

# Cracking in Poly(trimethylene terephthalate) Spherulites

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**ABSTRACT:** The crack behavior of poly(trimethylene terephthalate) spherulites was studied mainly by polarizing optical microscopy, along with scanning electron microscopy (SEM) and atomic force microscopy (AFM). In addition to the effects of temperature and constraining substrate, another important factor, film thickness, on the formation of crack was first put forward and investigated. The emergence of the first crack occurred at 120°C during cooling after crystallization at 190°C for the sample with a thickness of 31.0  $\mu\text{m}$ . For the spherulites growing between glass sheets, it was interesting that the sample with a thickness of 26.0  $\mu\text{m}$  exhibited the largest number of

cracks measured per 200  $\mu\text{m}$  of radius, whereas samples thicker than 100  $\mu\text{m}$  or thinner than 1  $\mu\text{m}$  did not induce the formation of crack. Also, spherulites growing between two polyimide and two Teflon sheets showed no crack. Glass sheets lubricated with silicon oil restrained the number of cracks but did not eliminate cracks. SEM revealed that the cracking was about 900 nm in width. In addition, the AFM results suggest that the cracks had a depth of at least 150 nm. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1713–1719, 2009

**Key words:** crazing; spherulites

## INTRODUCTION

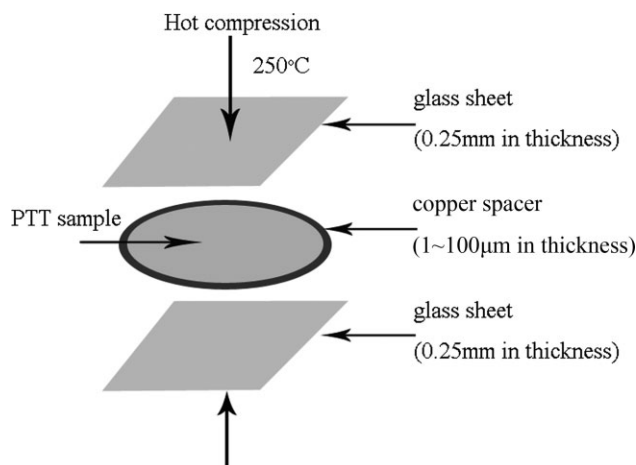
Poly(trimethylene terephthalate) (PTT) is a newly commercialized aromatic polyester. Although available in commercial quantities only as recently as 1998,<sup>1</sup> it was one of the three high-melting-point aromatic polyesters first synthesized by Whinfield and Dickson<sup>2</sup> nearly 60 years ago. Recently, PTT has drawn much attention for its outstanding properties, such as good tensile behavior, resilience, outstanding elastic recovery, and dyeability.<sup>3</sup> Different from its neighbors, poly(ethylene terephthalate) and poly(butylene terephthalate), PTT has an odd number of methylene units. Whether the number of methylene units is odd or even dictates a fundamental difference in its lowest internal energy conformation and, thereby, also the equilibrium properties of the material.<sup>4</sup>

A spherulite morphology is usually observed for semicrystalline polymers. However, spherulitic crystallization often results in residual stresses and cracks. The cracks within polyhydroxybutyrate (PHB)<sup>5–11</sup> and polylactide (PLLA)<sup>12,13</sup> spherulites have already been observed and studied. In the case of PHB, Friedrich<sup>5</sup> advocated for the first time that the very regular concentric rings within PHB spher-

ulites were found to have cracks. Then, Barham and Keller<sup>10</sup> further demonstrated that these cracks, which were either radial or circumferential within the spherulites, depending on the crystallization temperature ( $T_c$ ), formed under conditions of no externally applied stress. More recent studies by Hobbs et al.<sup>8</sup> showed that cracks formed during cooling because of differences in the radial and circumferential thermal expansion coefficients. That is, the cracks were in fact due to differences in the thermal expansion between the PHB film and the constraining glass slides. In the case of PLLA, Fraschini et al.<sup>12</sup> also found concentric cracks that showed up on cooling on top of the spherulites were completely reversible during subsequent heating and cooling cycles. In addition to concentric cracks, He et al.<sup>13</sup> detected hexagonal cracks in PLLA spherulites. They concluded that rhythmic growth and thermal shrinkage were the two main factors accounting for the formation of periodic cracks.

In this study, we investigated the spherulite morphology and crack behavior of PTT crystallized from the melt. In addition to the effect of temperature and constraining substrate, another important factor, the thickness of the film on the formation of cracks within the spherulites, was comprehensively studied. Polarizing optical microscopy (POM) and scanning electron microscopy (SEM) were used to characterize the plane circles of the PTT spherulites. In addition, atomic force microscopy (AFM) was

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**Figure 1** Schematic illustration of the preparation of a certain thickness of PTT film. The PTT grain was first sandwiched between two glass, polyimide, or Teflon sheets and then compressed at 250°C.

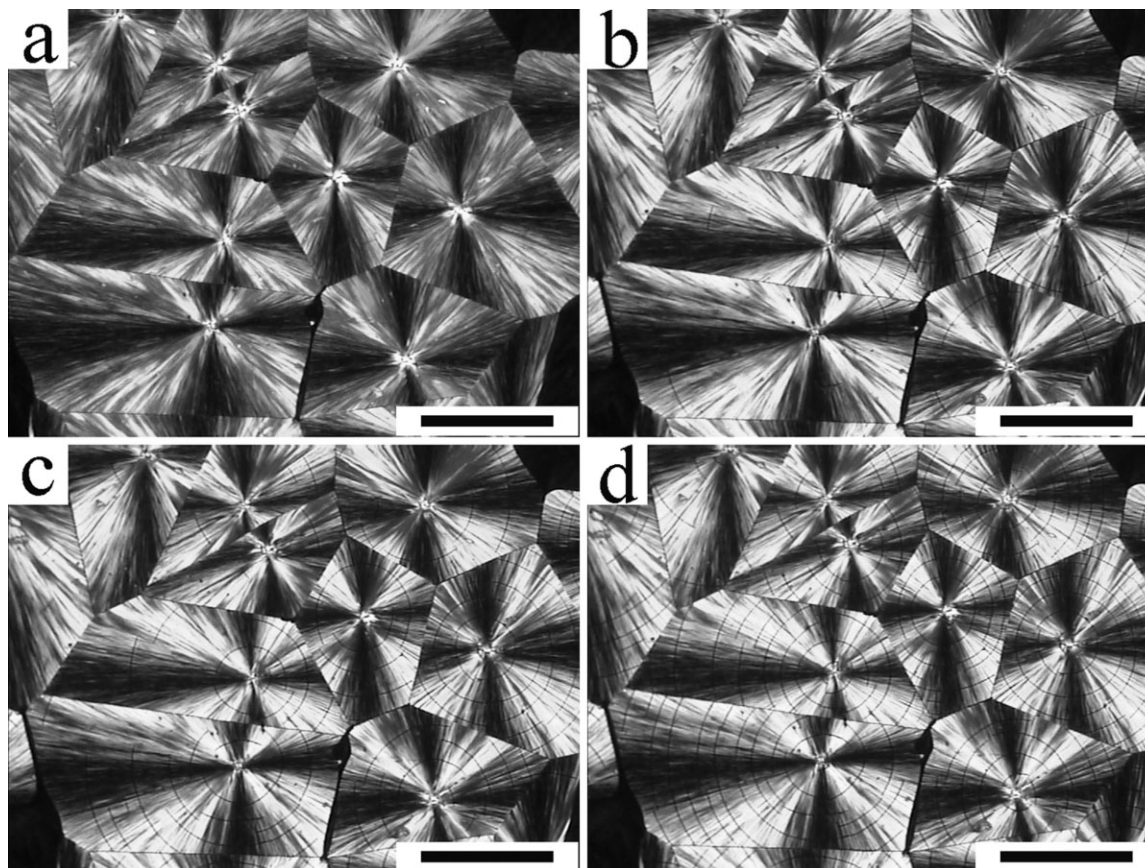
used to determine the depth profile of the circles. This was the first time, to our best knowledge, that the cracks within PTT spherulites were found and characterized.

## EXPERIMENTAL

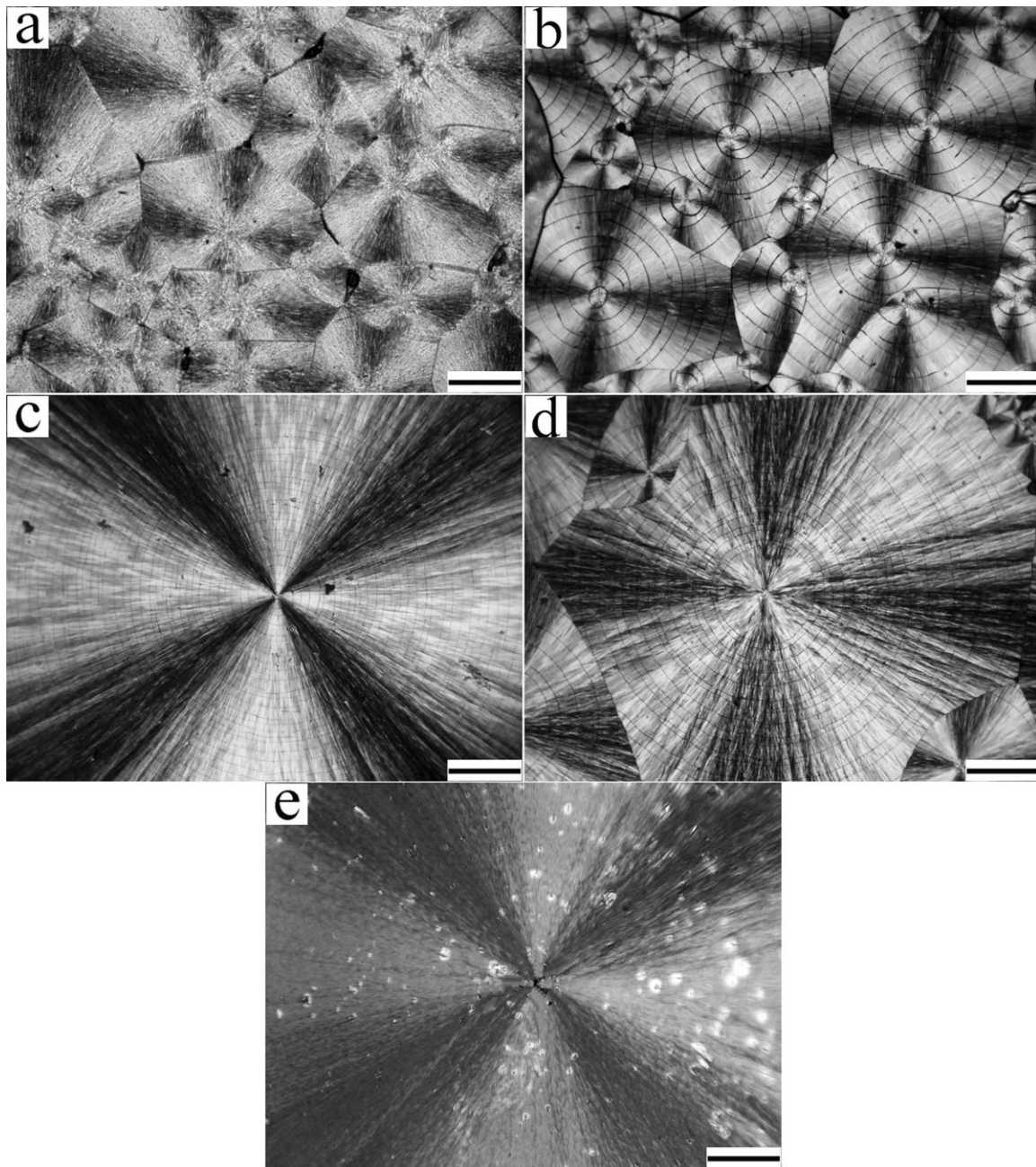
The PTT homopolymer used in this study was supplied by Shell Chemicals (Houston, TX). It had an intrinsic viscosity of 0.94 dL/g in a phenol/tetrachloroethane (50/50 w/w) solution at 25°C, a glass-transition temperature of 50.5°C, and a melting temperature of 230°C.

Samples films with thicknesses in the range 1–100 μm were deliberately produced. Figure 1 illustrates the schematic graph for the preparation method. A series of copper spacers (Longmei Copper Foil Co., Nanjing, China) with thicknesses ranging from 1 to 100 μm were used as a mold. However, the thicknesses of the films obtained were a little higher than the theoretical value. So a focusing ring of an optical microscope was used to measure the precise thickness of the polymer films. Three kinds of surface materials were investigated, including glass, polyimide, and Teflon. In addition, glass sheets lubricated with silicon oil were also studied.

The spherulite morphology of PTT was observed with POM (Olympus BX51-P) [Japan] coupled with a computer-controlled charged coupling device camera (Tota, Japan). A hot stage (Linkman CI93) was



**Figure 2** POM micrographs of PTT captured at (a) 190, (b) 120, (c) 90, and (d) 40°C during the cooling process after crystallization at 190°C. The scale bar represents 200 μm.



**Figure 3** POM micrographs of PTT films with different thicknesses [(a) 92.4, (b) 51.8, (c) 26.0, (d) 10.7, and (e) 1.3  $\mu\text{m}$ ] after crystallization at 190°C. The scale bar represents 200  $\mu\text{m}$ .

used for *in situ* monitoring of the crack propagation during the cooling process. In all cases, the specimens were first melted at 250°C for 3 min, then rapidly cooled to the designated  $T_c$  (200°C/min) with liquid nitrogen, held for certain time to ensure completion of the crystallization, and cooled to room temperature at a rate of 20°C/min. POM micrographs were captured either during the cooling process or at room temperature.

The morphology of the PTT spherulites was characterized with a JSM 5600 LV scanning electron microscope (Tokyo). For this observation, one of the

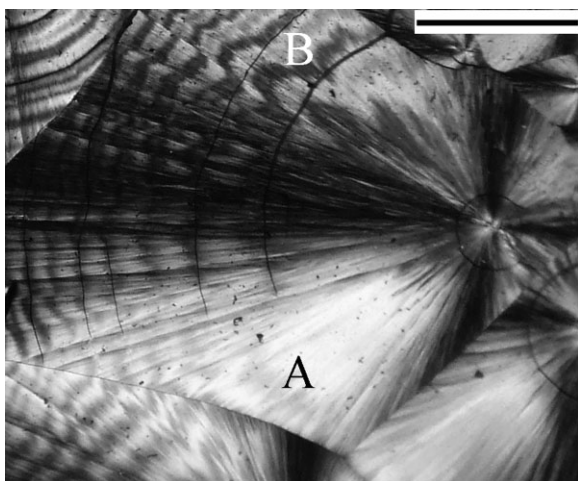
two glass slides was carefully removed from the sample.

AFM studies were performed with a Digital Instruments Nanoscope III (Santa Barbara, CA) in tapping mode. The instrument was operated in air at room temperature.

## RESULTS AND DISCUSSION

### Effect of the temperature on crack propagation

Figure 2 shows the POM micrographs of the PTT spherulites during the cooling process after



**Figure 4** POM micrographs of PTT films with thickness gradients ranging from 1 to 6  $\mu\text{m}$  after crystallization at 195°C: (A) thin and (B) thick parts. The scale bar represents 200  $\mu\text{m}$ .

crystallization at 190°C. The spherulites grew between two glass sheets, and the thickness of the film was controlled to be 30  $\mu\text{m}$  and was measured to be 31.0  $\mu\text{m}$ . Figure 2(a) reveals the well-defined spherulite morphology of pure PTT. Spherulites impinged on one another and formed particular polygonal spherulites with clear boundaries. The spherulites had a diameter of 200–350  $\mu\text{m}$ . However, no crack was detected. The first crack appeared at 120°C, as shown in Figure 2(b). Unlike Hobbs et al.'s<sup>8</sup> claim that cracks on PHB spherulites appeared at the growth front, the cracks on PTT appeared randomly within the spherulites, either at the front or in the middle of the spherulites. With decreasing temperature, cracks appeared progressively. At 90°C [Fig. 2(c)], cracks appeared in all of the spherulites. At 90°C [Fig. 2(d)], cracks further developed, and the mean spacing between two neighboring cracks decreased.

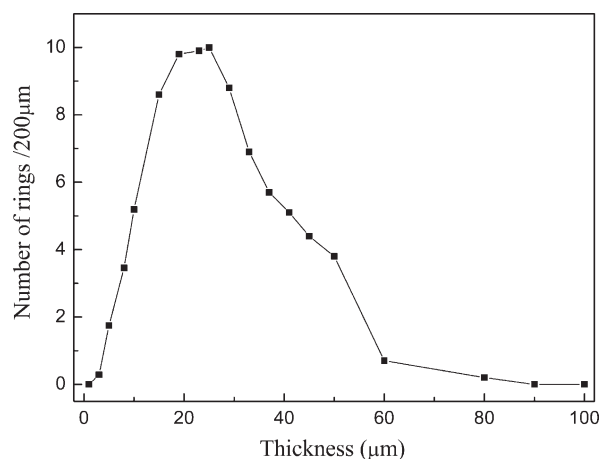
For the cracks of PHB, both Hobbs et al.<sup>8</sup> and Barham and Keller<sup>10</sup> reported two types: one running circumferentially around the spherulites and the other running radially through them. For PLLA, not only regular concentric cracks<sup>12</sup> but also hexagonal cracks<sup>13</sup> were detected. In this case, the cracks were similar but not identical to those found. The radial cracks appearing in PHB and the hexagonal cracks appearing in PLLA have never been found in PTT. In our samples, only one type of crack was identified, which ran tangentially along the radius of the spherulites.

#### Effect of the thickness on crack propagation

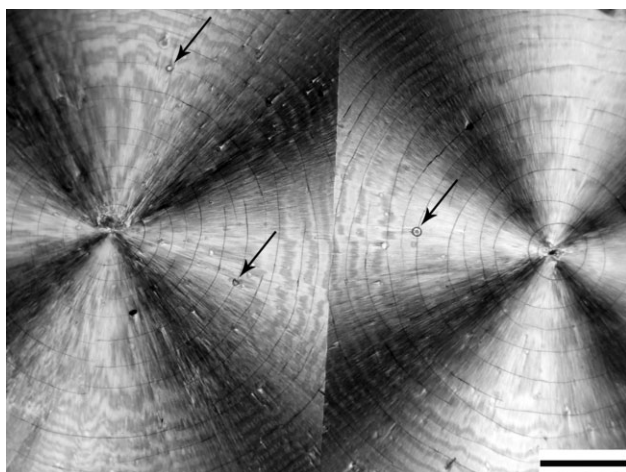
Figure 3(a–e) presents a series of POM micrographs of PTT films with thicknesses ranging from 1 to 100

$\mu\text{m}$ . Those pictures were captured at room temperature after the completion of crystallization at 190°C. The film thicknesses of Figure 3(a–e) were 92.4, 51.8, 26.0, 10.7, and 1.3  $\mu\text{m}$ , respectively. Figure 3(a) reveals a weak Maltese cross pattern, which is an evidence that the film was relatively thick. There was no circumferential feature; namely, cracks on the film with a thickness of 92.4  $\mu\text{m}$  were not detected. However, cracks appeared in Figure 3(b). In most cases, the cracks ran completely around the spherulite circumference, whereas some showed corkscrews at the center of spherulites. When the thickness was decreased to 26.0  $\mu\text{m}$ , the cracks propagated progressively. As shown in Figure 3(c), not only did the spherulites become bigger but also the circle spacing decreased. In addition, cracks appeared at regular intervals within PTT spherulites, and the mean spacing between two neighboring cracks was about 20  $\mu\text{m}$ . Figure 3(d) shows micrographs of PTT films with a thickness of 10  $\mu\text{m}$ . It was obvious that many cracks were present. Moreover, the mean spacing increased compared to that shown in Figure 3(c). An interesting occurrence was found in the case of the film shown in Figure 3(e); that is, the film with a thickness of 1.3  $\mu\text{m}$  exhibited no crack.

To further confirm that a very thin film could prevent cracks from propagating, a unique scheme was adopted to prepare a film with a thickness gradient range from 1 to 6  $\mu\text{m}$ . Several steel stainless fibers (diameter  $\phi = 7 \mu\text{m}$ ) and a PTT grain were sandwiched between two glass sheets. The steel stainless fibers were sandwiched on one side of the glass sheets to ensure that a thickness gradient was formed. The POM micrograph of the sample crystallized at 195°C is shown in Figure 4. The deep color [Fig. 4(B)] represents the thick part (ca. 5.3  $\mu\text{m}$ ), and



**Figure 5**  $N$  per 200  $\mu\text{m}$  of the spherulite radius as a function of the thickness of the PTT film for the samples crystallized at 190°C.



**Figure 6** POM micrograph of the PTT spherulites grown between glass sheets lubricated with silicon oil. The arrows denote the silicon oil. The scale bar represents 200  $\mu\text{m}$ .

the light color [Fig. 4(A)] represents the thin part (ca. 1.4  $\mu\text{m}$ ). It was apparent that the cracks originating from the thick part ceased at the thin part of the film. Moreover, Figure 4 shows banded spherulites; this was different from the previous POM micrographs. The appearance of banded spherulites in PTT was strongly dependent on the level of  $T_c$ ; at lower  $T_c$  values ( $<195^\circ\text{C}$ ), the banded morphology disappeared, and a regular spherulite image was exhibited. Temperatures higher than  $195^\circ\text{C}$  induce the formation of banded spherulites.<sup>17</sup> In our study,  $T_c$  of the sample was  $195^\circ\text{C}$ , so banded spherulites were observed as expected.

From the previous discussion, one may conclude that a film thicker than 100  $\mu\text{m}$  or thinner than 1  $\mu\text{m}$  will not induce the formation of crack for PTT. There may be a thickness in which the density of the cracks is at a maximum. Figure 5 illustrates the number of rings ( $N$ ) measured per 200  $\mu\text{m}$  of radius as a function of the thickness for the sample crystallized at  $190^\circ\text{C}$ . It was clear that the film with a thickness of approximately 26  $\mu\text{m}$  showed the maximum  $N$ . Films thicker or thinner than that value exhibited digressive  $N$  values.

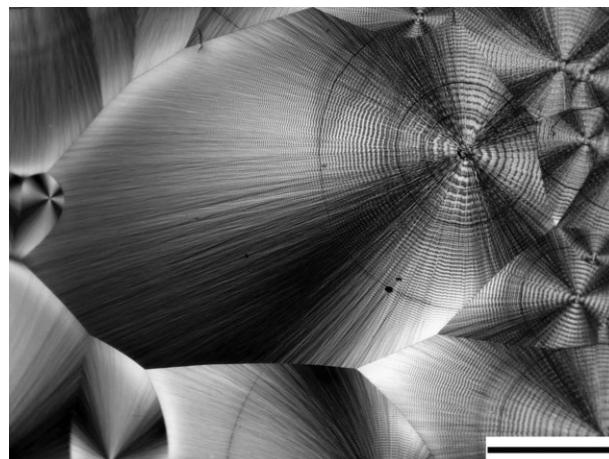
Actually, the origin of cracks was attributed to differential thermal expansion (or shrinkage) between the glass (or other) substrate and the polymer. The extent of expansion or shrinkage had some relationship with the thickness of the film. When the melt was constrained by two stiff foreign surfaces during cooling, a significant negative pressure could be built up because of the volume shrinkage on crystallization. The difference in the extent of shrinkage between the glass substrate and the PTT film may have reached a maximum at a thickness of 26  $\mu\text{m}$  for the PTT film, so the maximum stress was likely

to occur, which led to a maximal  $N$ . For thick films, the size of spherulites was relatively small. The stress in small spherulites was accordingly puny. Moreover, thicker films had higher strengths. Both of these factors led to a crackless film. For very thin films, there was still a shrinkage in volume on crystallization, but much of this volume change could, at least in part, be accommodated by a reduction in the thickness of the melt.<sup>8</sup> In addition, very thin films of a polymer have outstanding toughnesses,<sup>14–16</sup> which could have also resulted in crack resistance in PTT spherulites.

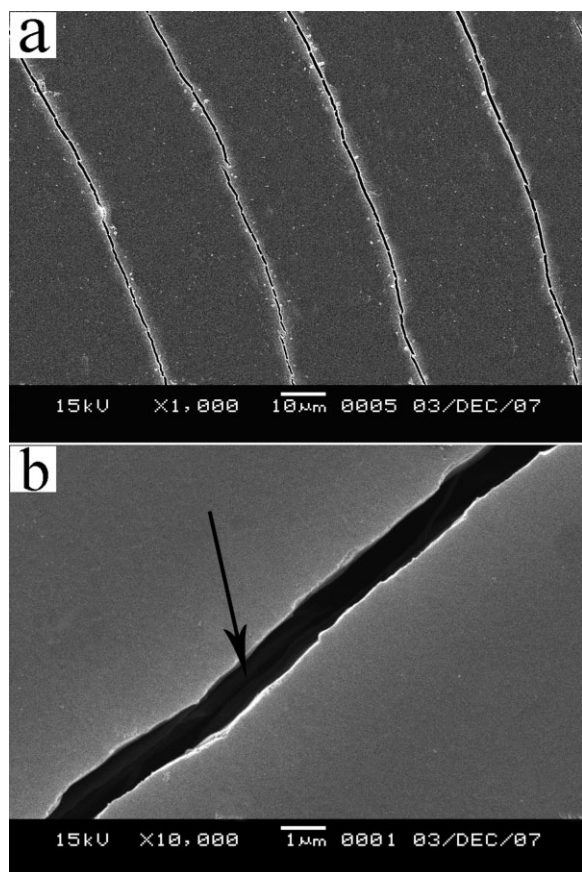
### Effect of the substrate on crack propagation

It has been reported before<sup>8,12</sup> that the nature of the substrate has a significant effect. Therefore, in addition to common glass sheets, polyimide and Teflon sheets were investigated. The thickness was set as 25  $\mu\text{m}$ , and the obtained values were 27.3 and 27.9  $\mu\text{m}$  for polyimide and Teflon, respectively. The average diameter of the PTT spherulites between both of these sheets was about 600  $\mu\text{m}$ , which was a little smaller than that between glass sheets. Most important, all of the spherulites exhibited no crack features. The only obvious difference between the surfaces was that the polyimide and Teflon sheets were much more compliant than the glass sheets. These results indicate that surface material had a great effect on the formation of cracks and that compliant materials such as polyimide and Teflon could produce films consisting entirely of crack-free spherulites.

Figure 6 illustrates the POM micrograph of PTT spherulites grown between glass sheets. These glass sheets were lubricated with silicon oil. The thickness was set as 25  $\mu\text{m}$ , and the obtained value was 25.9  $\mu\text{m}$ . These pictures were captured at room



**Figure 7** POM micrograph of the PTT spherulites grown with one free surface for the samples crystallized at  $195^\circ\text{C}$ . The scale bar represents 200  $\mu\text{m}$ .



**Figure 8** SEM micrographs of the PTT spherulite cracks. (b) is a magnification of (a). The arrow indicates the bottom of crack.

temperature after the completion of crystallization at 195°C. The arrows denote the silicon oil in Figure 6. We tried to depress the friction between the substrate and the polymer with silicon oil to make the stresses induced by volume change on crystallization easily release. Unfortunately, the cracks presented as usual. However,  $N$  measured per 200  $\mu\text{m}$  of radius was obviously lower than that without silicon oil [Fig. 3(c)]. The result indicates that silicon oil had some effect on restraining the formation of cracks.

### Growth with one free surface

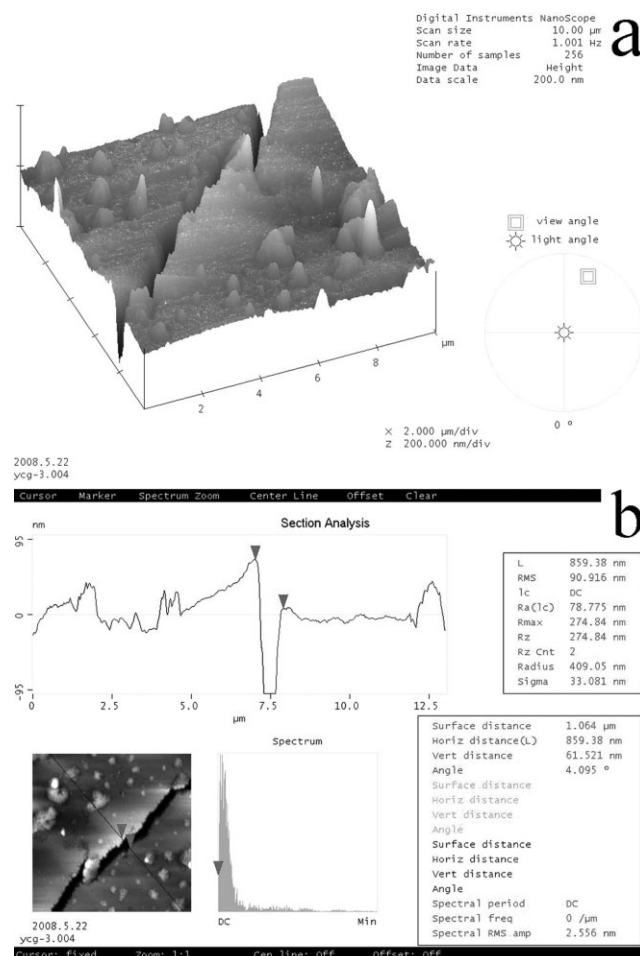
Because all of the previous experiments were carried out between two surfaces, we decided to investigate the crack behavior of spherulites grown with one free surface. Figure 7 shows the POM micrograph of PTT spherulites with one glass substrate crystallized at 195°C. The thickness was measured to be 30.2  $\mu\text{m}$ . In addition to the expected bands, cracks also appeared. Whereas their number was very low compared to that of spherulites growing between two surfaces, in much thicker films (>30  $\mu\text{m}$ ), cracks were still occasionally found. However, cracks were never seen when the thickness was smaller than 21.3

$\mu\text{m}$ . Similar results have been found in the case of PHB.<sup>8</sup>

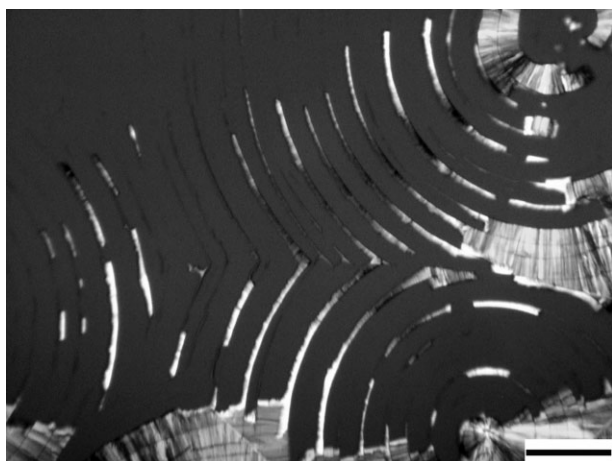
### Characterization of the cracks

After the picture in Figure 2(d) was captured, the upper glass of this sample was carefully removed, and the lower part was gold-coated with an Au/Pd mixture for SEM observation. Figure 8(a,b) shows the SEM micrographs of the PTT spherulites. It was apparent that the dark circular rings seen before were real cracks. Figure 8(b) is a magnification of Figure 8(a). Figure 8(b) suggests that the crack was about 900 nm in width, which was larger than Frascini's result. By careful observation, one can see the bottom of the crack, as indicated by the arrow.

After the upper glass was carefully removed, the lower sample was examined with AFM to determine the depth and profile of these surface features. Figure 9 illustrates the AFM images of the PTT spherulite cracks in detail; Figure 9(a) shows the three-dimensional height image, and Figure 9(b) shows the section analysis. As shown in Figure 9(b), the



**Figure 9** (a) Three-dimensional AFM height image and (b) section analysis of the PTT spherulite cracks.



**Figure 10** POM micrograph of the PTT spherulites. The picture is the micrograph of the upper glass after removal from the sample. The scale bar represents 200  $\mu\text{m}$ .

features had a width of about 510 nm, which was a little lower than that in the SEM observation, and a depth of at least 150 nm. However, the recorded images and the resulting measurements depended strongly on the geometry of the probe tip used, which did not have the ideal geometrical shape (perfect cone- or square-based pyramid) often suggested.<sup>12</sup> Thus, the bottom of the crack may not have been successfully imaged. So the depth of cracks could have been deeper than what was experimentally measured. Also, the crack may have propagate during removal of the upper glass, which would have increased the depth. Figure 10 presents the POM micrograph of the upper glass after removal from the sample. It was clear that there was some concentric residue on the surface, which resulted from the adhesion between the glass and polymer. When the two glass sheets were detached, some uplifts or valleys formed, as shown in Figure 9(b).

### CONCLUSIONS

The effects of temperature, constraining substrate, and film thickness on the cracking of PTT spherulites were comprehensively investigated, mainly by

POM and also by SEM and AFM. The first crack appeared at 120°C during cooling after crystallization at 190°C for the sample with a thickness of 31.0  $\mu\text{m}$ . For the spherulites growing between glass sheets, it was interesting to find that the sample with a thickness of 26.0  $\mu\text{m}$  exhibited the largest number of cracks measured per 200  $\mu\text{m}$  of radius, whereas films thicker than 100  $\mu\text{m}$  or thinner than 1  $\mu\text{m}$  did not induce the formation of cracks. No cracks were found for PTT spherulites grown between polyimide or Teflon sheets, regardless of the thickness. The spherulites grown between glass sheets lubricated with silicon oil still showed rare cracks. Similarly, spherulites grown with one free surface exhibited obviously fewer cracks compared to those grown between two sheets. SEM revealed that the cracks were about 900 nm in width. In addition, AFM suggested that the cracks had a depth of at least 150 nm.

### References

1. Semas, J. H. *Int Fiber J* 1997, 12, 12.
2. Whinfield, J. R.; Dickson, J. T. *Br. Pat.* 578,079 (1946).
3. Run, M. T.; Yao, C. G.; Wang, Y. J.; Song, H. Z. *J Appl Polym Sci* 2007, 106, 1557.
4. Fakirov, S. In *Handbook of Thermoplastic Polyesters*; Wiley-VCH: Weinheim, 2002; Chapter 12, p 551.
5. Friedrich, K. *Adv Polym Sci* 1983, 52, 225.
6. Scandola, M.; Ceccorulli, G.; Pizzoli, M. *Makromol Chem Rapid Commun* 1989, 10, 47.
7. Barham, P. J. *Mater Sci Technol* 1993, 12, 153.
8. Hobbs, J. K.; McMaster, T. J.; Miles, M. J.; Barham, P. J. *Polymer* 1996, 37, 3241.
9. Salazar, J. M.; Cuesta M. S. *J Mater Sci Lett* 1989, 8, 490.
10. Barham, P. J.; Keller, A. *J Polym Sci Part B: Polym Phys* 1986, 24, 69.
11. Xu, J.; Guo, B. H.; Chen, G. Q.; Zhang, Z. M. *J Polym Sci Part B: Polym Phys* 2003, 41, 2128.
12. Fraschini, C.; Plesu, R.; Sarasua, J. R.; Prud'homme, R. E. *J Polym Sci Part B: Polym Phys* 2005, 43, 3308.
13. He, Y.; Fan, Z.; Wei, J.; Li, S. M.; Li, S. M. *Polym Eng Sci* 2006, 46, 1583.
14. Ram, A. *Fundamentals of Polymer Engineering*; Plenum: New York, 1997; Chapter 4, p 83.
15. Zhang, T. Y.; Qian, C. F.; Wang, T. H.; Tong, P. *Int J Solids Struct* 2000, 37, 5465.
16. Morasch, K. R.; Bahr, D. F. *Thin Solid Films* 2007, 515, 3298.
17. Ho, R. M.; Ke, K. Z.; Chen, M. *Macromolecules* 2000, 33, 7529.