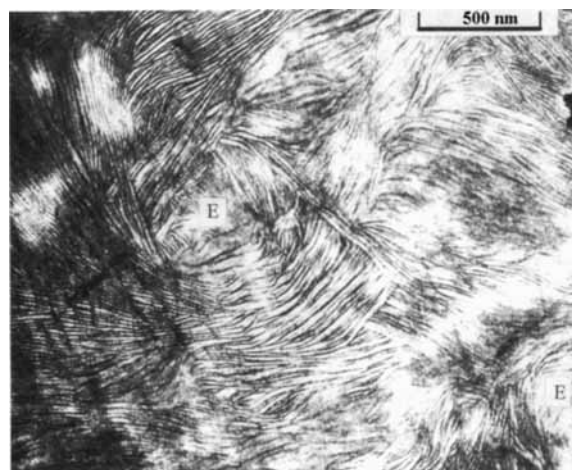


Figure 6 TEM micrograph of the center region of a POM spherulite; branching and fanning are apparent around the "eye" on the right.

the lamellar structure will appear as shown in Figure 6.

CONCLUSION

The ruthenium tetroxide solution prepared *in situ* by oxidation of ruthenium dioxide in a saturated aqueous solution of sodium periodate was able to stain crystalline polymer POM. It affected not only the amorphous region but also the crystals in the spherulites. During the early stage of the staining process, ruthenium tetroxide reacted with the amorphous material which was washed away after the rinsing process and caused an apparent increase in the crystallinity. Prolonged staining would cause more crystals to degrade, resulting in a substantial drop of crystallinity. The two-stage complementary staining technique improved the contrast among the amorphous and crystalline regions of the ultrathin samples. The TEM examination showed that spherulites in POM have a category 2 structure. Branching, fanning, and twisting of lamellae were found to occur during the growth of the spherulites. The long period of the lamellae was determined to be about 7 nm.

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