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# Orientational phase-separated domains in a polyolefin blend under a temperature gradient field

Hua Jiang [a,b], Nannan Dou [a,b], Guoqiang Fan [c], Xiaohua Zhang [a,*], Zhaohui Yang [a,*]

[a] Center for Soft Condensed Matter Physics and Interdisciplinary Research, Soochow University, Suzhou 215006, China
[b] College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China
[c] SINOPEC Beijing Research Institute of Chemical Industry, Beijing 100013, China

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ABSTRACT

We investigate the effect of a temperature gradient on the orientation of phase-separated structures in a polyolefin blend system. Phase contrast optical microscopy (PCOM) has been used to measure the morphology of phase separation via spinodal decomposition as a function of phase separation time and temperature gradient. The bicontinuous and interconnected tubelike structure, the characteristic morphology of the spinodal decomposition process, exhibits a preferential alignment along the direction of temperature gradient after phase separation. The orientation of the bicontinuous and interconnected tubelike structures gradually increases with phase separation time and temperature gradients. Also the orientation of phase-separated domains can respond really quickly to the change in the direction of external temperature gradient field. The results suggest that "thermal force" induced by the temperature inhomogeneity might play an important role in aligning phase-separated domains preferentially along the temperature gradient direction.

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## 1. Introduction

The phase separation, especially spinodal decomposition in the field of small molecule, such as the multicomponent liquids, binary alloys and inorganic glasses has fascinated researchers for a long time [1,2]. Over many years the study on the phenomenon of spinodal decomposition has become the subject of many theoretical and experimental investigations in polymer blends because of the ease with which the different regimes of the phase diagram can be probed for a wide range of time scales [3–8] and more importantly because of possibility of fabricating regular structures for their potential applications in a wide range of manufacturing and patterning fields [9,10]. The phase separation under non-equilibrium conditions has attracted much attention in soft matter system like polymer mixtures. In fact, polymer mixtures can undergo dramatic changes in morphologies and length scales in response to externally applied perturbations such as shear flow [11–13], concentration gradient [14], patterned surface [15], or temperature inhomogeneity [16–19]. The analysis of the behavior of liquid–liquid phase separation driven by spinodal decomposition in the non-equilibrium conditions or in external fields may shed additional light on many structural features of the polymer blend systems that are not well understood. In the presence of a temperature gradient, polymer chain dynamics show the different characteristics during the thermal-induced phase separation duo to the complexity of polymer chain structure and mobility [20]. Also due to the unique long-chain molecule characteristics of high viscosity through polymer–polymer entanglements, large correlation length and relatively slow dynamics, the polymer blend systems has become the ideal candidates for investigating the influence of thermal gradient field on the phase separation process. However, almost all authors of the experimental and theoretical papers describe the phase behavior of the blend by means of an equilibrium phase diagram. Recently, Voit et al. [21] investigated the influence of an inhomogeneous temperature field on the phase behavior of a polymer blend. Their results show that in an inhomogeneous temperature field the equilibrium phase diagram, where the locus of the mixture is characterized by its average composition and a constant temperature, is shifted toward a higher temperature and higher concentration. There have been some reports concerning the local thermal patterning in the polymer blend under inhomogeneous temperature fields by using a focused laser beam [16,17]. As the laser is switched on, the spinodal patterns around the focused laser beam, where the material was locally heated to temperature above the critical point, completely

* Corresponding authors.
*E-mail address:* zhangxiaohua@suda.edu.cn (X. Zhang).

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disappear. Their results indicated that in the two-phase regime of phase diagram of a polymer blend the spinodal decomposition patterns can be manipulated on a mesoscopic length scale in a controlled way by using a local laser heating technique. Our previous studies [22] suggest that the in-plane thermal gradient accelerates phase separation through the enhancement in concentration fluctuations in the early and intermediate stages of spinodal decomposition. However there are few (if any) experimental reports on the response of orientation of the phase-separated domains to a temperature gradient. Understanding the effect of the temperature inhomogeneity on the orientation of phase-separated domains will provide a great deal of insight into many features of the structures and dynamic behavior of blend systems in non-equilibrium conditions. Here, a typical two-component polyolefin blend system, a statistical copolymer blend of poly(ethylene-co-hexene) (PEH) and poly(ethylene-co-butene) (PEB) was selected, which exhibits an upper critical solution temperature (UCST)-type of phase diagram with the critical temperature at 146 °C at the composition of $\Phi_c = 0.44$ in melt [23]. We describe the optical microscopy measurements of the phase-separated domains as a function of temperature gradient and phase separation time. By estimating the orientation of characteristic structure of spinodal decomposition from the scattering patterns obtained numerically by the two-dimensional fast Fourier transform (2D FFT) of phase contrast micrographs, we quantify the evolution of the orientation of phase-separated domains with temperature gradient and phase separation time as it passes through the regime of phase separation, in an effort to understand the influence of thermal gradient on the orientation behavior of phase separation via spinodal decomposition in two-phase regime of the phase diagram. We previously studied the effect of the temperature gradient and phase separation temperature on the phase separation kinetics [22]. This former work is a natural reference for our discussion below, where we focus specifically on the orientation behavior of the phase-separated domains under thermal gradient field and reveal how the orientation of phase-separated domains responds to the change in the direction of external temperature gradient field.

## 2. Experimental section

### 2.1. Materials and sample preparation

The statistical polyethylene copolymers, polyethylene-co-hexene (PEH) ($M_w$ = 110 kg/mol, 2 mol% hexene comonomer) and polyethylene-co-butene (PEB) ($M_w$ = 70 kg/mol, 15 mol% butene comonomer), were supplied by ExxonMobil Co. Ltd. They were both synthesized with metallocene catalysts, and have relatively narrow molecular weight distributions, *Mw/Mn* ~ 2, and uniform comonomer distributions. The blend of PEH and PEB, which has PEH mass fraction of 50%, was prepared by coprecipitation method. The blend was first dissolved in the hot xylene at 120 °C, and then the solution was cooled to 100 °C and kept for 24 h. Afterward, the solution was poured into a chilled methanol to precipitate the blend. After filtering, the blend was washed with methanol and dried in air for 24 h and further dried in vacuum oven for 3 days before use, and then the blend was hot-pressed at 120 °C between the round cover glass and microscope slice on a hot plate to form a film of ca. 120 μm in thickness and 12 mm in diameter, which can be considered as a bulk sample in our study.

### 2.2. Characterization and experimental procedure

The phase contrast optical microscope observations were carried out using a Zeiss (Axio. imager. A2) optical microscope and a Zeiss (AxioCam HRC) CCD. Linkam LTS420 and GS350 hot stages were used to provide the homogeneous temperature control and temperature gradient, respectively. A schematic of the temperature gradient hot stage is shown in Fig. 1(a). An in-plane temperature gradient is established by independently temperature-controlled plate I and plate II. Two heating plates of the temperature gradient hot stage are perfectly aligned to ensure uniform thermal contact between the temperature controlled surface and the sample substrate. The heating plates are laterally separated from each other by a 2 mm air gap and can be controlled to 0.1 °C, allowing precise temperature gradients to be set up. The air gap is used to separate two heating plates and maintain a temperature gradient between them. The thermal stability of two heating plates is less than 0.1 °C. The samples were annealed in the chamber of hot stage without an inert gas. A stage lid with rubber sealing O-ring and a shallow pure silver heat shield covering the sample are used to prevent the airflow. Annealing blends at 160 °C for 10 min prior to any annealing step can heat the air in hot stage chamber to reduce the vertical temperature gradient. The temperature distribution between two heating plates was obtained by directly measuring the actual temperatures on the bare substrate using thermocouple. The results presented in Fig. 1(b) show the temperature profiles on the substrates between two heating plates are linear. The temperature at each observation position along the sample between two heating plates can be obtained from the fitting straight line in Fig. 1(b). The size of observed region on the sample is ca. 80 μm × 80 μm and much smaller as compared to the size of sample between the two plates of hot stage. The temperature variations at the observed regions are neglected and local temperatures at observed regions are considered to be homogeneous. The observed region on the

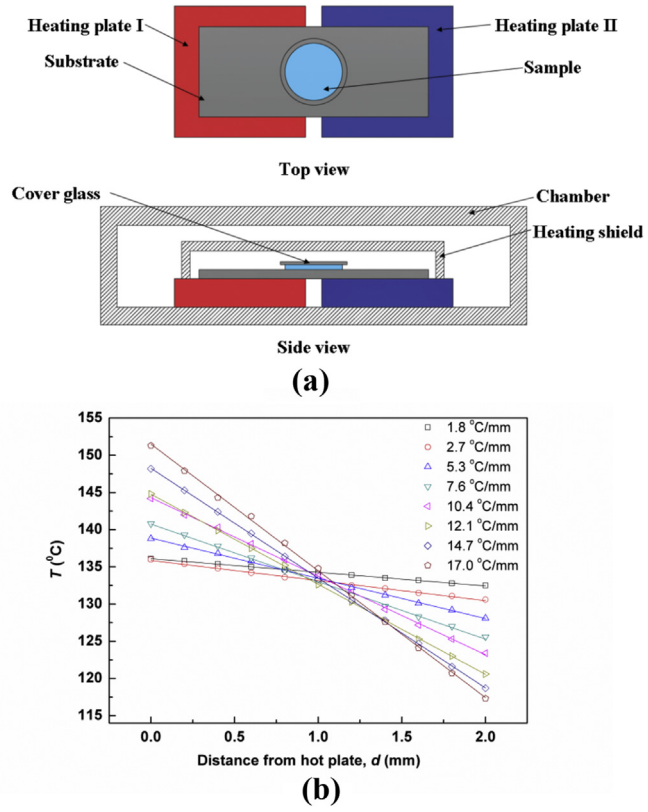


**Fig. 1.** (a) Schematic of the thermal gradient annealing system. The temperatures of plate I and plate II are controlled independently to form a temperature gradient. (b) The temperature distribution on the bare substrate sitting on the temperature gradient hot stage measured by thermocouple.

sample is away from the edges of the air gap, where the temperature gradient does not show significant influence on the orientation of the phase-separated domains. The parameters for generating all temperature gradients are listed in Table 1. The phase diagram of PEH/PEB blends has been determined previously [23], as shown in Fig. 2. The diagram exhibits an upper critical solution temperature with critical temperature of 146 °C at the composition of $\Phi_c = 0.44$ in melt. Also shown in the diagram is the equilibrium melting temperatures of blends determined by the Hoffman-Weeks extrapolation method. The $T_m o$ of blend decreases with increasing PEB concentration in one-phase regime, whereas $T_m o$ remains relatively constant in two-phase regime, at ca. 127 °C.

## 3. Results and discussion

As described in the previous studies [24,25], phase separation from the original homogeneous sample can be observed by PCOM and the bicontinuous and interconnected tubelike structure keeps on growing with annealing time, which is characteristic of the late stages of spinodal decomposition. The growth of the correlation length, $\xi$, between phase-separated domains can be predicted by the dynamic scaling hypothesis, $\xi \sim t^{\alpha}$. The growth exponent, $\alpha$, depends on the mechanism of domain coarsening. In the late stage of spinodal decomposition the amplitude of fluctuation reaches the equilibrium value and phase-separated structures have self-similarity. The growth exponent $\alpha$ of the correlation length of phase separated domains in the late stages is between 0.5 and 1.0. Our previous paper [22] has confirmed the power law slope of $\xi$ versus time for the zero temperature gradient film. For this PEH/PEB system, the coarsening mechanism-dependent growth exponent $\alpha$ on the whole annealing time scale remains invariant, ca. 0.62 and independent of temperature gradients. It indicates that the phase separation process under thermal gradient and homogenous temperature annealing (zero temperature gradient) is in the late stage of spinodal decomposition. The phase separation mechanism of late stage is the coarsening of microphase domains occurred by self-similarity. The hydrodynamic flow drives coarsening of phase-separated domains. First, we give an overview of our morphological development of PEH/PEB blends in the homogeneous temperature and temperature gradient fields. Fig. 3(a) shows the time evolution of the phase-separated structures for PEH/PEB blends annealed at 135 °C in the temperature gradient and homogeneous temperature fields. The corresponding digitized optical images and two-dimensional fast Fourier transform images are shown as insets in Fig. 3(a). For PEH/PEB blends annealed in the temperature gradient field, the optical microscopy images captured at the same in-plane spot, but different focus planes in the vertical direction are also included in Fig. 3(a) (center and bottom rows). Our results show that phase separation morphologies and the size of phase-separated domains captured at different focus planes do not change. The sample phase separates into the bicontinuous and interconnected tubelike structures, which is a characteristic of the late stage of spinodal decomposition. Annealing in a homogenous

**Table 1**
The parameters for generating temperature gradients.

| $\nabla T$ (°C/mm) | $T_{high}$ (°C) | $T_{low}$ (°C) |
|---|---|---|
| 1.8 | 136.1 | 132.5 |
| 2.7 | 136.0 | 130.6 |
| 5.3 | 138.8 | 128.1 |
| 7.6 | 140.8 | 125.6 |
| 10.4 | 144.2 | 123.4 |
| 12.1 | 144.8 | 120.6 |
| 14.7 | 148.2 | 118.7 |
| 17.0 | 151.3 | 117.3 |

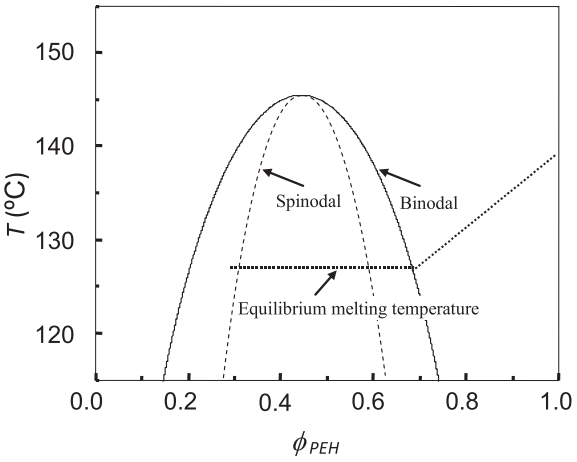


**Fig. 2.** Phase diagram of PEB/PEH blends based on Ref.23. The solid, dash and dot line correspond to the binodal temperature profile, spinodal line and equilibrium melting temperature profile, respectively.

temperature field yields a random spinodal demixing patterns. For PEH/PEB blends annealed at 135 °C under the temperature gradient of 5.3 °C/mm, however, the bicontinuous and interconnected tubelike structures are oriented parallel to the temperature gradient. The FFT images of phase-separated structures obtained by the thermal gradient annealing can be used to determine the orientation of bicontinuous and interconnected tubelike structures. As a reference case, a blend sample in which all the phase-separated domains are oriented randomly would generate a uniform so-called "spinodal ring" from the 2D FFT power spectra of the optical micrograph (see insets in Fig. 3(a)). An inspection of the FFT images shown in Fig. 3(a) indicates that the anisotropy of phase-separated domains exists during phase separation under temperature gradient field. These experimental results suggest that the anisotropy comes from the effect of the temperature gradient on the orientation of phase-separated structures of the blend. As the phase-separated domains gradually grow with annealing time, the bicontinuous and interconnected tubelike structures oriented parallel to the temperature gradient are predominantly observed. The orientation behavior of the phase-separated domains can be understood more precisely by an analysis of power spectra of the optical micrographs. The correlation length, $\xi$, can be obtained from the power spectra of the optical microscopy image of phase-separated structure. We can obtain the characteristic wave vector, $q^*$, from the peak in the FFT image. The correlation length is then evaluated from the relation, $\xi = 2\pi/q^*$. The FFT images of phase contrast micrographs obtained under the temperature gradient field exhibit an anisotropy with the reduced power spectra intensity at the azimuthal angle of 0° and enhanced intensity at the azimuthal angle of 90° (indicated in Fig. 3(a)). This enhanced and reduced intensity can be ascribed to the phase-separated domains that are aligned parallel to and perpendicular to the temperature gradient, respectively. To check for the effect of a temperature gradient on the correlation length of phase-separated domains along and normal to the temperature gradient direction, we compare the 1D power spectra at the azimuthal angles of 0° and 90° (Fig. 3(b) and (c)). Careful inspection of the locations of the peaks of 1D power spectra shows that the locations of peaks at the azimuthal angles of 0° and 90° are same. It indicates that the correlation lengths of phase-separated domains parallel to and perpendicular to the temperature gradient remains invariant under the thermal gradient annealing. For the phase-separated domains of the blend sample annealed under homogeneous temperature field the intensities of peaks of 1D power spectra at the azimuthal angles of 0° and 90° are almost identical. The

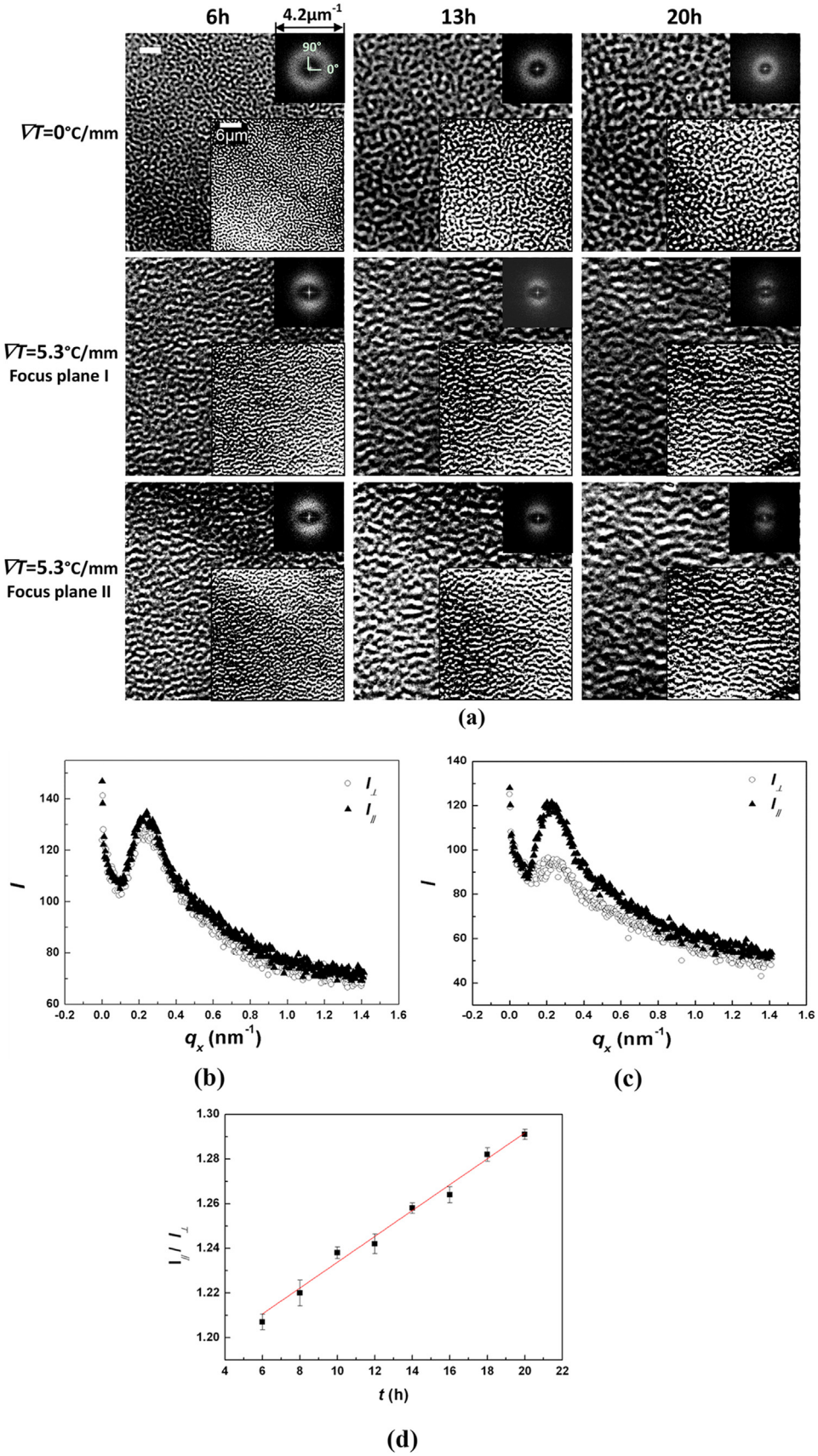


**Fig. 3.** (a) The phase contrast optical micrographs of PEH/PEB blends annealed at 135 °C for 6 h, 13 h and 20 h at 0 °C/mm (top row) and 5.3 °C/mm (center and bottom rows). The 1D power spectra intensity of the optical micrograph of sample annealed at 0 °C/mm (b) and 5.3 °C/mm (c) for 13 h at the azimuthal angles of 0° and 90°. (d) Plot of $I_{//}/I_{\perp}$ as a function of phase separation times. The direction of the temperature gradient is indicated by the arrow. The scale bar corresponds to 10 μm and applies to all images. The error bars are based upon the standard deviation of replicate optical images and fresh samples are used for each of independent experiments to avoid the effect of thermal history.

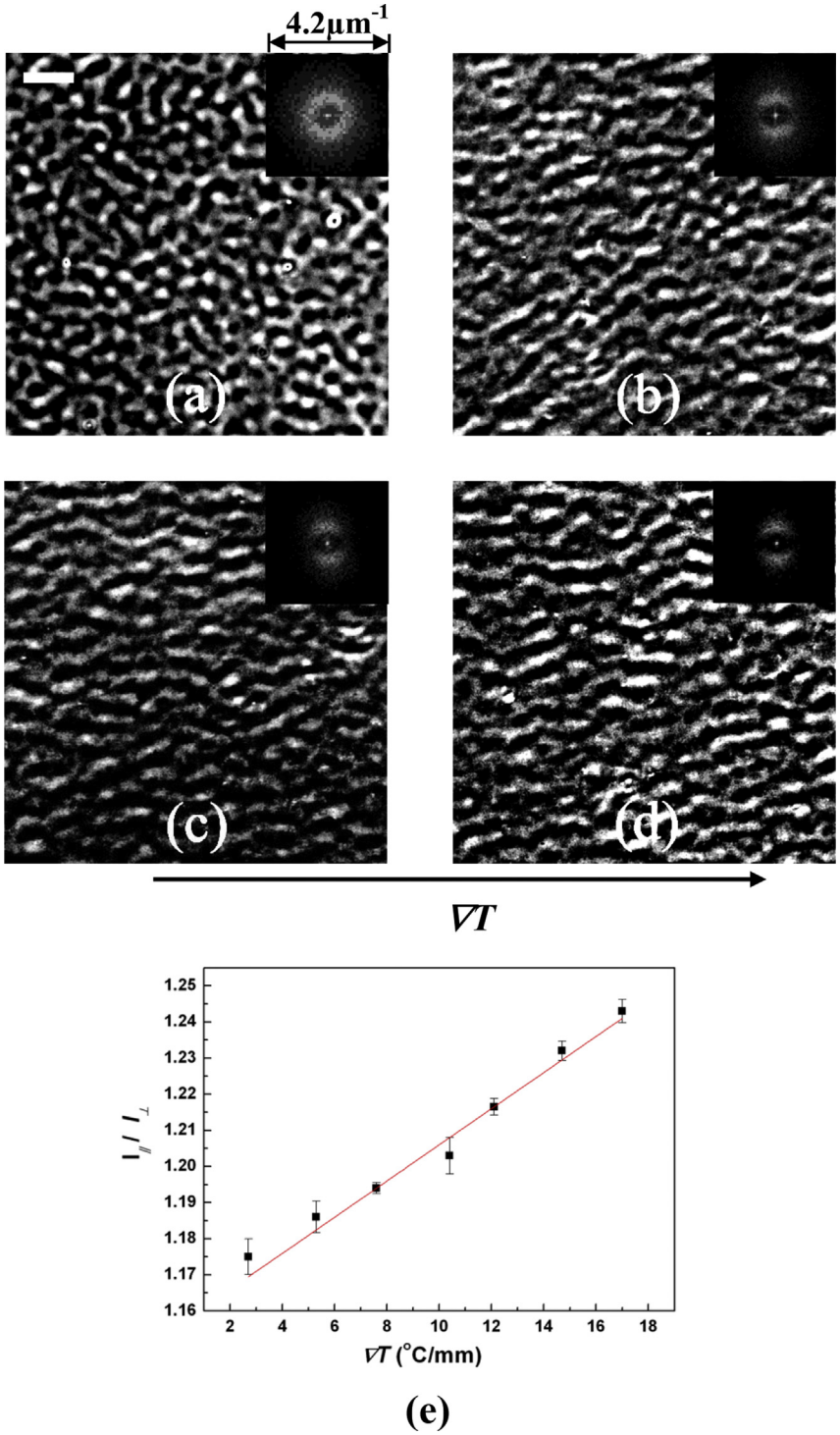


**Fig. 4.** The phase contrast optical micrographs of PEH/PEB blends annealed at 135 °C under the temperature gradients of (a) 0 °C/mm, (b) 2.7 °C/mm, (c) 7.6 °C/mm and (d) 14.7 °C/mm. (e) Plot of $I_{//}/I_{\perp}$ as a function of temperature gradient. The direction of the temperature gradient is indicated by the arrow. The PEH/PEB blends were first annealed at 135 °C for 13 h under the temperature gradient of 2.7 °C/mm. After that, the samples were further annealed at $\nabla T$ ranging from 2.7 °C/mm to 17 °C/mm for 15 min. The scale bar corresponds to 10 μm and applies to all images.

asymmetry of 2D power spectra indicates the phase-separated domains oriented along the temperature gradient direction. The strength of power spectra intensity from phase-separated domains along the direction of the temperature gradient, $I_{//}$, relative to the intensity from phase-separated domains normal to temperature gradient, $I_{\perp}$, slightly increases with phase separation time (Fig. 3(d)). The ratio of the intensities between $I_{//}$ and $I_{\perp}$ provides a measure of the anisotropy of phase-separated domains. The rate of change of anisotropic intensity with phase separation time is the slope of the curve. In Fig. 3(d), the slope of the curve is 0.006. Our observations clearly suggest that this anisotropy gradually increases with phase separation time.

We also observe that $I_{//}/I_{\perp}$ is temperature gradient dependent. To quantify the $\nabla T$ dependence of orientation of the phase-

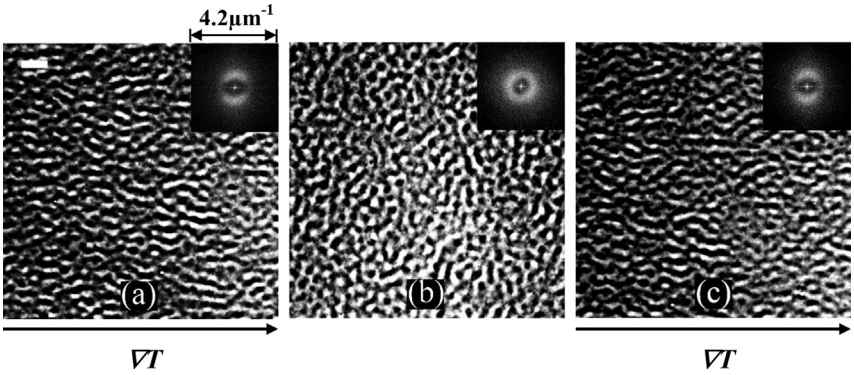


**Fig. 5.** The phase contrast optical micrographs of PEH/PEB blends annealed at 135 °C under temperature gradient (a, c) and homogenous temperature field (b). The direction of the temperature gradient is indicated by the arrow. The temperature gradient is 5.3 °C/mm. The scale bar corresponds to 10 μm and applies to all images.

separated domains, the PEH/PEB blends were annealed at 135 °C for 13 h under the temperature gradients from 0 °C/mm to 17 °C/mm. We previously studied the effect of temperature gradient on kinetics of phase separation via spinodal decomposition in the PEH/PEB blends [22]. Within the two-phase regime of phase diagram, the thermal gradient considerably changes the phase separation process and greatly accelerated domain growth through the enhancement in concentration fluctuation in the early and intermediate stages. As temperature gradient is gradually increased, the correlation lengths of bicontinuous phase-separated domains increase. At the same annealing time, the sample annealed under higher temperature gradient field has the larger phase-separated domain size. In our system, the temperature gradient leads to the reorganization of bicontinuous and interconnected tubelike structure parallel to the temperature gradient direction. The orientation involves only the large length-scale rearrangement of phase-separated domains. In order to avoid the influences of the size of phase-separated domains obtained in the different temperature gradients and also avoid the bicontinuous and interconnected tubelike structures to coalesce to the very "late" stage of LLPS during the long time annealing under the relatively high temperature gradient, we subjected the PEH/PEB blends to a long thermal annealing process (13 h) in a shallow temperature gradient field so that the sizes of phase-separated domains of PEH/PEB blends are same. After that we varied the temperature gradients to investigate the response of orientation of phase-separated domains to the externally applied perturbations. The representative phase contrast optical microscopy images of the samples annealed under the different temperature gradients are shown in Fig. 4. The scattering patterns obtained numerically by 2D FFT of phase contrast micrographs are indicated in Fig. 4 as insets. For the sample annealed under temperature gradient field there exists the anisotropy for the phase-separated structures as revealed by the 2D FFT. The optical micrographs also show that the orientations of phase-separated domains are not random and the bicontinuous and interconnected tubelike structures are oriented parallel to the direction of temperature gradient. The formation of the anisotropic morphology under the temperature gradient field appears to be a general phenomenon in our systems. In order to quantify the domain orientation of the blend, we measure the intensities of peaks in 1D power spectra at the azimuthal angles of 0° and 90°. The ratio of the intensities between $I_{//}$ and $I_{\perp}$ is shown in Fig. 4(e). A slight increasing in $I_{//}/I_{\perp}$ with $\nabla T$ is observed. The rate of change of intensity anisotropy with temperature gradient (the slope) at late stage for Fig. 4(e) is 0.005. It indicates that this anisotropy gradually increases with temperature gradients.

We next take a closer look at the response of orientation of phase-separated domains to the temperature gradient. In this experiment the PEH/PEB blend was first annealed at 135 °C for 13 h at the temperature gradient of 5.3 °C/mm (Fig. 5(a)). The phase separation of PEH/PEB blend under temperature gradient field leads to an anisotropic morphology of bicontinuous and interconnected tubelike structures. As the temperature gradient is set to zero, the anisotropy of phase-separated domains disappears and the distribution of domain orientations suddenly becomes random, as illustrated in Fig. 5(b). The isotropy of "spinodal ring" of FFT image indicates the random distribution of the bicontinuous and interconnected tubelike structures. After that, the temperatures of two heating plates of hot stage are reset to be different values (138.8 °C, 128.1 °C), a temperature gradient generates along the sample. The temperature at the observed region on sample is kept at 135 °C. The preferential alignment of bicontinuous and interconnected tubelike structures are recovered as evidenced by the FFT image in Fig. 5(c). The bicontinuous and interconnected tubelike structures exhibit a preferred orientation along the temperature gradient direction. The impact of the temperature gradient is apparently similar to observations on the preferentially aligned patterns in the block copolymer film under the temperature gradient annealing, where the direction of the temperature gradient acts to select a preferred orientation of the mesophases [26]. In our system, the orientation involves only the large length-scale rearrangement of phase-separated domains. The temperature gradient leads to the reorganization of bicontinuous and interconnected tubelike structure from random to parallel to the temperature gradient direction.

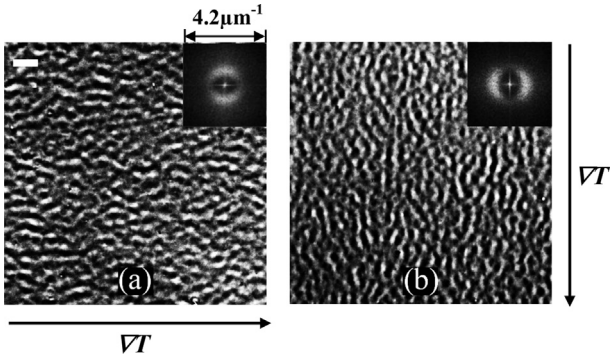


**Fig. 6.** The phase contrast optical micrographs of PEH/PEB blends annealed at 135 °C for 13 h under temperature gradient field. The direction of the temperature gradient is indicated by the arrow. The temperature gradient is 5.3 °C/mm. The scale bar corresponds to 10 μm and applies to all images.

We also address the morphology variation with the direction of temperature gradient. Subjecting the blend film to thermal gradient annealing at the temperature of 135 °C for 13 h causes the phase-separated domains oriented along the temperature gradient direction (Fig. 6(a)). By changing the direction of the temperature gradient field, we then expect to see an orientation variation of phase-separated domains. We rotated the temperature gradient field 90° with respect to original direction in order to examine the response of domain orientation to external filed. The result is shown in Fig. 6(b), which corresponds to the same spot in the sample as Fig. 6(a), except for the change in direction of temperature gradient. After changing the direction of temperature gradient field to perpendicular to the initial temperature gradient, the orientation of phase-separated domains immediately switches to parallel to the temperature gradient accordingly (Fig. 6(b)). It is really surprising that these phase-separated domains are reoriented parallel to the direction of temperature gradient in such a short time (less than 30 s). We also investigated the response time of re-orientation or disordering of phase-separated domains to the temperature gradient using the blends pre-annealed in a temperature gradient field for 6 h, 9 h and 15 h (images not shown). The response times of re-orientation or disordering of phase-separated domains of the blends pre-annealed at different times to the temperature gradient field did not show significant change.

In addition to the phase separation time and temperature gradient, the influence of the annealing temperature was addressed (see Fig. 7). As mentioned in the experimental section, the observed region on the sample is away from the edges of the air gap. Our recent measurements show that the phase-separated domains of the sample near the edges of the air gap do not show obvious preferential alignment along the temperature gradient [22]. The $I_{//}/I_{\perp}$ values for the samples annealed in the $T$ range of our measurements remain constant at 1.14 ± 0.003, 1.16 ± 0.004 and 1.22 ± 0.007 for 1.8 °C/mm, 2.7 °C/mm and 5.3 °C/mm, respectively. It indicates the phase separation temperature does not influence the orientation of phase-separated domains.

What factors control the orientation of the phase-separated domains under temperature gradient field? We then consider some of the basic phenomenological characteristics of these spinodal demixing patterns. This orientation behavior of phase-separated domains is somewhat similar to the measured orientation of phase-separating fluids under steady shear [11,12], suggesting one possible physical explanation. There are many interesting and complicated physical effects associated with the orienting process of phase-separated structures actually interacting directly with the shear field. Hashimoto et al. [12] investigated the detailed morphology of phase-separating fluids under shear. A string-like phase-separated structures oriented parallel to the shear field direction was observed. For the polymer blend system, under a shear flow field the phase-separated domains might respond like rigid rods, aligning with the flow direction [11]. Upon considering the matter, it is entirely possible that in the presence of a temperature gradient a “thermal force” acting like a shear force might exist in the blend system. Thus, there is a need for a greater consideration of the nature of the temperature gradient. The Soret effect (thermal diffusion) is a phenomenon observed in fluid mixtures where different species exhibit different responses to a temperature gradient [27,28]. Due to the Soret effect, a temperature gradient can cause all species in the mixture to become activated and move. In the presence of a thermal gradient, macromolecular solutes or single-phase drop-like structures tend to migrate along the temperature gradient [29,30]. In a polymer blend system undergoing phase separation via spinodal decomposition, the thermal diffusion plays an important role in the presence of inhomogeneous temperature distributions. As pointed out before by Eslamian [28], the temperature gradient can work as a thermal driving force for mass flow. The spatial temperature variation can lead to a spatial force in a blend system with a conserved order parameter [16]. The spatial force is caused by an interplay of the temperature variation and thermal diffusion. The thermal diffusion plays a crucial role in generating the spatial force in the phase separating systems. Once a thermal gradient field switches on, it immediately exerts thermal forces on all species in the mixture. The “thermal force” causes the rearrangement of the phase-separated domains. The “thermal force” exists in a material whenever temperature gradient is present and drives the phase-separated domains oriented along temperature gradient direction. This probably explains the orientation behavior of phase-separated domains along temperature gradient direction. After phase separation of PEH/PEB blend at 135 °C, the viscosities of PEH-rich and PEB-rich domains are on the same order and very close to each other. The small viscosity difference between co-existing phases might not drive the alignment of phase-separated domains.

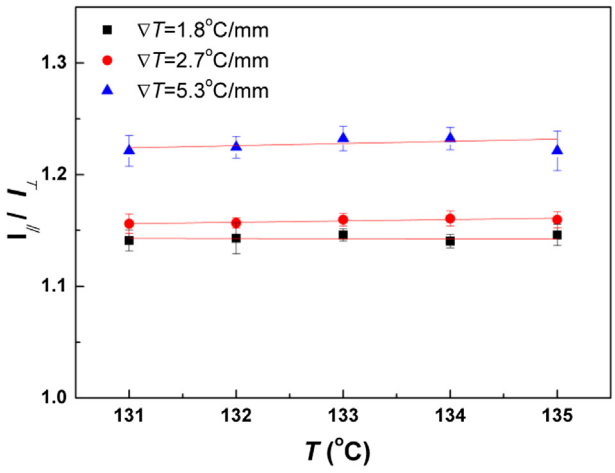


**Fig. 7.** Plot of $I_{//}/I_{\perp}$ as a function of the annealing temperature. The PEH/PEB blends were annealed at different temperatures for 9 h under the temperature gradients of 1.8 °C/mm, 2.7 °C/mm and 5.3 °C/mm.

Taken together, these results suggest that static in-plane thermal gradients can lead to a preferential alignment of phase-separated structures in polymer blend system, and that gradients of higher magnitude have greater effects. The mechanism by which this occurs is not immediately obvious, although it may be related to the Soret effect [26,31], or to forces generated by phonons traveling along the gradient [32,33]. Establishing a connection between the mesoscale dynamics, and fundamental molecular-scale physical effects, is an exciting area for future research.

## 4. Conclusion

By using the phase-contrast optical microscopy and digital image analysis, we investigate the orientation behavior of phase-separated domains in a temperature gradient field. The PEH/PEB blend exhibits the inhomogeneous phase-separated structures, indicating the temperature gradient has influenced the orientation of phase-separated domains. A preferential alignment of phase-separated domains is observed by phase contrast optical microscopy in the presence of a temperature gradient. The ratio of the intensities between $I_{//}$ and $I_{\perp}$, providing a measure of the anisotropy of phase-separated domains slightly increases with growth of phase-separated domains and temperature gradients. We have further found that the orientation of phase-separated domains responds to the changes in the direction of temperature gradient

in a very short time. It is possible that the temperature gradient can be used to manipulate the spinodal decomposition patterns in the two-phase region of phase diagram. The orientation of phase-separated domains along the temperature gradient direction probably arises from the "thermal force" induced by the temperature inhomogeneity. An understanding of the methods of manipulating the orientation of the phase-separated domains in the polymer blend system by temperature gradients is important as a means of producing oriented materials of practical use and understanding the orientation process of these materials. The experiments also give an insight into the strategy for the morphology control of multiphase polymer materials during processing.

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