Chinese Journal of Polymer Science Vol. 32, No. 9, (2014), 1260−1270

Chinese Journal of Polymer Science
© Chinese Chemical Society
Institute of Chemistry, CAS
Springer-Verlag Berlin Heidelberg 2014

Uniform to Accelerated Crystal Twisting Transition in Deuterate Polyethylene/Poly(ethylene-*alt*-propylene) Blend Films*

Li-na Zhang, Wei-chao Shi and Charles C Han**
State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
He Cheng*
China Spallation Neutron Source, Institute of High Energy Physics, Chinese Academy of Sciences, Dongguan 523803, China

Abstract A uniform to accelerated crystal twisting transition is observed in deuterate polyethylene/poly(ethylene-*alt*-propylene) (d-PE/PEP) blend films. And the band period is a function of initial d-PE concentration, quench depth and annealing time of phase separation. As Keith and Padden suggested, twisting of lamella is due to the unbalanced stress on its both sides, which can supply a satisfying explanation to banded spherulites formed in homogeneous systems. When it comes to d-PE/PEP blend system, in homogeneous 99% d-PE/PEP (weight fraction of d-PE) blend film, the formation of banded spherulite is observed as a result of uniform twisting of ribbon like d-PE lamellae along the radial direction. With the amorphous PEP piling up, it transfers into accelerated edge-on to flat-on twisting due to crystallization assisted phase separation. The mechanism can be interpreted as following: d-PE molecules must inter-diffuse to the twisting growth front to continue the secondary nucleation and growth process. Meanwhile, the amorphous PEP molecules are rejected and accumulated at the twisting growth front. Once the d-PE lamella begins to twist because of unbalanced stress on both sides, the accumulated rubber phase at the growth front strengthens the unbalance and accelerates the edge-on to flat-on twisting. The concentration wave propagates further away with constant speed, and leads to concentric ring pattern with periodic nonuniform twisting along the radial direction. Since this is a kinetic effect, the band period can be controlled through initial d-PE concentration, quench depth and annealing time of phase separation. Our result shows that crystallization assisted phase separation can modify lamella growth kinetic pathway, thereby assisting concentric ring pattern formation.

Keywords: Polyethylene/poly(ethylene-*alt*-propylene) (d-PE/PEP) blend; Phase separation; Crystallization.

INTRODUCTION

Concentric ring pattern formation in spherulites[1−19] has been intensely studied for decades. Twisting model[3] describes the concentric ring pattern with alternating bright and dark rings in polarized optical microscopy (POM) as a result of gradual change of the refractive index with twisting of the lamellar stacks along the radial direction. Many models[3, 4, 7, 9, 14, 20–22] have been proposed to explain the energetic driving force that makes the crystal twisting. There are two basic approaches to interpret the origin of lamellar twisting, *i.e.*, the twisting is coming from the characteristics of lamellae themselves[6, 21, 23], or is generated from the growth process[4, 9]. Keith and Padden[20] proposed initially in 1984, Lotz and Cheng[10] summarized in 2005, that the unbalance in surface stress from differential congestion of fold surfaces led to the twisting of lamellar stacks. Bassett[21, 24] suggested that screw dislocation can also induce lamellar reorientation. On the other hand, Kyu[22] suggested that the

* This work was financially supported by the National Natural Science Foundation of China (Nos. 50930003 and 21174152).
** Corresponding authors: Charles C Han (韩志超), E-mail: c.c.han@iccas.ac.cn
He Cheng (程贺), E-mail: chenghe.iccas@gmail.com
Invited paper for the special issue of "Polymer Crystallization"
Received April 27, 2014; Revised May 10, 2014; Accepted May 13, 2014
doi: 10.1007/s10118-014-1500-3

nonlinear diffusion of 'nutrient' to the growth front during growth should twist the lamella. And Schultz[4, 9] introduced the idea that lamellar twisting happened when self-induced compositional or mechanical fields were generated at the growth front. Because twisting is not a universal feature of lamellar growth, and the two approaches explained lamellar twisting separately from secondary nucleation and lamellar growth process, there might be some common features.

Polymer blends, especially those involving semicrystalline polymers, are of particular interest[25–30], and some progress has been achieved on the control of concentric ring morphology. It was found that the band period can be adjusted by incorporation of a second segment[16] or a second component, or by changing the molecular weight[31]. However, these strategies are limited in block copolymer systems or systems that a wide range of molecular weight fractions are available. Recently, Li *et al*.[32] studied the effect of inter-diffusion on the crystallization dynamics in PE/PEP blend, and they found that the slower PE inter-diffusion coefficient in the amorphous PEP rich region greatly influenced the crystallization dynamics. Shi *et al*.[33] examined the interplay between crystallization, phase separation and glass transition in a dynamically asymmetric poly(ethylene oxide)/poly(methyl methacrylate) (PEO/PMMA) blend, and showed that concentric ring pattern can also be formed because of lamellar growth along the tangential direction without any twisting. Different chain sizes or other transitions may enhance the dynamical asymmetry between the two components, resulting in a new type of phase separation, known as asymmetric phase separation[33]. The interplay between asymmetric phase separation and crystallization suggests another possible way to control crystallization morphology.

Motivated by previously reported works, the role of crystallization assisted phase separation on the concentric ring pattern formation in d-PE/PEP blend films (1 μm and 20 μm in thickness) has been studied. The simplest polymer, d-PE, is chosen as the crystallizable component to make our model non-specific, while PEP is used as a rubbery component to manifest the effect of phase separation on the concentric ring pattern formation process. A continuous to accelerated crystal twisting transition is observed due to the crystallization assisted phase separation at the growth front. The effect of initial d-PE concentration, quench depth and annealing time of phase separation on band period are also studied. Our results demonstrate that the kinetic pathway can be used to adjust the morphology of concentric ring pattern in polymer blends.

EXPERIMENTAL SECTION

Materials and Blend Sample Preparation

PEP and d-PE homopolymers used in this study are prepared by saturation of mono-disperse anionically polymerized polyisoprene (PI) and polybutadiene (PB), respectively. PB is saturated with D_2 gas instead of H_2 gas. There is no special reason to select this d-PE in this study. The weight average molecular weight of d-PE and PEP is 13000 $g \cdot mol^{-1}$ and 4200 $g \cdot mol^{-1}$, respectively, measured by gel permeation chromatography. ^{1}H-NMR analysis indicates that the conversion of unsaturated bonds is more than 99%. Differential scanning calorimetry measurement indicates the melting temperature of d-PE is 104 °C.

d-PE and PEP with a given weight fraction are dissolved in cyclohexane with 1% by weight. The solution is stirred at 60 °C for 24 h. Films, with thickness of about 1 μm, are prepared by spin coating the solution onto silica substrates. On the other hand, to prepare blends, d-PE and PEP are coprecipitated from the hot cyclohexane solution into cold methanol. After filtration, the blends are dried in vacuum oven at room temperature for 3 days until constant weight. Then, films, with thickness of about 20 μm, are hot pressed between two glass slides.

For the etching process, cyclohexane is chosen as the solvent for PEP and amorphous d-PE. The sample is immersed in cyclohexane for 24 h at room temperature, and most of the amorphous PEP and uncrystallizable d-PE are etched away.

Optical Microscopy

Phase contrast optical microscopy (PCOM) and polarized optical microscopy (POM) experiments are carried out using an Olympus (BX51) optical microscope and Olympus (C-5050ZOOM) camera. The experimental temperature is controlled by a Linkam (LTS350) hot stage.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) images of samples are observed by a JEOL 6700 microscope with 5 kV accelerating voltage. Samples are coated by platinum before observation.

Atomic Force Microscopy

Atomic force microscopy (AFM) measurements are performed on a Multimode 8 AFM (Veeco Nanoscope). All images are taken with the tapping mode at ambient temperature.

Differential Scanning Calorimetry

Thermal diagrams are obtained by differential scanning calorimetry (DSC) (Q2000, TA Instrument) under nitrogen atmosphere. Samples are encapsulated in aluminum pans for DSC measurements.

RESULTS AND DISCUSSION

Phase Diagram

The d-PE/PEP blend has an upper critical solution temperature (UCST) phase diagram and the equilibrium melting curve of crystallizable d-PE is lower than the binodal line, as illustrated in Fig. 1. The red line represents the binodal line obtained from optical microcopy examination. The green line stands for the spinodal line calculated by Wang's equation[35]. The blue line is the melting depression line calculated using Hoffman-Weeks approach[36]. The black line represents the transition line which stands for the lowest temperature to form concentric ring pattern. A similar UCST phase diagram was observed and reported by Bates[34] before.

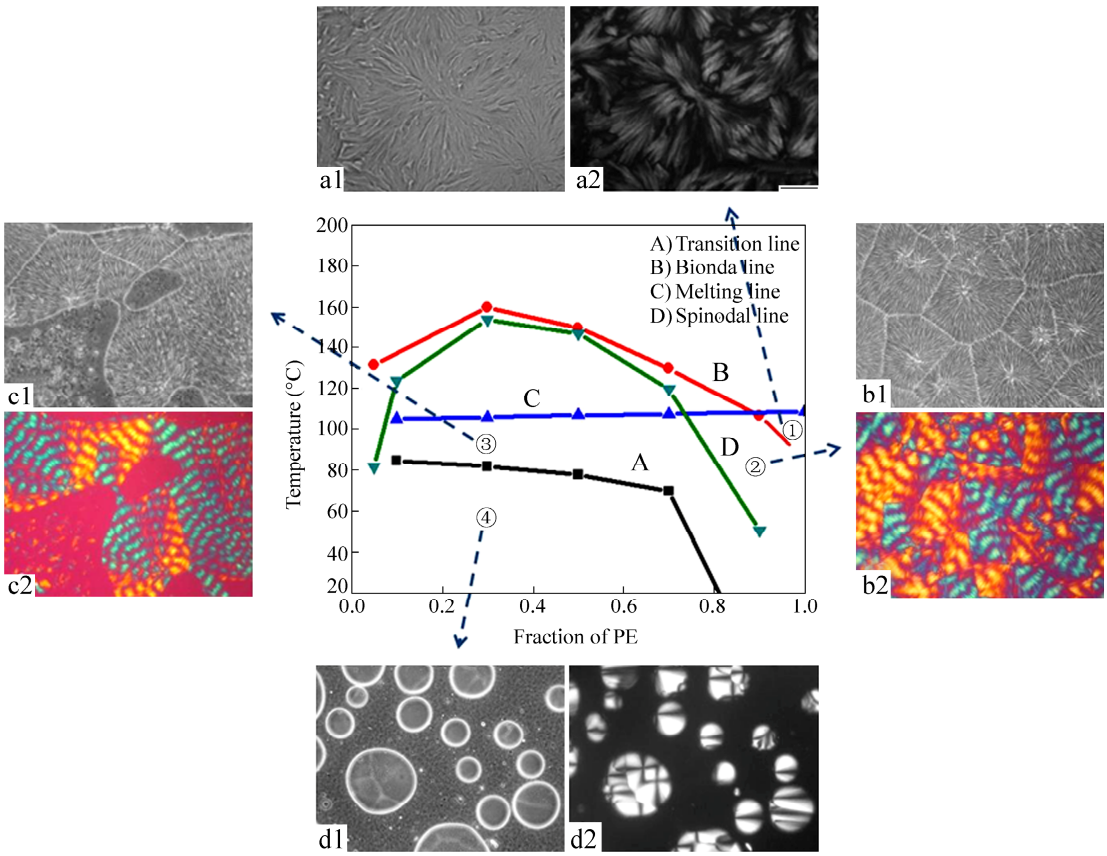


Fig. 1 Schematic phase diagram of d-PE/PEP blend system
Phase contrast (a1, b1, c1, d1) and polarized (a2, b2, c2, d2) optical micrographs are used to illustrate the crystallization morphologies in the corresponding regions (1, 2, 3 and 4), with d-PE weight fraction of 99%, 90% and 30% at 95 °C, 30% at 70 °C. The scale bar is 50 μm.

When quenching below the equilibrium melting line of d-PE, the blend can be in miscible region (region 1), metastable liquid-liquid phase separation (LLPS) region (region 2) or unstable LLPS region (region 3), depending on initial d-PE concentration. Region 1 is the uniform one phase region, and amorphous PEP concentration is very low and the blend behaves like pure d-PE. Regions 2 and 3 are in the binodal and spinodal region, respectively. And the relative speed of phase separation and crystallization can be adjusted through initial d-PE concentration and quench depth. While, in deep quench region (region 4), the speed of crystallization is so fast that it freezes the morphology and no concentric ring pattern can be observed. Therefore, there is a transition line stands for the lowest temperature to form concentric ring pattern.

In the following sections, we will discuss two types of regions according to the phase diagram: one phase region and two phase region. In one phase region, classical banded spherulites should be observed, as have been intensely investigated by Keith and Padden[7, 37]. On the other hand, in two phase region, crystallization will be coupled with phase separation. The interplay between them as well as morphology evolution will be discussed.

Concentric Ring Pattern Formation in Thin Films

By controlling solution concentration and spinning rate, a 99% d-PE/PEP blend film is obtained, with a thickness of about 1 μm.

There is no concentric ring pattern in phase contrast optical microscopy (PCOM) (Fig. 2a). The grey and white regions here are corresponding to amorphous and crystalline rich regions, respectively. Both of them arrange along the radial direction. On the other hand, concentric ring pattern is observed in polarized optical microscopy (Fig. 2b). The negative spherulite indicates that the chain folding is perpendicular to the radial direction. In order to examine the detailed organization of lamellar stacks, solvent etching is implemented to remove amorphous phase. After etching, SEM (Figs. 2c–2e) reveals the morphology of lamella twisting. The detailed kinetics of lamellar twisting in PE spherulite has been clearly described by Barham and Keller[3]. The unbalanced surface stresses twist the d-PE lamella continuously along the radial growth direction, as shown in Figs. 2(c–e). Since the amorphous PEP concentration is low, the amorphous d-PE and PEP are rejected and occupy inter-lamellae spaces. Therefore, radial growth of crystal lamellae can be observed in PCOM and concentric ring pattern can only be seen in POM as a known result of uniform twisting, with amorphous PEP located in the inter-lamellae spaces.

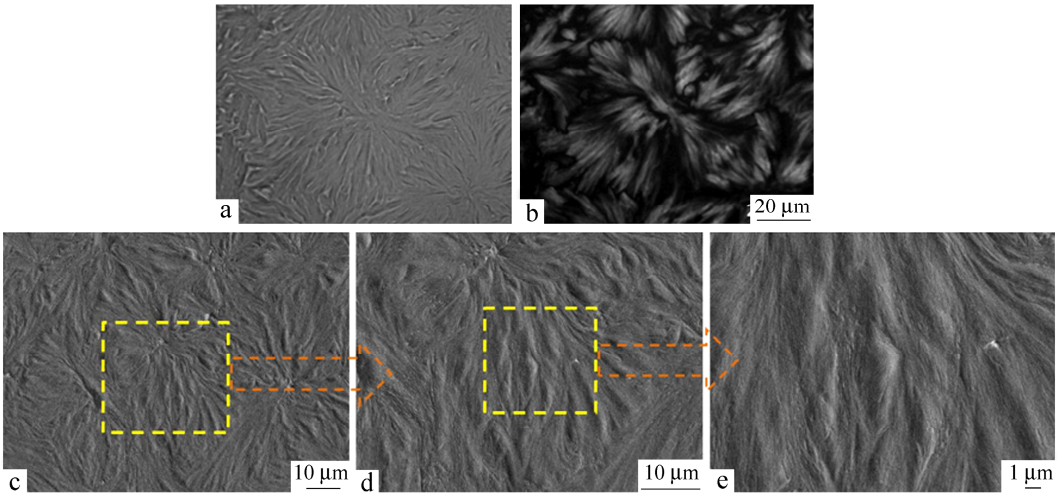


Fig. 2 Phase contrast (a) and polarized (b) optical micrographs of a 99% d-PE/PEP blend film at 95 °C, and corresponding scanning electron micrographs of etched sample (c), enlarged images of corresponding part indicated in squares (d) and (e) (The white arrow is used to guide the eyes.)

In the 70% blend film, crystallization assisted phase separation begins to play its role with amorphous PEP piling up. Figure 3 is the phase contrast (a) and polarized (b) optical micrographs of the 70% blend film at 95 °C,

and corresponding SEM images (c–e) after being etched by cyclohexane. Regular concentric ring pattern is observed in both POM and PCOM. The former is due to the twisting of lamellae along radial direction. Contrary to 99% blend in one phase region with absence of concentric ring in PCOM, the latter ring pattern indicates that a ring like amorphous rich region is formed as a result of the coupled effect of crystallization and phase separation.

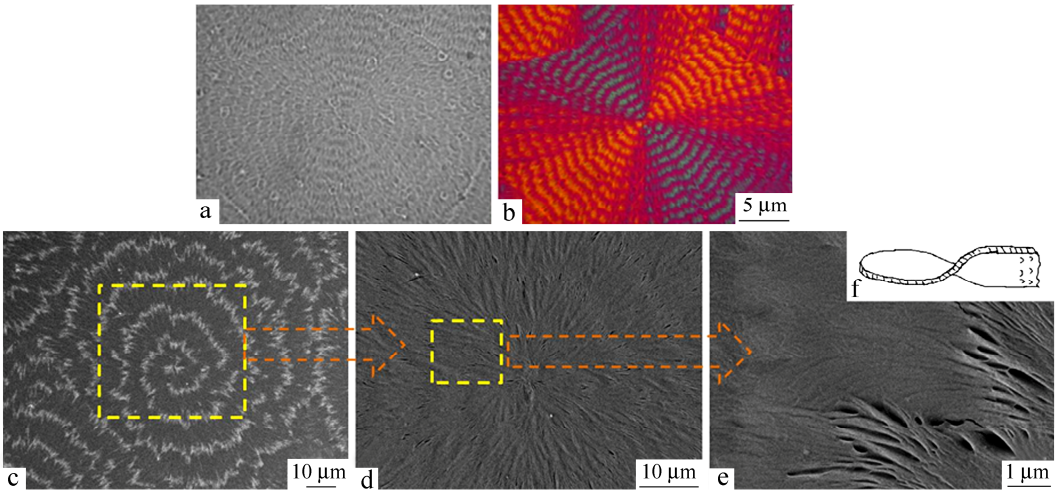


Fig. 3 Phase contrast (a) and polarized (b) optical micrographs of 70% d-PE/PEP blend film at 95 °C and scanning electron micrographs of etched sample: Overall morphology of a concentric ring pattern (c), and magnified image of twisting lamella indicated by the square (d) and (e) respectively, with the inset (f) representing a schematic picture of twisting lamella from edge-on to flat-on (The white arrow is used to guide the eye.)

Concentric rings in SEM images are consistent with those in OM. Unlike the uniform twisting in one phase region as shown in Fig. 2, lamellar stacks change their orientation from edge-on to flat-on abruptly during confronting with amorphous rich region at the growth front. As demonstrated in Fig. 3(c), the edge-on part takes about 1/4 in one banding period which can be deduced form secondary electron imaging mode SEM which is sensitive to surface roughness[38]. And the transition from uniform to accelerated twisting is probably related to the ring like amorphous rich region during spherulite growth. The coupled effects can be interpreted as following: After the formation of crystal nuclei, crystallizable d-PE must inter-diffuse to the growth front to continue the secondary nucleation and growth process, while amorphous polymers are rejected to the growth front. In the secondary nucleation step, the crystal lamella begins to twist because of unbalanced stress on both sides. While in the growth process, the faster depletion of crystallizable d-PE at the twisting growth front strengthens the unbalance, leading to an intensified reorientation from edge-on to flat-on. Note that crystallization assisted phase separation introduces amorphous PEP to pile up at the crystal growth front. And the propagation of this kind of "concentration wave" leads to the concentric ring pattern formation in PCOM picture shown in Fig. 3(a).

AFM is another effective way to test the role of crystallization assisted phase separation on concentric ring pattern formation because it can supply a direct description of the surface height variation. The location of amorphous rich region can be confirmed through the height variation between original and etched samples.

Figure 4 is the AFM height profiles of 70% d-PE/PEP blend film before (a) and after (b) amorphous parts being etched, and the corresponding height profiles (c, d) along the white lines in (a) and (b). The d-PE/PEP blend film before etching is relatively smooth with most of amorphous PEP covered the valley part of the ring structure, while it becomes exposed and reveals the lamellar structure after etching. The height variation between peak and valley changes from about 130 nm to about 270 nm after etching, which suggests that most of

amorphous parts are accumulated in the valley before etching. For an ideal twisting lamella with periodic abrupt edge-on to flat-on transition, its height profile should be a square wave. Since the mild solvent etching should not have damaged the original lamella crystal, the AFM height profile of d-PE/PEP blend film indicates that the accelerated edge-on to flat-on transition is not ideal.

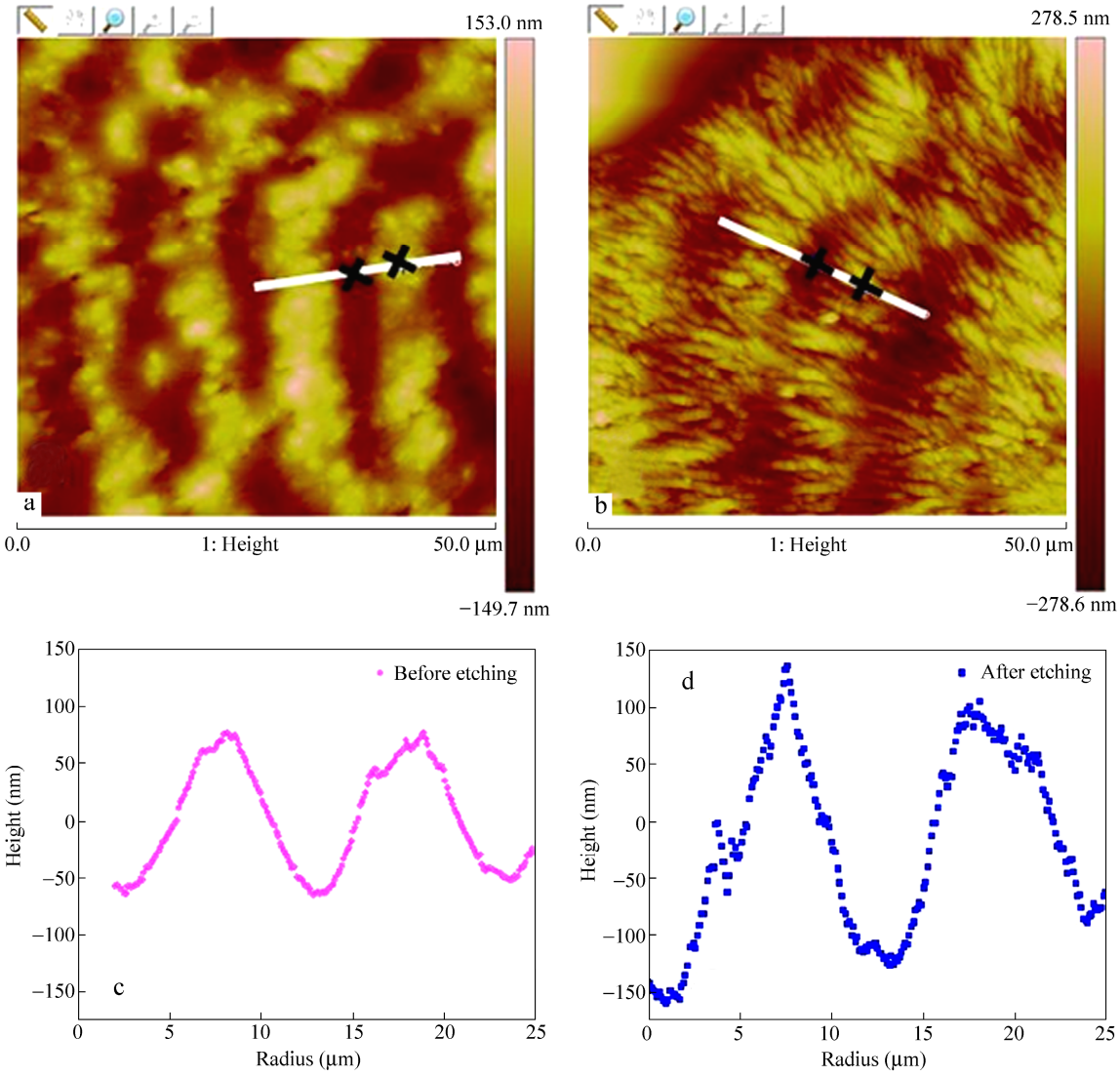


Fig. 4 Atomic force microscopy height images of 70% d-PE/PEP blend film before (a) and after (b) etching and corresponding height profiles (c, d) along the white line in (a) and (b), respectively

Concentric Ring Pattern Formation in Thick Films

It has been reported[39] that for a given film thickness, if the width of the lamella is commensurate with film thickness, the lamella will tend to have an accelerated twisting; if the lamella is thinner, the lamella will have enough space to twist, undisturbed by the presence of the substrate. Considering the possible effect of film thickness on concentric ring pattern formation, further experiments in much thicker samples have also been carried out.

The SEM image of hot pressed sample of 20 µm in thickness is presented in Fig. 5. The width of lamellae is about 1 µm, and it's much smaller than the film thickness. Thus a surface confinement should not be a major effect. It clearly demonstrates a concentric ring pattern, and the center of spherulite lies in the image center. In

order to gain a better observation of the organization of lamellar stacks, the yellow square region is enlarged. Figure 5(c) demonstrates that lamellar stacks do twist, and change their orientation from edge-on to flat-on which is consistent with the result of thin film of 1 μm in thickness as shown in the previous discussion. In the film of 20 μm in thickness, the orientation of lamellae should not be influenced by film thickness confinement, thus the accelerated twisting of lamellar stacks from edge-on to flat-on could be demonstrated as a common feature for asymmetric phase separating blend samples.

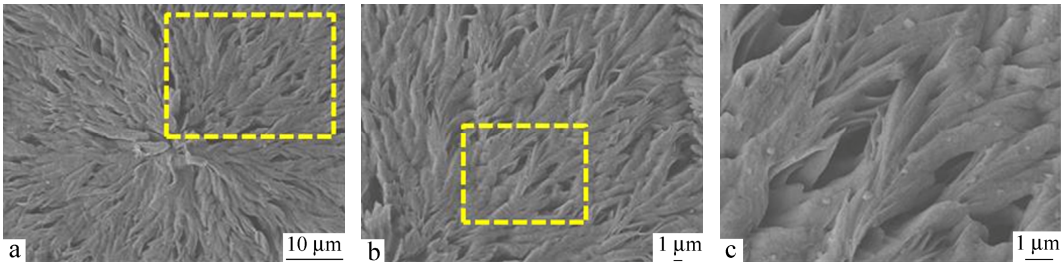


Fig. 5 (a) Scanning electron microscopy iamges of an etched sample of 70% d-PE/PEP blend film with a thickness of about 20 μm at 95 °C and (b, c) enlarged images of corresponding part indicated by squares in (a) and (b)

To further prove this, kinetic pathway of concentric ring pattern formation at different d-PE concentrations, quench depths and annealing time lengths of phase separation in 20-μm-thick films have also been studied.

Kinetics Effects on Band Period

Band period is the distance between the nearest dark rings or white rings in POM, and it is a key parameter to describe the concentric rings pattern morphology. It is mainly determined by twisting intensity and amorphous volume fraction[40].

Effect of quench depth

Figure 6 shows that the change of band period of d-PE spherulites is a function of crystallization temperature and initial blend composition. First, it is evident that the band period of d-PE spherulites increases with crystallization temperature, while the tendency of band period with initial blend ratio cannot be simply classified into previous conclusions. The increase of band periodicity with temperature is expected as frequently reported in many other polymer systems with extinction features[41–44]. However, the trend of band period with the increase of the second component is quite different from the results of other blend system, where a reduction of band period is usually observed[45, 46] and also some exceptions[47]. In this d-PE/PEP blend system, for initial blend ratio of 30% and 50%, their band periods are almost the same, while for 90% blend the band period is a little larger. Considering that crystallization of d-PE is coupled with liquid-liquid phase separation, which can give a good explanation for this different trend of band period with initial blend ratio. Let's resort to the phase diagram in Fig.1, 30% and 50% falls into two phase region and follows a coupled LLPS and crystallization, and hence a similar trend of band period; while 90% falls into metastable region, and hence a lower PEP concentration in d-PE rich region and a larger band period compared with that in 30% and 50% blends. D/G (diffusion/growth) ratio is determined by crystallization temperature (T_c). Keith and Padden[5, 48] termed it as diffusion length to determine lateral dimensions of the fibers. Noncrystallographic branching should be observed when D/G is small enough to be commensurate with the sizes of disordered regions on their surfaces. However, in a system when crystallization is coupled with phase separation, the "impurity concentration" in the work of Keith and Padden is not only determined by its initial fraction, but also affected by the phase separation process.

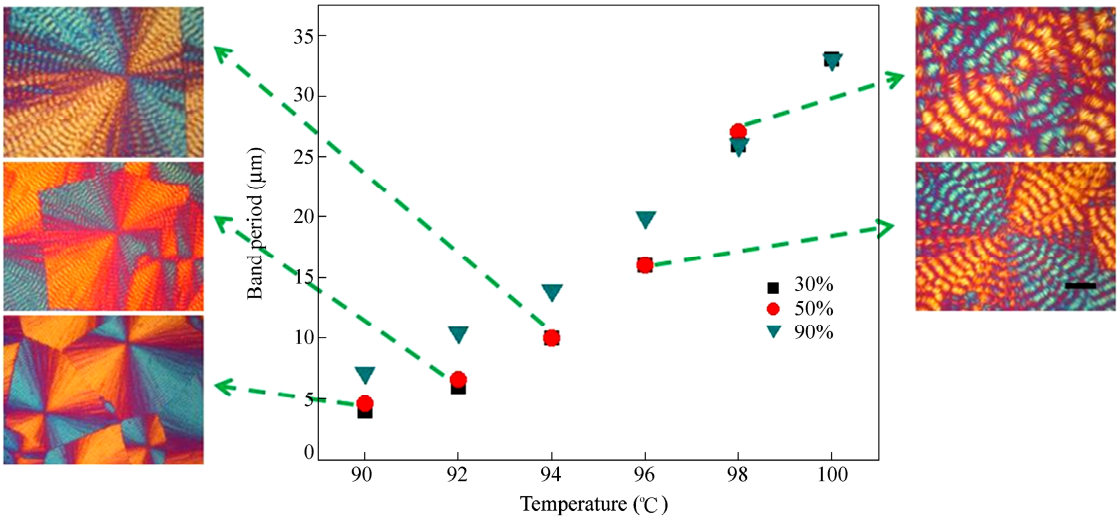


Fig. 6 Band periods at different crystallization temperatures for 30%, 50% and 90% d-PE/PEP blends quenched from homogeneous state (The scale bar is 50 μm.)

Effect of initial concentration

To demonstrate the role of initial concentration, three d-PE fractions, 30%, 50% and 90% are investigated, as represented in Fig. 6. The 30% and 50% samples have similar band periods which are a little smaller than that of the 90% sample at larger quench depths. And the band periods for all the three fractions become similar with decreasing quench depth.

The effect of initial composition is associated with phase separation and its competition with crystallization after quenching. Upon cooling a homogeneous blend melt, liquid-liquid phase separation will take place either by the nucleation and growth mechanism or by the spinodal decomposition, which will influence the d-PE composition evolution process. 30% and 50% blend samples fall into unstable region and follow similar spinodal decomposition kinetics, while 90% blend follows a nucleation and growth type of phase separation.

For a deep quench, the driving force of crystallization due to supercooling is strong, and crystal growth happens much faster than phase separation. d-PE crystal grows through secondary nucleation and growth process of d-PE chains and at the crystal growth front an amorphous rich region will be formed due to the rejection of non-crystallizable chains. Since the 90% blend is in the binodal region, and closer to the coexistent composition, therefore, it takes longer time for the d-PE to grow (to longer distance) before there are enough amorphous PEP being rejected in the growth front to produce a twist, and consequently the band period is larger. While, 30% and 50% blends are in spinodal region, and far away from the coexistent composition, so it takes less time to accumulate enough PEP in the growth front to form a twist, and the band period is smaller. Besides, the driving forces of phase separation in 30% and 50% d-PE blends are similar, thus they have similar liquid-liquid phase separation rates, and similar band periods.

For a shallow quench, the driving force of crystallization is reduced, while the driving force of phase separation is little influenced. All of the three samples have more time to reach to the coexistent composition, and the crystal growth essentially happens in a domain with the same coexistent composition. Therefore, they have similar band periods.

Effect of the annealing time of phase separation

Finally, we will discuss the effect of annealing time of phase separation through a two-step quench experiment. The experimental procedure is as following: firstly, 50% blend samples are quenched to 115 °C, which is higher than d-PE melting temperature, to undergo a phase separation process without crystallization coupled; then after varying annealing time of phase separation, they are quenched to 95 °C for crystallization. Band period is

obtained by OM to represent the corresponding morphology change as a result of annealing time of phase separation.

The dependence of band period on annealing time of phase separation is shown in Fig. 7. Band period increases with phase separation time at first; then it reaches a plateau after a longer annealing time. As is shown in Fig. 7, band period changes from 16 μm to 20 μm with annealing time of phase separation. In the first quench step, the blend system follows a liquid-liquid phase separation and as the phase separation goes on, the d-PE concentration in its rich region marches toward the coexistent composition. So band period increases correspondingly (it will takes longer time to accumulate enough amorphous materials to produce a twist). When the blend stays at 115 °C for a long enough time, liquid-liquid phase separation becomes more closer to the coexistent composition, correspondingly, band period dose not change any more.

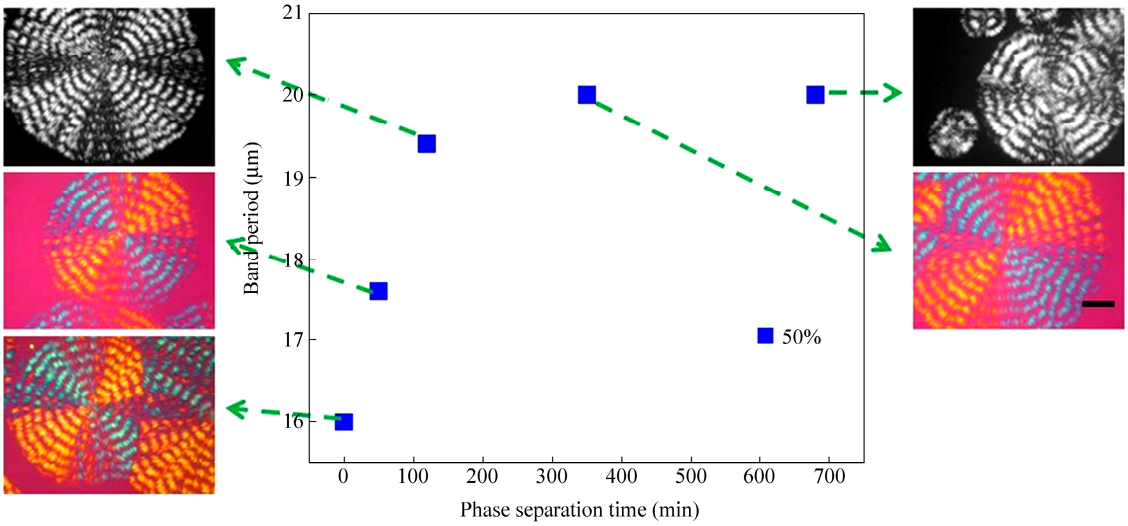


Fig. 7 Band period evolution in 50% d-PE/PEP blends with different annealing time of phase separation at 115 °C (The scale bar is 50 μm.)

The band period is determined by the competition between phase separation and crystallization, which proves that crystallization assisted phase separation is a major factor to accelerate lamella twisting in asymmetric d-PE/PEP blends.

CONCLUSIONS

In summary, concentric ring pattern with alternating bright and dark rings in POM can be either generated in secondary nucleation and growth process or in the crystallization assisted phase separation mechanisms. In secondary nucleation and growth process, which is the regular one component polymer crystal growth kinetics, the unbalanced stress on both sides of lamella leads to the twisting and gives the ring structure in POM; while in the crystallization assisted phase separation process, phase separation at the growth front enhances the refractive index difference of the interface (between rings) and produce also the image in PCOM. Our results demonstrate that crystallization assisted phase separation can generate a uniform to accelerated crystal twisting transition in d-PE/PEP blend films and hence concentric ring pattern with alternating bright and dark rings can be observed in both POM and PCOM by changing the d-PE crystallization kinetic pathway.

REFERENCES

1 Keller, A., J. Polym. Sci., 1959, 39: 151
2 Keller, A. and Machin, M.J., Macromol. Sci. Part B: Phys., 1967, 1: 41
3 Barham, P.J. and Keller, A.J. Mater. Sci., 1977, 12: 2141
4 Schultz, J. and Kinloch, D., Polymer, 1969, 10: 271
5 Keith, H.D. and Padden, F.J., J. Appl. Phys., 1964, 35: 1270
6 Bassett, D. and Hodge, A., Proc. R. Soc., London, 1981, 377: 25
7 Keith, H.D. and Padden, F.J., Macromolecules, 1996, 29: 7776
8 Bassett, D.C., Olley, R.H., Sutton, S.J. and Vaughan, A.S., Macromolecules, 1996, 29: 1852
9 Schultz, J.M., Polymer, 2003, 44: 433
10 Lotz, B. and Cheng, S.Z.D., Polymer, 2005, 46: 577
11 Fromsdorf, A., Woo, E.M., Lee, L.T., Chen, Y.F. and Forster, S., Macromol. Rapid Commun., 2008, 29: 1322
12 Xu, J., Guo, B.H., Zhou, J.J., Li, L., Wu, J. and Kowalczuk, M., Polymer, 2005, 46: 9176
13 Toda, A., Okamura, M., Taguchi, K., Hikosaka, M. and Kajioka, H., Macromolecules, 2008, 41: 2484
14 Hatwalne, Y. and Muthukumar, M., Phys. Rev. Lett., 2010, 105:10780101
15 Xu, J., Guo, B.H., Zhang, Z.M., Zhou, J.J., Jiang, Y., Yan, S., Li, L., Wu, Q., Chen, G.Q. and Schultz, J.M., Macromolecules, 2004, 37: 4118
16 Li, J., Li, Y., Zhou, J., Yang, J., Jiang, Z., Chen, P., Wang, Y., Gu, Q. and Wang, Z., Macromolecules, 2011, 44: 2918
17 Wang, Y., Chan, C.M., Li, L. and Ng, K.M., Langmuir, 2006, 22: 7384
18 Woo, E.M., Yen, K.C. and Wu, M.C., J. Polym. Sci. Part B: Polym. Phys., 2008, 46: 892
19 Ratner, S., Moret, P., Wachtel, E. and Marom, G., Macromol. Chem. Phys., 2005, 206: 1183
20 Keith, H.D. and Padden, F.J., Polymer, 1984, 25: 28
21 Bassett, D.C., Polym. J., 1999, 31: 759
22 Kyu, T., Chiu, H.W., Guenthner, A.J., Okabe, Y., Saito, H. and Inoue, T., Phys. Rev. Lett., 1999, 83: 2749
23 Toda, A., Taguchi, K. and Kajioka, H., Macromolecules, 2008, 41: 7505
24 Bassett, D. and Hodge, A., Proc. R. Soc. London, 1981, 61
25 Wang, T. C., Li, H. H. and Yan, S. K., Chinese J. Polym. Sci., 2012, 30(2): 269
26 Yang, J.A., Wang, Z.B., Wu, Y., Wu, X.F. and Gu, Q., Acta Polymerica Sinica (in Chinese), 2010, (8): 987
27 Luo, F.L., Zhang, X.Q., Li, R.B., Fu, D.S., Gan, Z.H., Ji, J.H. and Wang, D.J., Acta Polymerica Sinica (in Chinese), 2009, (10): 1043
28 Wu, N.J. and Yang, P., Acta Polymerica Sinica (in Chinese), 2010, (3): 316
29 Wei, J.C., Sun, J.R., Wang, H.J., Chen, X.S. and Jing, X.B., Chinese J. Polym. Sci., 2010, 28(4): 499
30 Hu, H.X., Shangguan, Y.G., Zuo, M. and Zheng, Q., Acta Polymerica Sinica (in Chinese), 2009, (2): 123
31 Kajioka, H., Yamada, K., Taguchi, K. and Toda, A., Polymer, 2011, 52: 2051
32 Li, J., Li, W., Li, Z., Cheng, H., Li, Y. and Han, C.C., J. Chem. Phys., 2011, 135: 0449021
33 Shi, W.C. and Han, C.C., Macromolecules, 2012, 45: 336
34 Maurer, W.W., Bates, F.S., Lodge, T.P., Almdal, K., Mortensen, K. and Fredrickson, G.H., J. Chem. Phys., 1998, 108: 2989
35 Wang, H., Shimizu, K., Hobbie, E.K., Wang, Z.G., Meredith, J.C., Karim, A., Amis, E.J., Hsiao, B.S., Hsieh, E.T. and Han, C.C., Macromolecules, 2002, 35: 1072
36 Hoffman, J.D. and Weeks, J.J., J. Res. Natl. Bur. Stand., 1962, 66: 13
37 Keith, H.D. and Padden, F.J., J. Polym. Sci., 1958, 31: 415
38 Goldstein, J., Newbury, D.E., Joy, D.C., Lyman, C.E., Echlin, P., Lifshin, E., Sawyer, L. and Michael, J.R., "Scanning electron microscopy and X-ray microanalysis", Springer, 2003
39 Barnes, J.D. and Khoury, F., J. Res. Natl. Bur. Stand., 1974, A 78: 363
40 Okabe, Y., Kyu, T., Saito, H. and Inoue, T., Macromolecules, 1998, 31: 5823
41 Wang, Z.G. and Jiang, B.Z., Macromolecules, 1997, 30: 6223

42 Xu, J., Guo, B.H., Zhou, J.J., Li, L., Wu, J. and Kowalczuk, M., Polymer, 2005, 46: 9176
43 Wang, H.J., Gana, Z.H., Schultz, J.M. and Yan, S., Polymer, 2008, 49: 2342
44 Su, C.C. and Lin, J.H., Colloid Polym. Sci., 2004, 283: 182
45 Wang, X.H., Zhang, H.X., Wang, Z.G. and Jiang, B.Z., Polymer, 1997, 38: 1569
46 Xiao, Q., Yan, S., Rogausch, K., Petermann, J. and Huang, Y., J. Appl. Polym. Sci., 2001, 80: 1681
47 Penning, J.P. and St. John Manley, R., Macromolecules, 1996, 29: 77
48 Keith, H.D. and Padden, F.J., J. Appl. Phys., 1963, 34: 2409