Large Area Orientation of Block Copolymer Microdomains in Thin Films via Directional Crystallization of a Solvent

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ABSTRACT: A fast method for inducing alignment of microdomains in noncrystalline block copolymers is presented. The method is based on the use of crystalline organic materials, which are solvents for the block copolymers above their melting temperatures, and, when cooled and directionally crystallized, act as a substrate on which thin films of the block copolymers are formed. Both lamellar and cylindrical type microdomains in a symmetric polystyrene-*block*-poly(methyl methacrylate) diblock copolymer and in an asymmetric polystyrene-*block*-polyisoprene respectively are globally aligned using either benzoic acid (BA) or anthracene (AN) as the crystallizable solvent. The fast directional solidification during the phase separation leads to alignment of the intermaterial dividing surface (IMDS) of both types of microdomains parallel to the fast growth direction of BA and AN crystals (*b* axis direction in both cases). Depending on film thicknesses, the block copolymers show various microdomain orientations such as vertical lamellae and parallel and perpendicular cylinders to the substrate. With respect to the processing methods currently used to induce orientation in block copolymers, our method allows attainment of ordered patterns over regions larger than 50 μm^2 within a few seconds without annealing.

Introduction

The self-assembly of block copolymers produces microstructures on the nanoscopic length scale.[1] Such periodic nanostructures are very useful, for instance, in thin films as templates for lithography.[2−6] By removing one polymer chemically, the patterns may be transferred to a substrate either through reactive etching or by thermal evaporation of a component into the previously removed regions.[2−6] Additionally, the domains can be used as a template for decoration with nanoparticles.[7−9]

Optimal utilization of nanoscopic patterns, however, requires spatial and orientational control of the microdomains. Indeed, the microdomains composed of the different blocks, having sizes of several tens of nanometers, typically nucleate randomly and grow into a polygranular texture, with periodic ordering maintained only over distances of about 50 lattice constants (i.e., a grain size of only 1−2 μm). A greater range of engineering applications demands control over the orientation and position of the microdomains. Thus, the development of processing techniques which create global orientation of the microdomains in block copolymer thin films is an important goal.

Several techniques are currently used for inducing alignment of the microdomains in block copolymers.[10−26] They rely on the ability to couple an externally applied field to some molecular and/or supermolecular feature in the polymer and thus achieve directional properties, such as transport, optical, and mechanical properties. Therefore, if an applied bias field (mechanical, electric, etc.) is present during the self-assembly process, then instead of random nucleation of microdomains, preferential orientation can develop.

Flow provides an efficient and versatile means of achieving global alignment. In typical processing methods involving flow fields, the material with an initial polygranular texture is subjected, for instance, to capillary extrusion,[10] oscillatory and steady shear,[11−15] and planar extensional flow.[16,17] The flow field causes certain domain orientations to be favored, and eventually a near-single-crystal structure can be developed in bulk materials. Alternatively, instead of realignment of an existing polydomain structure, use of low molecular weight samples for which the material is initially above its order−disorder transition temperature and subsequently cooled during processing can result in well-aligned samples within a few hours.[15] The roll-casting method utilizes a volatile solvent to permit processing of higher molecular weight polymers from an initially homogeneous solution through the order−disorder concentration into a well-aligned state in approximately 1 h.[18] Flow field techniques, however, cannot be easily applied to thin films due to flow instabilities.

Recently, Hashimoto et al.[19] have shown that a single grain lamellar microdomain orientation can be achieved using an applied temperature gradient. Also in this case, the process is very slow (~2 mm/day). The spatial variation of the dielectric constant of block copolymers is another means for alignment under electric fields of the nanoscale patterns in bulk[20] as well as in thin film.[21,22] In particular, Morkved et al. demonstrated that in-plane cylindrical poly(methyl methacrylate) (PMMA) microdomains were aligned along the electric field in a thin polystyrene (PS)/ poly(methyl methacrylate) (PMMA) block copolymer film.[21] Recently, Thurn-Albrecht et al. have also demonstrated that a vertically ordered cylindrical PMMA microdomain structure was achieved when an electric field was applied across the block copolymer thin film.[22]

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The simplest technique to make a uniform *thin film* is spin-casting. However, after long time annealing, the thin film typically displays a polygranular texture of microdomains.[2−4]

Control of film thickness is another way to vary the orientation of microdomains. Fasolka et al.[23] recently studied the phase behavior of a lamellar-forming block copolymer for film thicknesses less than the period of block copolymer on SiO_2/Si substrates. They showed that either parallel or perpendicular ordering can be obtained depending on film thickness and interfacial energy between the substrate and the block copolymer.

A bias field induced by surface interactions such as preferential wetting of the contact surface can also control the thin film microstructure.[24] Surface modification with a random copolymer provided a neutral surface upon which a perpendicular lamellae structure formed in approximately 100 nm thickness film. However, due to degenerate azimuthal orientations of the lamellae, a film containing many defects and grain boundaries is produced.[24]

Multiple interactions allow for more precise microdomain control. For example, the physical structure (topography) of the substrate surface and the chemical nature of both the copolymer and the substrate can be used to control microdomain orientation. Fasolka et al. employed a one-dimensional groove pattern from a miscut Si single-crystal wafer to create periodic substrate topography.[25] The period and amplitude of the surface grooves were controlled by the miscut angle, the annealing temperature, and time. By spin-coating a lamellar-forming block copolymer thin film two different film thicknesses resulted, and these exhibited a 1D patterned microdomain ordering.[25] In a subsequent work, the one-dimensional groove pattern was chemically patterned by evaporation of metal atoms at a low angle of incidence. This topographically and chemically (Au and SiO_2 regions) patterned substrate generated nanoscale pattern of a lamellar-forming PS/PMMA block copolymer where the PMMA blocks interact selectively with Au area.[26] A vertically ordered lamellar structure was obtained when the periodicity of block copolymer was comparable with that of a groove.[26]

Another approach to chemically modify substrates is by microcontact printing of self-assembled monolayers.[27] Parallel and perpendicular lamellar structures were formed on the patterned substrate depending on the two different surface properties (preferential (parallel) and neutral surfaces (perpendicular)).[27]

Recently, we employed the rapid solidification of semicrystalline block copolymers from an organic crystallizable solvent to control both the molecular and the microdomain orientation in thin films.[28,29] Depending on the nature of semicrystalline block copolymers and on the properties of organic crystallizable solvents such as melting temperature (T_m), crystalline structure, the fast growth direction of the crystals, and the epitaxial relationship between crystalline block and crystallizable solvent, versatile patterned textures have been achieved. The process involves two driving forces, i.e., (1) directional solidification and (2) epitaxy that together produce oriented microdomains via crystallization of the crystalline block onto the surface of the performed crystals of the organic solvent.[29] The combination of the two types of interactions determined the kinetically driven microstructures.[28,29]

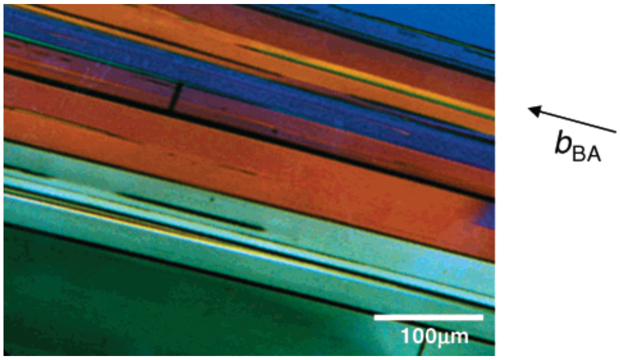

Figure 1. Polarized optical microscope image of directionally crystallized BA crystals. The large, flat, and elongated BA crystals are aligned with the *b* axis parallel to growth front direction. BA single crystals with various thicknesses lead to different colors under polarized light.

In this paper we show that the simple and fast process originally developed for PE homopolymer[30] as well as for semicrystalline block copolymers[28,29] can be employed to induce the alignment of lamellar and cylindrical microdomains of *amorphous* diblock copolymers. In this case of noncrystalline block copolymers, only directional solidification is involved. Understanding of this effect will give new insight into the physics of the ordering process in block copolymers.

Experimental Methods

We use a polystyrene-*block*-poly(methyl methacrylate), PS/PMMA (26/32), diblock copolymer and a polystyrene-*block*-polyisoprene diblock copolymer, PS/PI(45/12). The PS/PMMA(26/32) sample has a total molecular weight of 58 500 g/mol, a polydispersity of 1.06, with PS and PMMA blocks of 26 000 and 32 000 g/mol, respectively. This sample presents a bulk lamellar microstructure (evidenced by small-angle X-ray scattering (SAXS): $d_{100}^{\text{lam}} \approx 39$ nm), consistent with the 49% volume fraction of the PS block. The PS/PI(45/12) sample has a total molecular weight of 57 000 g/mol with PS and PI blocks of 45 000 and 12 000 g/mol, respectively. Since the volume fraction of the PI block is 24%, the bulk sample displays a hexagonally packed cylindrical microstructure of the minority PI component (evidenced by SAXS: $d_{10\bar{1}0}^{\text{cyl}} \approx 42$ nm). The PS/PMMA(26/32) was purchased from Polymer Laboratories, while the PS/PI(45/12) block copolymer was supplied by Dr. L. J. Fetters of Exxon Research and Engineering.

The processing method we employed is based on the use of low molecular weight crystallizable organic solvents such as benzoic acid (BA) and anthracene (AN). The process employs three main steps as described in previous papers:[28,29]

(1) Thin films of the block copolymer (∼100 nm thickness) were first formed on a carbon-coated coverslip glass, by evaporation of the solvent from a xylene solution (0.1−0.3 wt %).

(2) Crystalline BA or AN powders are then spread over a glass slide, and the coverslip is placed polymer side down on the BA or AN and melted at 150 and 240 °C, respectively, whereupon the molten BA or AN dissolves the block copolymer. The solution is then supercooled by placing the glass slide on a hot bar at 110 °C for BA and at 190 °C for AN and to induce directional crystallization of the BA (melting temperature $T_m \cong 123$ °C) or the AN ($T_m \cong 220$ °C). Rapid crystallization of BA or AN occurs (growth front velocity ≅ 2 mm/s), resulting in large, elongated crystals with the *b* axis parallel to growth front direction. Figure 1 shows a polarized optical microscope image of directionally crystallized BA. Large flat and elongated crystals of BA are seen. Finally, the slide is moved to a position on the hot bar with a temperature of 60 °C (or 140 °C) and held for a minute to complete the crystallization of the BA (or the AN) and then cooled to room temperature.

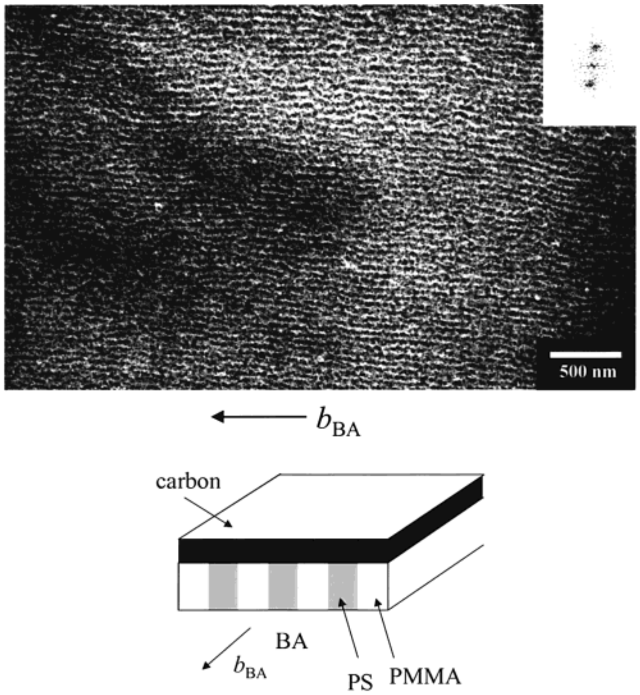

Figure 2. (a, top) TEM bright-field image of a thin film of PS/PMMA(26/32) block copolymer with the thickness of approximately 20 nm, directionally solidified with BA, and stained with RuO_4. The dark regions correspond to the stained PS microdomains. The lamellae are well-aligned along the fast growth direction of the BA crystals (crystallographic *b* axis). Inset shows the FFT power spectrum of the TEM micrograph. Spotlike first reflection located on the meridian shows the nearly single-crystal-like microstructure. (b, bottom) Schematic model of the microstructure of PS/PMMA processed with BA. Alternating lamellae of PS and PMMA microdomains are aligned along the *b* axis of BA crystal.

(3) A razor blade is then used to fracture-open the solidified material (cleavage occurs easily on the (001) BA and AN planes). Ethanol at 50 °C is then used to wash away either the BA or the AN from the coverslip.

The interior surface of the coverslip is then scored with a knife, and small sections of the carbon film are floated off onto distilled water and picked up onto transmission electron microscope (TEM) grids. Some pieces of PS/PMMA(26/32) were exposed to RuO_4 for 20 min to stain the PS microdomains, and pieces of the PS/PI(45/12) films were then exposed to OsO_4 for 2 h to stain the PI microdomains. The films were examined by a JEOL 200 CX TEM in bright field mode, operating at 160 kV. Polarized light microscopy of the films after BA or AN removal demonstrates that there is a strong texture, most apparent from some elongated regions of thicker polymeric material which formed between the crystals of the organic solvents. This direction corresponds to the fast growth direction of the BA or AN (the *b* axis). Fast Fourier transforms (FFTs) were made from the TEM images, using a software program, image SXM. This program performs the FFT and outputs the data on a log scale as a 2 D image.

Results and Discussion

A bright field TEM image of a thin film of PS/PMMA (26/32) block copolymer prepared using BA is shown in Figure 2a. The darker regions correspond to the RuO_4-stained PS microdomains. Edge-on parallel lamellae of PS and PMMA are well-aligned along the fast growth direction of the BA crystals. The PS lamellae appear thicker than the PMMA lamellae because the PMMA microdomains beam damage and shrink under electron irradiation. The well-aligned parallel lamellae extend over regions larger than 50 μm^2. The FFT power spectrum in the inset of Figure 2a shows a spotlike first reflection located on the meridian, indicating the nearly single-crystal-like microdomain structure.

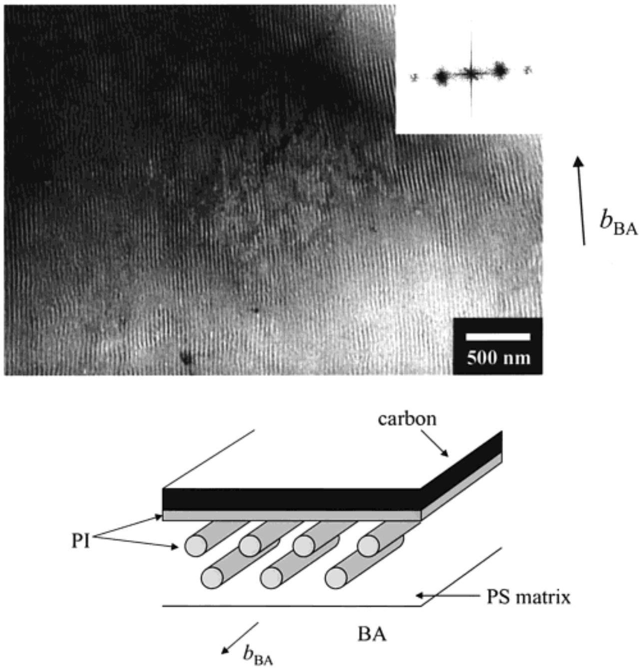

Figure 3. (a, top) TEM bright-field image of a thin film of PS/PI(45/12) block copolymer with the thickness of approximately 50 nm, directionally solidified with BA, and subsequently stained with OsO_4. The dark regions correspond to the stained PI cylinders, while the white regions correspond to the PS matrix. The cylindrical PI microdomains are well-aligned along the fast growth direction of the BA crystals. No grain boundaries are evident. A few dislocation defects are seen. Inset shows the fast Fourier transform (FFT) power spectrum of the TEM micrograph. Spotlike reflections located on the equator at q_0 and $2q_0$ indicate a nearly single-crystal-like microstructure. In particular, absence of the $\sqrt{3}q_0$ reflection in this FFT power spectrum demonstrates that there is no rotation and tilting of microdomain lattice along the cylinder axis. (b, bottom) Schematic model of the microstructure of PS/PI processed with BA. Cylindrical PI microdomains are edge-on to the crystalline substrate and aligned along the *b* axis of BA crystal.

The schematic model of the microstructure of the PS/PMMA block copolymer after directional solidification with BA is shown in Figure 2b. Vertically alternating PS and PMMA lamellae are very well oriented along the *b* axis of BA crystal. The fast directional microstructure formation during the phase separation with a thin film thickness approximately less than a half lamellar period avoids preferential wetting of one of the blocks on the substrate, leading to the oriented lamellae microdomain structure where the interface of the microdomains is parallel to the normal of the substrate surface. The structure is kinetically driven and subsequently vitrified at room temperature. Importantly for regions thicker than approximately a half lamellar period, the perpendicular lamellae orientation switches to an in-plane parallel one, and large planar regions (hence no TEM contrast) are produced.[31]

A bright-field TEM image of a thin film of the PS/PI(45/12) block copolymer with the thickness of approximately 50 nm, directionally solidified with BA, is shown in Figure 3a. The darker regions in Figure 3a correspond to the OsO_4-stained PI microdomains. It is apparent that the PI cylinders, lying in-plane, are well-oriented along the crystallographic *b* axis of the BA. The

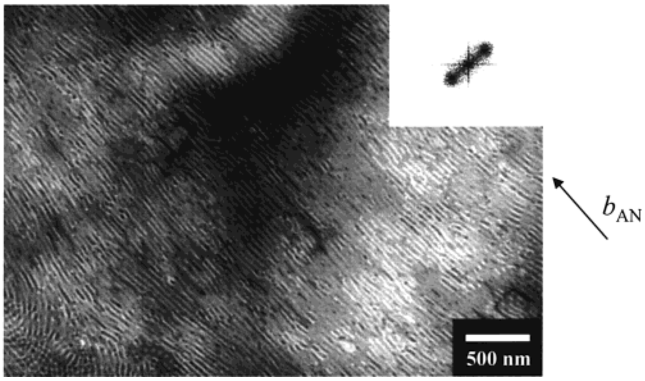

Figure 4. TEM bright-field image of a thin film of PS/PI(45/12) block copolymer with the thickness of approximately 50 nm, directionally solidified with AN, and stained with OsO_4. The dark regions correspond to the stained PI cylinders, while the white regions correspond to the PS domains. The cylindrical PI microdomains are not so well aligned along the fast growth direction of the AN crystals. Many dislocation defects are observed. Inset is the FFT power spectrum of the TEM micrograph. The arced first-order reflection perpendicular to *b* axis of AN crystals demonstrates the orientation of the PI microdomains observed in TEM, which is not as good as when the PS/PI copolymer is processed with BA.

ordered parallel cylinder structure also extends over regions larger than 50 μm^2. The average diameter of the PI cylindrical microdomains is approximately 20 nm, while the average distance between the cylinders is 40−50 nm consistent with the bulk SAXS data. A schematic model of microstructure of PS/PI block copolymer after directional solidification with BA is shown in Figure 3b. In-plane PI cylinders are aligned along the BA *b* axis. We assume the lower surface tension PI block is preferentially at the carbon interface while the PS block forms the interface with the BA surface due to its more favorable interaction.

To confirm that this simple process can be applied with other organic crystallizable solvents, we employed anthracene which has a melting temperature 100 °C higher than that of benzoic acid. A TEM bright-field image of a thin film of the PS/PI(45/12) block copolymer, directionally solidified with AN, is shown in Figure 4. A microstructure similar to that obtained with BA is observed. The cylindrical PI microdomains are again aligned along the fast growth direction of AN crystals. However, in terms of the perfection of ordering, the microstructure produced with AN is much more defective with many more dislocations than when BA is used. The FFT power spectrum of Figure 4 (inset) shows only one arced reflection, whereas the FFT power spectrum of Figure 3a (inset) clearly shows spotlike multiorder reflections perpendicular to the cylinder axis of PI microdomains. This decrease in microdomain ordering is due in part because the shape anisotropy of the AN crystals is lower than that of BA crystals as observed with optical microscopy.

The mechanism of pattern formation in the block copolymer induced by the crystallizable solvent is related to that previously reported for a semicrystalline block copolymer.[29] The key difference is that, for the present noncrystalline block copolymer materials, only the effect of directional solidification is involved. The essential aspects of overall phase transformation can be understood assuming the possible formation of an eutectic mixture of the block copolymer and the crystallizable solvent.[29] In a hypothetical solvent−polymer phase diagram an eutectic may be present due to the intersection of the melting point depression liquidus curve of the crystallizable solvent and the microphase separation transition depression liquidus curve of the block copolymer.[29] The initial homogeneous solution confined between the glass substrates transforms due to the imposed directional solidification into large crystals of BA (or AN) having (001) surfaces coexisting with a thin liquid layer near the eutectic composition. Dropping the temperature further then causes this layer to also directionally solidify by thickening the preexisting (BA or AN) crystal with simultaneous formation of a thin, metastable vertically oriented *lamellar* microdomain film.[29] In the case of the PS/PMMA block copolymer, the vertical lamellar structure is vitrified due to the high glass transition temperatures of both blocks. In the case of PS/PI block copolymer with a low volume fraction of PI block, however, we hypothesize that the vertical lamellar microstructure is transformed into in-plane cylindrical microstructure due to the interfacial instability of thin lamellae, film thickness, and preferential wetting of PI block.

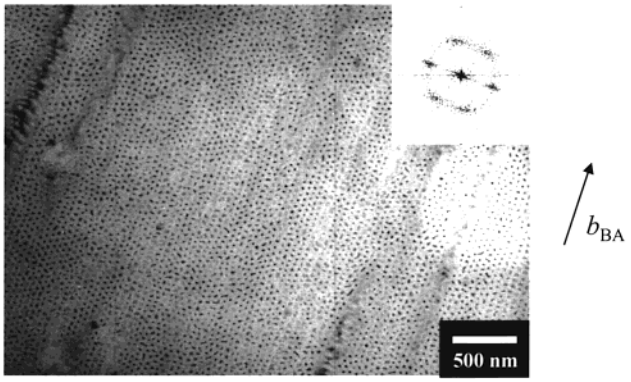

Figure 5. TEM bright-field image of a thin film of PS/PI(45/12) block copolymer with the thickness of approximately 20 nm, directionally solidified with BA, and stained with OsO_4. The dark regions correspond to the stained PS microdomains. Vertically oriented PI cylinders are well-aligned along the fast growth direction of the BA crystals (crystallographic *b* axis). Fast microstructure formation leads to noncircular shape of PI cylinders. Inset shows the FFT power spectrum of the TEM micrograph. Spotlike first reflections with 6-fold symmetry show the nearly hexagonally packed microstructure.

An interesting possibility to achieve vertically aligned cylinders is to employ ultrathin films of a cylinder-forming block copolymer. As first shown by van Dijk and van den Berg, the cylindrical microdomains orient vertically for relatively thin film due to incommensurability effects, which is similar to what observed for lamellar diblock copolymers.[32] An initially thinner PS/PI film (approximately 20 nm thickness) prepared from a more dilute solution probably first forms a thin metastable vertically oriented lamellar film which undergoes a vertical undulation instability, resulting in a vertically aligned cylindrical structure. Figure 5 shows a bright-field TEM image of PS/PI (45/12) block copolymer directionally solidified with BA and stained with OsO_4. The dark OsO_4-stained vertically aligned cylindrical PI microdomains are oriented into rows along the *b* axis of BA crystal. The aligned vertical cylinder extend over regions larger than 50 μm^2. The FFT power spectrum in the inset of Figure 5 shows spotlike first reflections with 6-fold symmetry, indicating approximate hexagonal packing of the PI microdomains.

We have also processed several noncrystalline block copolymers with different molecular weights, compositions, and architectures, using BA. In general, our kinetically controlled process gives poorer orientation with higher molecular weight block copolymers. Better orientation is achieved with higher PS-containing block copolymers probably because of better solubility of the PS block in BA. At high PI block content, the block copolymer film dewets on the glass substrate after removal of BA at room temperature.

Conclusions

Orientation of block copolymer microdomains via directional crystallization of a solvent is an effective way to develop unidirectional long-range ordering of conventional amorphous block copolymers. The orientation of microdomains occurs within a few seconds without any long time annealing procedures. Several types of microdomain alignment were possible: (1) vertical lamellae, (2) in-plane cylinders, and (3) vertical cylinders, depending on film thickness. The method could be applied to different block copolymers with various compositions and generalized by using other crystallizable provided the solvents dissolve block copolymers above their melting temperature and directionally crystallize into large, elongated single crystals. In addition, this process can be combined with topologically and/or chemically modified patterned substrates for better control of microdomain structures.

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