

博士論文

Nanoscale periodic patterning in polymer blends via epitaxial
crystallization directed by solvent crystallization

(溶媒結晶化により誘導されるエピタキシャル結晶化を利用したポ
リマーブレンドのナノ周期構造形成)

張 鑫

Chapter 1. Introduction

Creating nanostructures via bottom-up assembly of molecules has been attracting increasing interest in various fields of applications. Most studies on creating nanopatterns using self-organization of polymers have focused on block copolymers. Covalently linked two blocks in a block copolymer tend to segregate into different domains due to their mutual repulsion, followed by the formation of thermodynamically stable nanostructures. Micropatterning has also been tried using polymer blends, as they have more potential on polymer variety and simpler sample preparation process, which is especially attractive for industrial applications. By external confinements during phase separation which is induced by functionalized substrate for example, directional orientations have been realized. However, the patterns obtained so far are all in micrometer or larger scale, and the nanopatterns are not yet realized.

Feasible nanopatterning in polymer blends was first achieved by our group via epitaxial crystallization of crystalline polymer onto crystallizable solvent^[1]. In this process, quick directional solidification restricts the phase separation between the component polymers to a nanometer scale. The epitaxial crystallization of the crystalline polymer on a crystallizable solvent generates oriented lamellae of the crystals, resulting in directional periodic nanopatterns. Comparing with other nanopatterning strategies, it has the advantages on polymer variety and changeable component. However, many issues on the formation mechanism, pattern structures and processing parameters are still unclear. Moreover, extensions on applications such as reproducibility, large patterned area, changeable component and polymer variety are highly required to be further discussed. To achieve progresses on these issues, vast investigations on preparation and characterization of patterned films from various pairs of blends have been performed in my work. The scope of my Ph.D. project includes fundamental mechanism (*e.g.* pattern evolution, pattern structure, as well as effects of processing parameters on the patterns), and the demonstration of key aspects for potential applications (*e.g.* the enlargement of pattern area). Throughout the following three chapters, I will show that my methodology is feasible and easy with considerable potential on polymer variety and periodicity control.

Chapter 2. Effects of processing parameters on the nanopatterns of poly(L-lactic acid) (PLLA) /poly(vinylphenol) (PVPh) blends

In this chapter, blends composed by crystalline PLLA and amorphous PVPh were employed. This blend is partially miscible. PLLA is known to epitaxially crystallize on hexamethylbenzene (HMB) crystals. Crystallinity of PLLA is influenced by PVPh content and sensitive to thermal conditions due to the hydrogen bonds between the hydroxyl group of PVPh and the carbonyl group of PLLA. The intermolecular force reduces the crystallizability of PLLA, which helps us study the influence of

the crystallization process on the formation and control of nanopatterns.

The patterning process is briefly depicted as following. Patterning began with a homogenous solution composed of PLLA, PVPh and HMB at 200 °C. A temperature gradient from 200 °C to r.t. was applied to induce the crystallization of HMB. The direction of HMB crystal growth was parallel to the direction of temperature gradient. At the growing front of HMB crystals, the polymer concentration concomitantly increased and finally reached saturation, followed by solidification of polymers. The embryos of lamellar pattern are produced through epitaxy between PLLA and HMB and tend to assemble parallel to *b* axis of HMB. Then, epitaxial crystallization of PLLA further proceeds onto HMB with its *c* axis vertical to the (001) face of HMB. The phase separation between PLLA and PVPh during the solidification is frozen and kinetically trapped within a very short time, forming nanometer scaled amorphous domains and embryos of PLLA epitaxial crystals. The subsequent isothermal annealing induces further growth of PLLA embryos into crystalline lamellae, giving clear and well-ordered nanopatterns.

Through the patterning process above, clear lamellar nanopatterns in PLLA/PVPh blends were formed. The crystalline and amorphous domains in the patterned films can be distinguished by AFM images. The bright domains in the height images, which correspond to the dark domains in the phase images, represent the PLLA crystalline domains.

Well-aligned patterns with monodispersed periodicity could be fabricated in PLLA/PVPh with optimized blend compositions of 8/2 and 7/3. For pure PLLA, as driving force of phase separation was absent, the grown lamellae were unequal in width, resulting in the irregular periodicity. This result suggests that the phase separation induced by the presence of PVPh during the directional solidification is necessary for well-ordered lamellar patterns. At PVPh contents over 50 wt %, aligned lamellar patterns were absent. The absence of ordered nanopatterns is due to the reduction of the PLLA crystallinity caused by the intermolecular hydrogen bonding with PVPh.

The sample prepared without annealing after the directional solidification had only the crystalline embryos in a halfway to grow into elongated lamellae with lower degree of alignment. With increasing annealing time, the periodic morphologies of the patterns were evolving gradually, indicating that evolution into sharper and well-ordered nanopattern requires a certain period of thermal annealing time. This period of time would be necessary to complete the epitaxial crystallization of PLLA accompanying with phase segregation between crystalline and amorphous domains.

Samples under different annealing temperatures require different time periods to complete epitaxial crystallization for lamellar pattern formation. 8/2 samples annealed at 80 °C exhibited a gradual formation of patterns from 0 to 60 min, while the samples annealed at 100 °C did not show any substantial changes of the morphology after 30 min, indicating the faster formation of the periodic patterns at this temperature than at 80 °C. The temperature dependence of the kinetics of lamellar evolution in the thin films is in agreement with the temperature dependence of the spherulite growth rate of the blends.

At 120 °C, however, longer annealing time led to slight deformation of patterns in the 8/2 blend. Moreover, the area of defects increased substantially with increasing PVPh content. These results indicate that the thermal motions of amorphous domains may compete with epitaxial crystal growth of PLLA at high annealing temperature.

Polymer ratio and annealing temperature influence on the periodicity of patterns. Compared with the 8/2 films, the periodicity in the 7/3 films is wider. This can be attributed to the higher volume of amorphous parts, which enlarges the distance between crystalline domains. Compared with the samples annealed at 80 °C, the samples annealed at 100 °C exhibit wider periodicity. As mentioned above that PLLA crystals grow faster at 100 °C than at 80 °C, the wider periodicity for the blend at 100 °C annealing suggests further phase segregation between crystalline and amorphous domains at 100 °C than at 80 °C.

Chapter 3. Selective removal of one component from patterned PLLA/polybutene (PB)

In this chapter, the nanostructures of crystalline domains were further investigated by selective removal of amorphous PB from the patterned PLLA/PB blend films. Patterning process was the same with chapter 2. Cyclohexane (CyH), known as good solvent for PB but poor solvent for PLLA, was used for selective solvent extraction of the patterned films.

Before and after the removal of PB, the periodicity of patterns did not change, suggesting that crystalline PLLA domains were not affected by the CyH wash. However, the depth of patterns increased, as PB which had composed the main part of amorphous domains was etched. These results directly prove that amorphous PB domains are trapped between crystalline PLLA domains.

By removing PB, the morphology of PLLA crystalline domain was clearly revealed. The crystals of PLLA exhibited hierarchical lamellar structures, with daughter lamellae aligning inside a parent lamella perpendicularly to the parent lamella. The presence of the daughter lamellae was confirmed at various blending ratios and annealing temperatures, while they were absent in the quenched samples. The encouraged formation of daughter lamellae during isothermal annealing indicates that they should be considered as crystalline domains of PLLA.

The growth of the patterned structure is affected by annealing temperature. Compared with 80 °C, the daughter lamellae grew longer at 100 °C, resulting in a wider periodicity of parent lamellae. This result also agrees with the statistic results PLLA/PVPh blend, where annealing at 100 °C led to the wider periodicity of parent lamellae than at 80 °C, indicating the influence of annealing temperature on pattern periodicity. Compared with the 8/2 blend, the 5/5 blend annealed at the same condition exhibited shorter length of the daughter lamellae. These results give insight into the formation mechanism of crystalline domains. First, embryos of PLLA crystals are formed on the freshly grown HMB crystals during solidification of polymers. During the subsequent annealing process, these embryos grow as the daughter lamellae via epitaxial crystallization onto HMB with the direction perpendicular to HMB extending direction. Daughter lamellae with a certain length in a line further

assemble as a parent lamella, whose width also represents the length of daughter lamellae inside. The length of daughter lamellae is affected by annealing temperature and blending ratio.

Chapter 4. Precise control of patterning direction in large area using guided crystallization of HMB

The precise control of patterning direction in large area is pivotal for various applications. In this chapter, large scale (centimeter scale) nanopatterns were realized by using a trenched substrate which precisely regulated the orientation of HMB crystals during their growth.

First, I investigated the guiding effects of the line spacing of trenches (the width of the trenches) on the orientation of HMB crystals, confirming that 5 and 10 μm were the optimum. Then, the polymer blends were patterned on the HMB crystals prepared by using this optimum substrate. The 8/2 PLLA/PB blend was firstly investigated. Patterning process was the same with chapter 2 and 3. AFM images of several positions show that all the lamellae in these positions oriented in the same direction, indicating the nanopatterns have seamlessly extended into a centimeter scale. Enlarged images of these spots further confirm the well-ordered morphology and relatively monodispersed periodicities of lamellae.

Favorable interaction between polymer and substrate is not necessary in this strategy. Various polymer blends, including miscible and immiscible pairs, can be applied.

Chapter 5. Conclusions

Significant insights and progresses on the polymer blend nanopatterning were achieved by detailed investigations on the formation of patterns (pattern morphology, periodicity, and depth) and key processing parameters (polymer ratio and annealing conditions) in immiscible blends and blends having relatively strong intermolecular force. The results do not describe only the morphology, size, and distribution of patterns with details but also reveal the underline mechanism of pattern evolution and the effects of polymer interactions. These conclusions help us optimize patterning conditions and control the morphology as well as the size of nanopatterns. Moreover, the success on enlarged nanopatterns into centimeter scale by simply using a trenched substrate shows great potential on both scientific study of nanopatterning via polymer blends and state-of-the-art applications in near further.

References

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