Observation of the Concentric Diffractive Banding on the Spherulites of Poly(ethylene oxide) by a Dynamic Method

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ABSTRACT: The growth of poly(ethylene oxide) (PEO) spherulites was observed synchronously with a polarized optical microscope, which was equipped with a video detector, and so the whole growing process of the PEO spherulites was dynamically recorded as a movie. There was a series of concentric diffractive bands on the surface of the PEO spherulites; furthermore, the diffractive banding did not exist until at least two independent PEO spherulites came into contact with each other. However, the formation of the diffractive banding on the PEO spherulites was also related to the crystallization conditions. It was concluded qualitatively that the diffractive banding formed more easily at the crystallization temperature with a high degree of supercooling, and this was explained in kinetic terms. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 96: 2454–2458, 2005

Key words: spherulites; structure; water-soluble polymers

INTRODUCTION

Poly(ethylene oxide) (PEO) is not only a well-known water-soluble polymer but also a flexible and crystalline one. Until now, the crystalline morphology and structure of PEO have been widely studied as functions of different crystallization conditions.[1–9] In the 1960s, Keller et al.[9] observed PEO spherulites in the bulk state under polarized optical microscopy (POM) and saw concentric diffractive banding on the surface of the spherulites, in addition to the typical extinction cross. They believed that the concentric banding resulted from lamellar twisting of the spherulites. They also observed similar phenomena previously on spherulites of polyethylene and several other materials,[10,11] and they called them *banded spherulites*. However, further work proved that the banding on PEO, reported by Keller et al., was a kind of irregular banding unrelated to the typical banding exhibited the normal banded-spherulite polymers. Recently, Yang et al.[12,13] also investigated diffractive banding on PEO spherulites, and they found that banding could also be observed without polars, so they ascribed the formation of the irregular concentric banding to the step growth or spiral growth of the spherulites.

In our group, diffractive banding on PEO spherulites has also been studied.[14] Synchronous observations were carried out with a video detector on a polarized optical microscope during the growth of PEO spherulites. Diffractive banding formed only just when two or more independent PEO spherulites came into contact with one another. Different crystallization conditions were also tried to investigate the formation of the diffractive banding.

EXPERIMENTAL

Materials

PEO was purchased from Shanghai Reagent Factory (Shanghai, China); its number-average molecular weight was 6000 g/mol, and its molecular weight distribution (weight-average molecular weight/number-average molecular weight) was 1.83 according to size exclusion chromatography results.

POM measurements

A model DMLP polarized optical microscope from Leica Co. (Wetzlar, Germany) was used with a THMSE-600 heat stage from Linkam Co. (Surrey, En-

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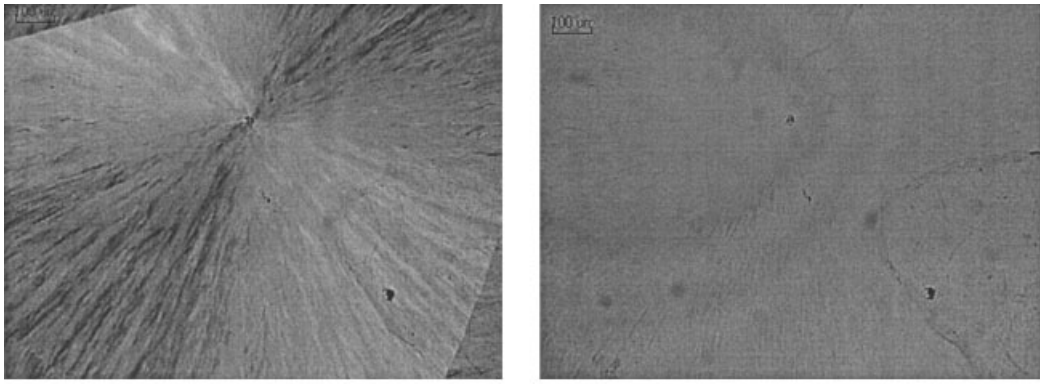

(a) (b)

Figure 1 POM images of PEO spherulites under nonisothermal crystallization conditions at a cooling rate of 10°C/min: (a) with polars and (b) without polars.

gland), and the controlled temperature range was −196 to 600°C. A JVC video was used as a detector, and the shoot rate was 1 f/s.

Before observations were made, the PEO sample was placed on a heat stage under the polarized optical microscope, and the system temperature was increased to 100°C at a heating rate of 20°C/min under nitrogen and kept at 100°C for 3 min. Then, two different sets of crystallization conditions were tried. Under nonisothermal conditions, the temperature was reduced from 100 to 0°C at a cooling rate of 10°C/min; under the other conditions, the sample was quenched from 100°C, and the temperature was kept at 45°C with isothermal crystallization. The entire processes of PEO crystallization were recorded with the video detector and a $\lambda/4$ compensator plate was used during the POM observations under both sets of conditions.

Differential scanning calorimetry (DSC) experiments

The thermal behavior of PEO was measured with a Pyris 1 differential scanning calorimeter (Perkin Elmer Cetus Instruments, Norwalk, CT) under nitrogen. First, the temperature was increased from 0 to 100°C at a heating rate of 20°C/min; then, the temperature was kept at 100°C for 3 min and reduced from 100 to 0°C at a cooling rate of 10°C/min. In succession, the temperature was increased from 0 to 100°C at the same heating rate; after 100°C was reached, the sample was quenched to 45°C, and the system temperature was kept at 45°C for 10 min.

RESULTS AND DISCUSSION

Figure 1 shows POM images of the PEO spherulites with and without polars under the nonisothermal crystallization conditions, as discussed in the Experimental section. The radius of the spherulites was approximately 1000 μm [Fig. 1(a)], whereas the thickness of the spherulites was approximately 4 μm (measured with a micrometer). Therefore, all the observed PEO spherulites were disklike and not really spherical; the growth of the spherulites was limited to two-dimensional space. Interestingly, concentric diffractive banding could be seen with POM not only with polars but also without polars [Fig. 1(a,b)]. These results agree with Yang et al.'s reports.[12,13] Figure 1(a) shows that the average number of the banding was 5–6, and the banding space was approximately 100 μm equably in single PEO spherulites.

To investigate the formation of the concentric diffractive banding on the PEO spherulites, we dynamically recorded the whole growing process of the spherulites with the video detector with POM. Figure 2 shows POM images of PEO spherulites at different time during the spherulite growing process, with the time increasing, under nonisothermal crystallization conditions. The concentric diffractive banding did not appear before two single spherulites met each other [Fig. 2(a–c)]. However, once two independent spherulites came into contact with each other, the diffractive banding appeared immediately and grew from the periphery of the spherulites to the center, step by step. Because the diffractive banding appeared after the spherulites came into contact with each other, we concluded that the formation of the diffractive banding on the PEO spherulites was related to the stress force of the PEO spherulites after they collided, and we assumed that the stress effect led to the change in the spherulite growth to form the diffractive banding. We believed that there could be two different growth steps during the growing process of the PEO spheru-

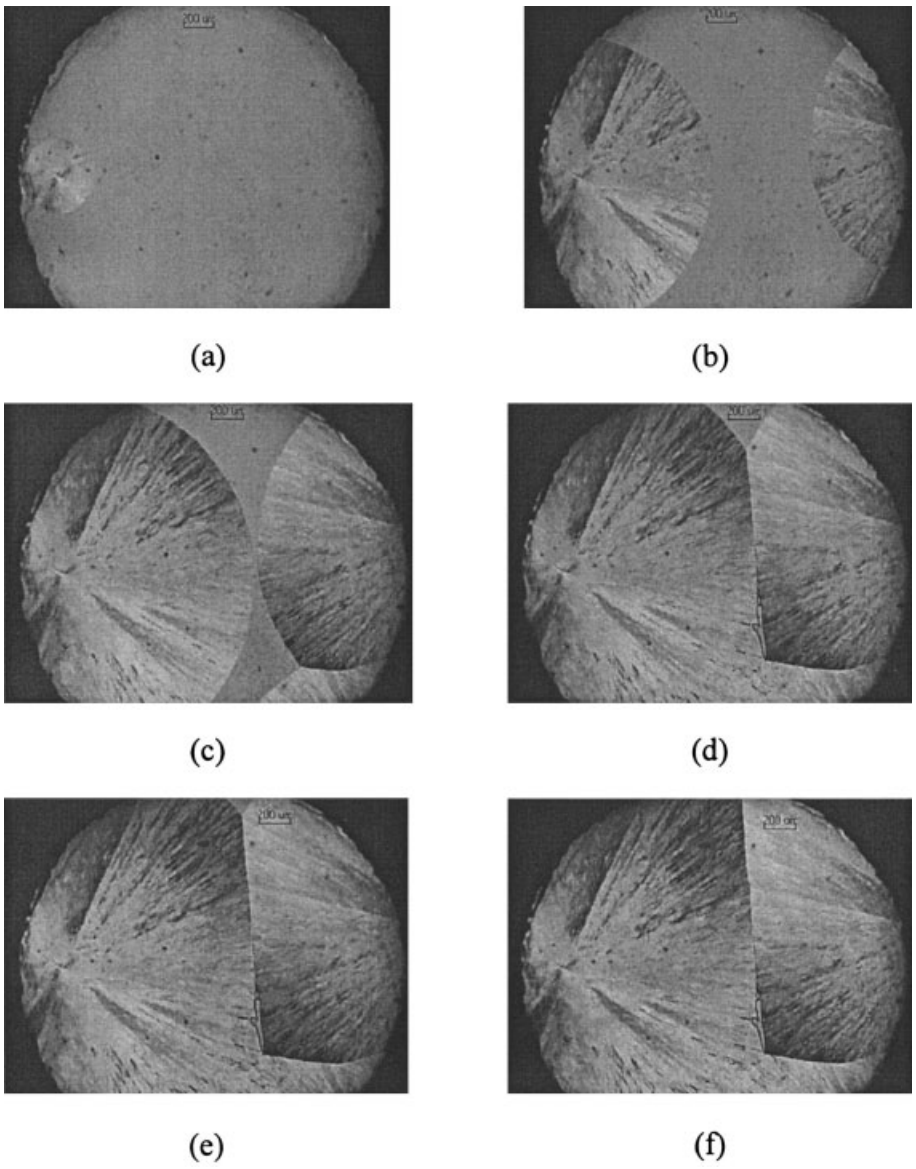

Figure 2 POM images of PEO spherulites at different time during the growing process under nonisothermal crystallization conditions at a cooling rate of 10°C/min: (a) 0, (b) 25, (c) 32, (d) 36, (e) 38, and (f) 54 s.

lites before and after the appearance of the diffractive banding. Moreover, the DSC results supported this viewpoint. Figure 3 shows the DSC curve of PEO; it describes the nonisothermal crystallization process of a PEO sample as the temperature decreased from 100 to 0°C at a cooling rate of 10°C/min. There are two peaks in the DSC curve, and they may indicate two different steps during the crystallization process.

Moreover, the formation of the concentric diffractive banding was also related to the crystallization conditions; that is, the concentric diffractive banding could not appear at any arbitrary crystallization conditions. Figure 4 shows the growth of the PEO spherulites under the isothermal conditions with a crystallization temperature (T_c) of 45°C; on the PEO spherulite surface, diffractive banding was never observed like that growing under the nonisothermal conditions [Fig. 1(a)]. Figure 5 shows that the detected melting point of PEO was near 62°C; the temperature of PEO spherulite growth under the isothermal conditions was just 17°C lower than the melting point. At this T_c, the growth of PEO spherulites took nearly 3.7 min according to Figure 6. However, looking back at the growth of PEO spherulites under the nonisothermal conditions at a cooling rate of 10°C/min, we can see that the crystalline nucleus began to appear at approximately 44°C, and the whole growing process lasted just 54 s. It was also easy to estimate the velocity of the PEO spherulites qualitatively in this situation. Figure 2(a–c) shows that the radius increasing from 0 to

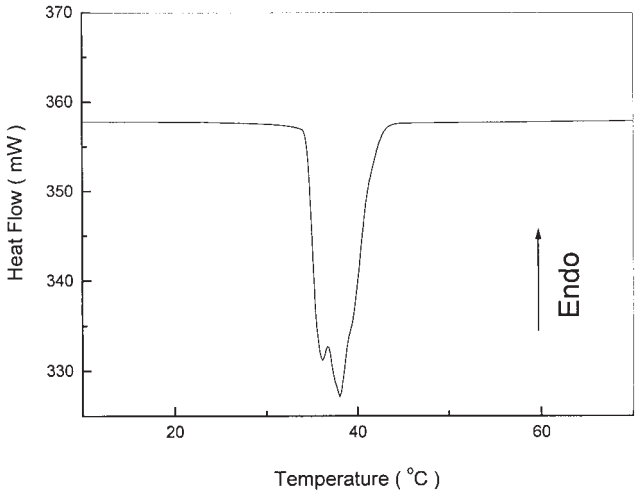

Figure 3 DSC curve of PEO, with the system temperature decreasing from 100 to 0°C at a cooling rate of 10°C/min.

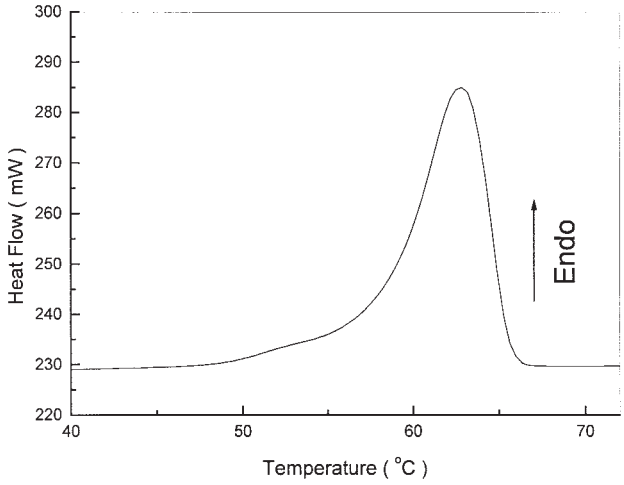

Figure 5 DSC curve of PEO, with the system temperature increasing from 0 to 100°C at a heating rate of 20°C/min.

1000–1100 μm took only about 32 s, and the growth velocity was much faster than that under the isothermal conditions, although the PEO spherulites growing under the isothermal conditions were more perfect.

However, we assumed that the stress force of the spherulites, after they came into contact with one another, enhanced the formation of concentric diffractive banding. Therefore, under crystallization conditions with a high crystal velocity, the more fiercely the spherulites collided, the greater the stress force was, and this was more beneficial to the formation of diffractive banding. In other words, it was believed that the velocity of the spherulite growth was just rapid enough to provide enough stress force to make the change in the spherulite growth needed to produce the concentric diffractive banding when the spherulites met. On the contrary, at a lower growth velocity, the stress force was not enough to change the spherulite growth or there may have been enough time to adjust the interior structure of the spherulites so that the diffractive banding did not form. Therefore, according to the before mentioned experimental results, PEO spherulites growing under nonisothermal conditions with rapid crystal velocity could form diffractive banding easily, whereas diffractive banding was never observed under crystallization conditions with a relatively slow crystal velocity.

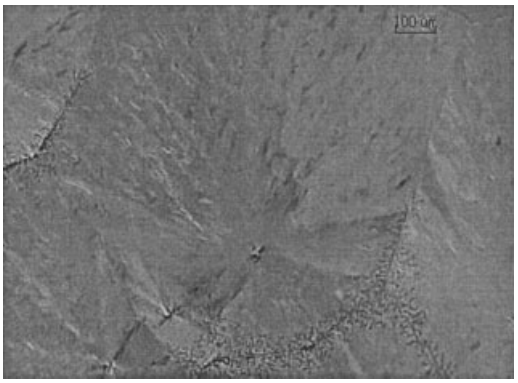

Figure 4 POM image of PEO spherulites under isothermal crystallization conditions with T_c = 45°C.

CONCLUSIONS

Observing the whole growing process of the PEO spherulites, we concluded that the formation of the diffractive banding was ascribable to kinetic factors, and these were related to the change in the spherulite growing step from the stress effect when two or more

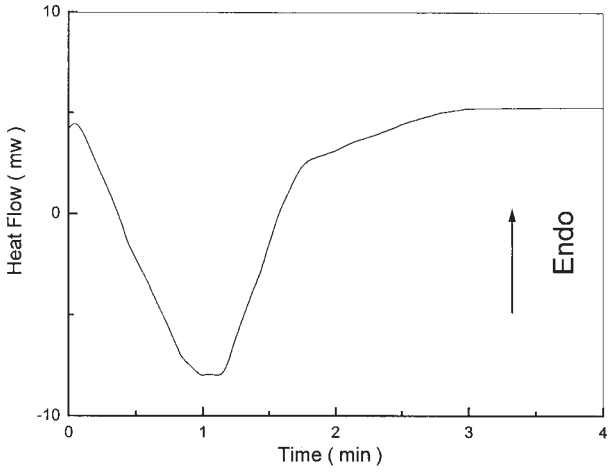

Figure 6 DSC curve of PEO, with the system quenched from 100 to 45°C and the temperature kept at 45°C for 10 min.

single spherulites collided. However, many factors related to the formation of the diffractive banding on the PEO spherulites, such as the molecular weight and molecular weight distribution and the other crystallization conditions, are still unknown, so further investigations should be made.

References

1. Kovacs, A. J.; Lotz, B.; Keller, A. L. J Macromol Sci Phys 1969, 3, 385.
2. Kovacs, A. J.; Gonthier, A.; Straupe, C. J Polym Sci Polym Symp 1975, 50, 283.
3. Cheng, Z. D.; Bu, H. S.; Wunderlich, B. J Polym Sci Part B: Polym Phys 1988, 26, 1947.
4. Song, D. D.; Bu, H. S.; Yu, T. Y. Acta Polym Sinica 1993, 6, 698.
5. Barnes, W. J.; Price, F. P. Polymer 1964, 5, 283.
6. Allen, R. C.; Mandelkern, L. J Polym Sci Polym Phys Ed 1982, 20, 1465.
7. Mihailov, M.; Nedkov, E.; Goshev, I. J Macromol Sci Phys 1978, 15, 313.
8. Schultz, J. M.; Miles, M. J. J Polym Sci Part B: Polym Phys 1998, 36, 2311.
9. Calleja, F. J.; Hay, I. L.; Keller, A. Kolloid Z Z Polym 1966, 209, 128.
10. Keller, A. J Polym Sci 1959, 39, 151.
11. Price, F. P. J Polym Sci 1959, 39, 139.
12. Ding, J. D.; Zhu, J. X.; Yang, Y. L. Chem J Chin Univ 1996, 17, 306.
13. Ding, J. D.; Zhu, J. X.; Yang, Y. L. Chem J Chin Univ 1996, 17, 498.
14. Yin, W. S.; Yang, H.; Cheng, R. S. Acta Chim Sinica 2004, 62, 610.