Macromolecules **2007,** *40,* 6445−6447

Nanostructured Thin Films of Polymer Blends by Directional Crystallization onto Crystallizable Organic Solvent

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Received May 23, 2007

Revised Manuscript Received July 12, 2007

Creating nanostructures via bottom-up assembly of molecules is attracting increasing interest in various fields of application. In particular, the nanometer-scale patterns given by self-assembled polymers are drawing extensive attention due to the relative ease of implementation and low cost compared with top-down methods.[1] In addition, bottom-up fabrication techniques have potential to provide access to a length scale that is not available by traditional optical lithography.[2] Therefore, periodic nanopatterns achieved by polymer self-organization take focus not only for fundamental science, but also for many emerging applications, such as nanochannels,[3] nanoparticle deposits,[4,5] nanolithographic masks for further etching,[6] and templates for the fabrication of nanodot[7] and nanowire arrays.[8]

Until now, in order to orient the microdomains of polymers and create well-ordered nanoarrays, various approaches have been examined (solution casting,[9] shear fields,[10] electric fields,[11] temperature gradients,[12] patterned substrates,[13] modification of base top,[14,15] and directional crystallization[16−21]). 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. However, in the synthetic process of block copolymers, monomers are often limited to those having no functional groups, since functional groups could react with propagating active-end anions to terminate the living polymerization.

As a method to overcome this limitation, we have employed directional crystallization of crystalline/amorphous miscible polymer blends onto crystallizable solvents. Polymer blends are just simple mixtures of two polymers without covalent bonds between them. Normally, an immiscible polymer blend tends to separate into large domain and is hardly used for patterning in nanoscale order. However, we show here that the use of phase segregation in a miscible blend upon rapid directional crystallization can make it possible to create nanoscale order in a thin film of crystalline/amorphous polymer blends.

Patterning with polymer blends, as we report in this Communication, may offer more versatile choices of polymer components including those having functional groups and easier ways to implement further selective chemical modification of the nanopatterned polymer templates when compared to traditional block copolymer lithography.

In order to demonstrate the development of periodic nanopatterns with polymer blends, we selected poly(L-lactic acid) (PLLA) as a blend component. PLLA is an aliphatic polyester useful for the preparation of nanopatterned templates attributed to the ease of degradation of ester groups.[22] Topographical patterns would be obtained readily by selective hydrolysis of PLLA from the nanoarrayed polymer blends. Additionally, PLLA is a biocompatible and environmentally conscious material, which is regarded as a promising candidate for increasing number of applications such as drug delivery systems (DDS),[23] and in vivo nanodevices. PLLA is known to be miscible with poly(3-hydroxybutyrate)(PHB),[24] poly(methyl methacrylate)(PMMA),[25] poly(vinyl acetate)(PVAc),[26,27] poly(vinylphenol)(PVPh),[28] and poly(ethylene glycol)(PEG).[29,30] We employ PVAc here as a blend partner of PLLA. Miscibility between PVAc and PLLA is kept over the entire composition range.[26] PVAc is a good candidate for a polymeric gate insulator in the organic thin film transistors.[31]

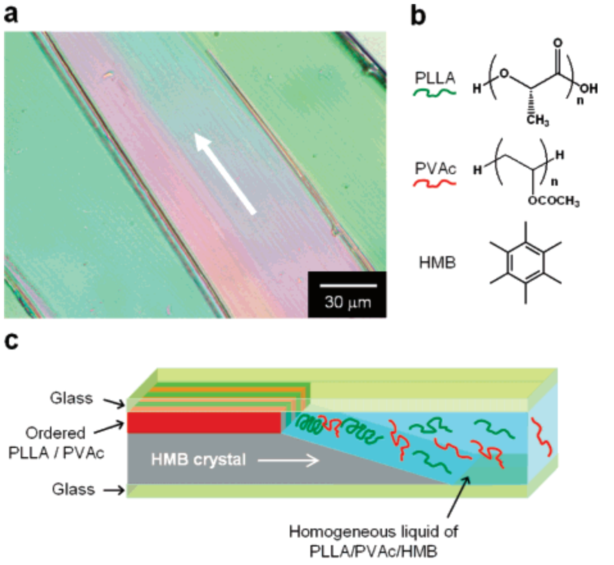

Figure 1. (a) Polarized optical microscope image of directionally crystallized HMB crystals. Various colors are caused by difference in thickness of HMB crystals. (b) Chemical structures of PLLA, PVAc, and HMB. (c) Schematic illustration of directional crystallization of the polymer blend. Solvents for polymers turn into crystals, and the polymer concentration increases simultaneously. Then, PLLA segregates from the blend and directionally crystallizes onto freshly formed HMB crystals.

In this study, directional crystallization of polymer blends was performed by a method similar to the one that De Rosa and co-workers[16−19] applied for block copolymers. First, we prepared thin films of PLLA/PVAc blends on glass coverslips (18 × 18 mm) by spin-coating from dilute chloroform solution (1 wt %) at spin rate of 2000 rpm. PLLA and PVAc were obtained from commercial sources; PLLA ($M_n = 91\,000$ g/mol, PDI = 1.58, kindly gifted from Mitsui Chemical) and PVAc ($M_w = 113\,000$ g/mol, Aldrich). Melting temperature (T_m) of PLLA, glass transition temperature (T_g) of PLLA and T_g of PVAc were 168, 63, and 38 °C from DSC, respectively. As a crystallizable solvent, hexamethylbenzene[32] (HMB) was selected. Crystalline HMB (Tokyo Kasei Kogyo) powders were spread over a glass slide (several tens of milligrams), and the coverslip with the polymer thin film (approximately 10 μg) was placed polymer side down on the HMB powders. Then the glass slide was put on a hot plate at 180 °C to melt HMB. The molten HMB dissolved the polymer thin films and a homogeneous solution was formed between two glasses. Then, the sample was rapidly transferred to another hot stage equilibrated at 80

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10.1021/ma0711543 CCC: $37.00

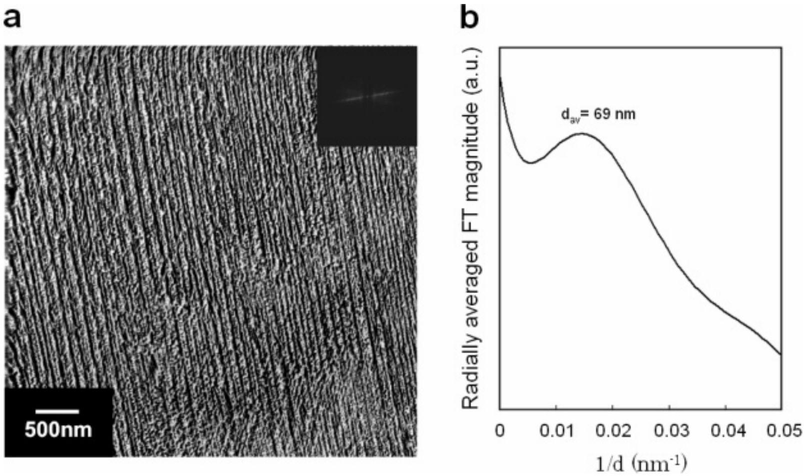

Figure 2. Well-ordered thin films of PLLA/PVAc. (a) An AFM phase image of the thin film of PLLA/PVAc 80/20 blend that is directionally crystallized onto HMB at 80 °C. Well-ordered lamellae are visible over the large area (5 μm × 5 μm). Inset shows the Fourier transform (FT) pattern of the AFM image. (b) Radially averaged magnitudes of the FT pattern of part a.

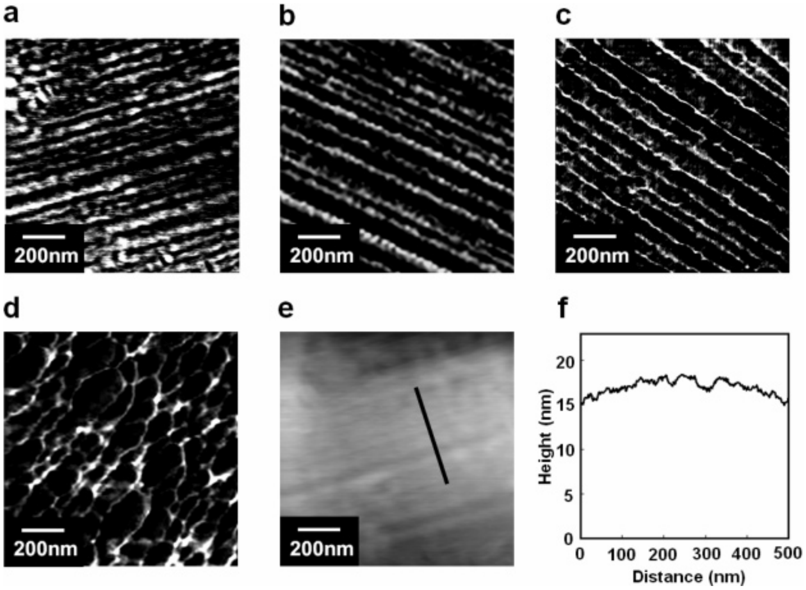

Figure 3. Higher magnified AFM phase and height images of thin films of PLLA/PVAc blends that were directionally crystallized onto HMB: (a) phase = PLLA/PVAc 80/20; (b) phase = PLLA/PVAc 60/40; (c) phase = PLLA/PVAc 40/60; (d) phase = PLLA/PVAc 20/80; (e) height = the same area as the phase image of part a. (f) height profile of part e.

°C. Rapid crystallization of HMB resulted in large, elongated crystals (Figure 1a). As the directional crystallization of HMB proceeds, the polymer concentration in the solution increases. Eventually, the polymer could not be dissolved any longer and began to crystallize directionally onto freshly formed HMB crystals (Figure 1c). The sample was kept at 80 °C for 1 h to complete the crystallization of PLLA. This sample was fractured open with razor blade. Cleavage was easily occurred at a HMB crystal plane. After sublimation of HMB, flat surface of the polymer blend film was obtained. The surface of the film was observed with atomic force microscopy (AFM, JEOL JSPM-4200).

A tapping mode AFM phase image of a thin film of PLLA/PVAc directionally crystallized onto HMB is shown in Figure 2a. Well-aligned lamellae over the large area are observed. Even on μm scale, the crystals form axiallite structure. On the contrary, usual spherulitic crystalline morphology was observed when the polymers had been crystallized without HMB (data not shown). From the radially averaged magnitudes (Figure 2b) of 2-D Fourier transform pattern of the AFM phase image, average spacing between lamellae was 69 nm.

We next examined the effect of the blend composition on the morphology. Higher magnification AFM phase images of various compositions are shown in Figure 3. In the phase images, soft amorphous layers and hard crystalline layers appear dark and bright, respectively. From these images, it is obvious that the amorphous layers become thicker with the increase of the noncrystalline-PVAc content. When the PVAc content reaches 80%, parallel lamellar orientation are broken into deformed honeycomb morphology. These results indicate that PVAc is located in the interlamellar regions after directional crystallization of PLLA, and the crystallization of PLLA is the key event in the ordered nanostructure formation. Ho et al. also showed crystallization of PLLA is the key process when forming the oriented nanostructures from PLLA-*b*-PS.[20] In PLLA/PVAc 80/20 thin film, the thickness of the crystalline layer is 30−50 nm (Figure 3a). With the increase in the PVAc content to 60%, the thickness of the crystalline layer decreases to 15 nm, coming along with the thickening of the noncrystallin layer to 50−100 nm (Figure 3c). Since the thickness of the crystalline layer of PLLA/PVAc (80/20) was approximately 30−50 nm, the crystalline layer consists of a stack of lamellae rather than a single lamella. Because of the flatness of HMB crystals, the surface of the polymer blend films was also very flat (Figure 3e,f).

The underlying mechanism of the morphological evolution of the PLLA/PVAc/HMB blend system can be explained as follows. Primary, the PLLA/PVAc/HMB system forms miscible melt. By placing the material on a hot plate equilibrated at 80 °C, HMB first starts to crystallize directionally into large flat crystals (Figure 1a) and then, PLLA starts to crystallize directionally onto the freshly formed HMB crystals. Through the directional crystallization of PLLA, phase segregation of crystalline PLLA from noncrystalline PVAc occurs. Therefore, alternate lamellae of crystalline and amorphous regions in nanoscale order are achieved.

Directional crystallization onto the aromatic coumpounds had been well studied for homopolymers by Wittmann and Lotz.[33] After De Rosa et al.[16] had successfully obtained ordered nanostructures in thin films of strongly segregated PS-*b*-PE block copolymer by applying directional solidification, they also showed that PE-*b*-PEP-*b*-PE triblock copolymer gave well ordered alternate lamellae of crystalline and amorphous regions, regardless of its miscibility in the melt, due to phase segregation during epitaxial crystallization.[17] More recently, Ho et al.[20] showed that microdomains of weakly segregated low-molecular-weight PS-*b*-PLLA were also well aligned as well as strongly segregated high-molecular-weight PS-*b*-PLLA, due to directional crystallization of PLLA component. Though our achievement is similar to these results in using crystallization-induced orientation, it should be emphasized that we first show that the covalent bond between two blocks in block copolymers is not always necessary for nanopatterning.

In the case of block copolymers, phase separation is limited by the covalent bond between the two blocks. Hence, the ordered morphologies of the block copolymers correspond to the thermodynamically stable structures. On the other hand, in polymer blends, ordered nanostructure is not the thermodynamically stable structure. Therefore, regulation of the progress of phase separation is required. We show here that directional crystallization of miscible polymer blends is an ideal method to preserve the ordered morphology during the processing stage in thin films.

In summary, we have demonstrated lamellar orientation by using directional crystallization of a crystalline−amorphous miscible polymer blends. To the best of our knowledge, this is the first report to make a well-ordered nanostructure over hundreds of square micrometers in polymer blend thin film. We also showed amorphous layer thickness is tunable to some extent by changing the composition of polymer blend. The power of using polymer blends, when compared to traditional block copolymers, is the ability to skip the synthesis of the block copolymer. Thus, this methodology would be a facile, efficient way to produce lamellar orientation in thin films that hold promise in the fabrication of nanostructural materials.

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MA0711543