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Spherical to cylindrical microdomain transformation by application of a flow field

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Abstract

A structural transformation from a spherical microdomain structure to a cylindrical one in a semicrystalline polystyrene-*b*-polyethylene-propylene-*b*-polyethylene (PS/PEP/PE) terpolymer having a total molecular weight of 103 kg/mol under a strong external flow field was observed. Quiescently formed samples made by evaporation of the polymer in decalin show the disordered spherical microdomain structure of polystyrene (PS). The roll cast process generated a cylindrical PS microdomain structure well oriented along the flow direction as determined by TEM and SAXS. We explain the observed structural transformation by an analogy to the behavior of surfactant systems under external forces and furthermore demonstrate that the cylindrical structure is an example of a facilitated equilibrium morphology development by an external force. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polystyrene-*b*-polyethylenepropylene-*b*-polyethylene; External flow field; Structural transformation

1. Introduction

The mechanical, transport and other properties of multi-component and multiphase polymer systems largely rely upon their phase morphology and the nature of the interface between these phases. Control of morphology is the key to manipulating the properties of such systems. In addition, controlling phase transitions is essential to advance our knowledge of material properties in multi-component and multi-phase systems.

A number of methods have been found which can induce a shape transformation in a self-assembled system. The transition from vesicle to cylindrical micelle has been observed in the surfactant/solvent systems in three different ways, namely, by an increase in temperature [1], an addition of a surfactant [2], or upon mechanical shearing [3,4]. Similar shape transitions from a randomly dispersed spherical structure to an elongated cylindrical structure have been observed in polymer systems including homopolymer/solvent systems [5], homopolymer/homopolymer/solvent ternary systems [6,7] and homopolymer/block copolymer surfactant systems [8] due to application of mechanical or electrical fields.

Phase transitions in block copolymers have been induced in many ways. Most of the phase transitions in block copolymers have been achieved by evaporating the solvent and altering the temperature [9] or pressure [10]. Block copolymer microdomain structure can also be altered by simply adding the homopolymer of one of the block components [11–14]. Here, solubilization of homopolymer into the same polymer component phase results in the change of the volume fraction of that component which induces a phase transition. A related approach to control the shape of the microdomain is to blend a low molecular weight additive that can preferentially swell one of the block components [15].

External forces such as shear flow [16–19], surface orientation [20], and electric fields [21–23] have generally been applied to obtain a well-oriented microphase separated structure rather than to induce phase transitions in block copolymer systems. Attaining a well-oriented structure is useful for both material characterization and a detailed investigation of the full tensor properties. The methods using surfaces with specific interactions and electrical fields, however, are limited to relatively thin films, and block copolymers composed of blocks with significantly different

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dielectric constants, respectively. The application of a flow field to a molten but already microphase separated sample, creates a highly aligned structure due to the forced rotation of the many originally misaligned grains (due to their individual mechanical anisotropy) but leads to numerous morphological defects in the final material.

An orientation method called 'roll casting' developed in our laboratory can be a good method to obtain a thick and relatively defect-free globally aligned film. This method subjects the material to a hydrodynamic flow as the solvent evaporates and the initially homogeneous solution undergoes microphase separation. Previous studies show that the resultant global orientation of block copolymer films with cylindrical or lamellar morphology is almost single-crystal like using this method [24–26]. Recently a highly oriented spherical microdomain structure arranged on a body-centered cubic lattice as well as an oriented double gyroid bicontinuous cubic microdomain structure have also been produced using the roll cast method [18,27].

Only a few reports have appeared on the effect of the external forces on the phase transformation of the block copolymer melts. Hamley et al. [28] detected various intermediate metastable phases between the lamellae and the cylindrical phases of a diblock copolymer upon shearing through the transition region. The nature of these intermediate structural states is related to the transformation pathway of the lamellar to the cylindrical microdomain structure. The intermediate structures are termed hexagonally modulated lamellae and layered hexagonal-packed channels. The coexistence of two cylindrical microdomain structures of different lattice symmetries has been observed in a sheared triblock copolymer as reported by Jackson et al. [29]. Shearing of a spherical domain structure near the order–disorder transition temperature was shown to transform the material into cylinders. Upon cessation of shearing, the material converts back to the spherical domain structure via epitaxial growth from the oriented cylinder structure resulting in a texture with the [111] direction in the cubic phase parallel to the [001] direction of the hexagonal phase [30]. Recently, Vigild et al. [31] showed a similar epitaxial growth of the double gyroid phase either from a hexagonal perforated layer phase or from a hexagonal cylinder phase obtained by shear aligning. Dair et al. [27] also reported an epitaxial growth of the gyroid phase from a roll cast oriented hexagonal phase of a PS/PI/PS triblock by annealing.

In block copolymer systems, it is well known that the microdomain geometry depends on the relative volume fraction of each segment and their respective degree of polymerization. Flow field energy can, however, shift the zero-field phase diagram, as observed in both experimental [32,33] and theoretical [34,35] studies. The suppression of composition fluctuations by external fields such as shearing drives the system towards the mean-field limit, resulting in an apparent increase of order–disorder transition temperature. For example, Amundson et al. [23] demonstrated that an ordered structure persisted even after heating the materials 14 K above the critical temperature of the zero electric field (electric-field-induced shift of the microphase separation).

Most of the phase transitions promoted by applied fields observed in block copolymer melts took place when the phase present under zero field conditions was not far from a phase boundary, in which case, the external forces need only to provide a small bias to affect the transition. In addition, the field-induced structures revert to the previous zero field (equilibrium) structures after cessation of the forces and annealing.

In the present work, we have employed TEM and SAXS to study structure formation in a crystallizable block terpolymer consisting of polystyrene (PS), polyethylene propylene (PEP), and polyethylene (PE) microphase separated with and without the presence of an applied flow field. We show that the development of the thermodynamically stable morphology can be facilitated by application of an external force during microphase separation. Such an ABC linear terpolymer with one glassy end block (PS) and a crystallizable end block (PE) which are connected via a rubbery midblock (PEP) presents a novel situation in which the crystallization of the end block within the microphase separated structure is partially screened by the rubbery midblock. Since PEP and PE are completely miscible above the T_m of PE, the microdomain morphology consists of PS domains segregated within a mixed matrix of PE and PEP [36]. The sample is allowed to microphase separate above the T_c of PE using both the roll casting and simple casting methods, and the films obtained are subsequently quenched in liquid N_2 to limit crystallization. When the temperature drops below the crystallization temperature of PE, phase separation between the PE and PEP blocks will take place within the matrix, leading to some type of crystalline PE morphology. The influence of the crystallization of the PE block on the microdomain structure will be described in another paper [37].

2. Experimental

The polymer used in the present study was derived by hydrogenation of a polystyrene-*b*-polyisoprene-*b*-polybutadiene (PS/PI/PB) terpolymer with block molecular weights of approximately 15, 70 and15 kg/mol synthesized at Exxon Research Co. The PS/PI/PB triblock was prepared by anionic polymerization in benzene at 20°C with s-BuLi as the initiator. The polymerization was done in a sequential fashion commencing with styrene. Conventional high vacuum techniques were used [38]. The resultant PI microstructure yielded, after hydrogenation, the essentially alternating copolymer of ethylene and propylene while the PB segment yielded a poly(ethylene–butene) copolymer having approximately two ethyl branches per 100 backbone carbons. The hydrogenation was carried out using the procedures given elsewhere [38]. The method used leads to the

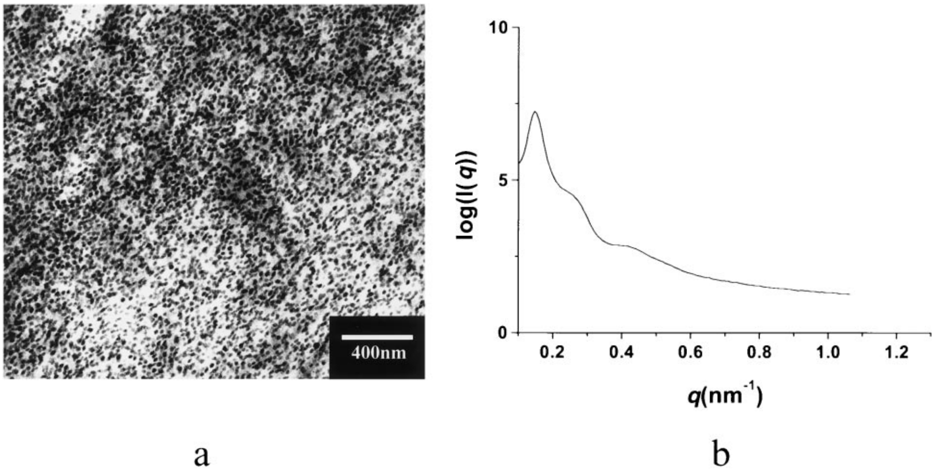


Fig. 1. (a) Bright field TEM micrograph for the simple cast PS/PEP/PE (15/70/15) film. The film was stained with RuO_4 for 20 min so that the PS domains appear dark. Poorly ordered PS spheres are shown. (b) SAXS profile at 140°C for the simple cast PS/PEP/PE film.

complete saturation of polydiene segments while leaving the polystyrene segment unchanged.

Polymer molecular weight characterization was done using a combination of size exclusion chromatography (SEC) and low-angle-laser-light-scattering. Tetrahydrofuran was the solvent in both cases. The weight average molecular weight, M_w (PS/PI/PB) via light scattering was 103,000 g/mol while SEC gave the M_z/M_w and M_w/M_n ratios as 1.02 and 1.04, respectively.

Isotropic thick films (1 mm thickness) of the terpolymer were simple cast from decalin solutions containing 5 wt% polymer at 110°C. Anisotropic thick films (1 mm thickness) were made by pouring the polymer solution between two *heated* counter-rotating adjacent cylinders while at the same time the solvent was allowed to evaporate. The angular velocity of each cylinder was about 30 rpm. The roll casting process was performed at an elevated temperature (90°C) that is higher than the crystallization temperature of polyethylene block (70°C), determined by DSC-7 at a cooling rate of 10°C/min, to avoid any effects of crystallization on structure. Simple cast films and roll cast films were dried in vacuum oven at 40°C for 24 h to remove the solvent. Both types of films were then annealed for an additional 10 days under vacuum at 140°C, significantly above both the glass transition temperature of the polystyrene block and the melting temperature of polyethylene block (98°C), determined at a heating rate of 10°C/min. Both types of films were then subsequently quenched into liquid N_2.

Thin sections of the simple cast and the roll cast films were prepared for transmission electron microscopy (TEM) using a Reichert-Jung FC4E Ultracut microtome at −110°C. Some samples from both types of preparation were subsequently stained for 20 min with RuO_4, a preferential stain for the PS block. Bright-field transmission electron microscopy was then performed with a JEOL 200 CX microscope operated at 200 kV.

Small angle X-ray scattering (SAXS) measurements were carried out at the Advanced Polymers beamline, X27C, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The wavelength used was 0.1307 nm, and the beam size was about 0.4 mm in diameter at the sample position. A three 2° tapered tantalum pinhole collimation system was utilized with a sample to detector distance of 1560 mm. Scattering angles down to 1.5 mrad corresponding to a d-spacing ($d = 2\pi/q_{\min}$) of about 100 nm were achieved. A single-cell heating stage (maximum temperature: 350°C) was used for high temperature measurement. Fuji imaging plates were used to collect the scattering data with exposure times of 1 min per frame.

3. Results

The morphology of the simple cast film is shown in the bright field TEM images of Fig. 1(a). A spherical microdomain structure of PS is clearly evident as the dark circular regions selectively stained with RuO_4. The PS spheres are arranged in the PEP/PE matrix without significant long-range order. This is likely due to the weak correlation between PS spheres at the low volume fraction of PS and/or possibly due to the crystallization of PE in the matrix which could disrupt the sphere packing at room temperature.

The possibility that crystallization of the PE lamellae disrupts the ordering of the PS spheres was investigated using temperature-controlled SAXS. Fig. 1(b) shows the SAXS scattered intensity vs. scattering angle at 140°C for the simple cast film. There is a distinct low angle reflection and with a shoulder at a q of approximately 0.27 nm^{-1} followed by a broad maximum centered at $q \sim 0.43$ nm^{-1}. This pattern is similar to those previously observed by Kinning and Thomas [39–41] and Bates et al. [42] for PB micelles packed on a bcc lattice in polystyrene homopolymer/PS-*b*-PB diblock blends. The average intersphere distance can be estimated as 42 nm from the first

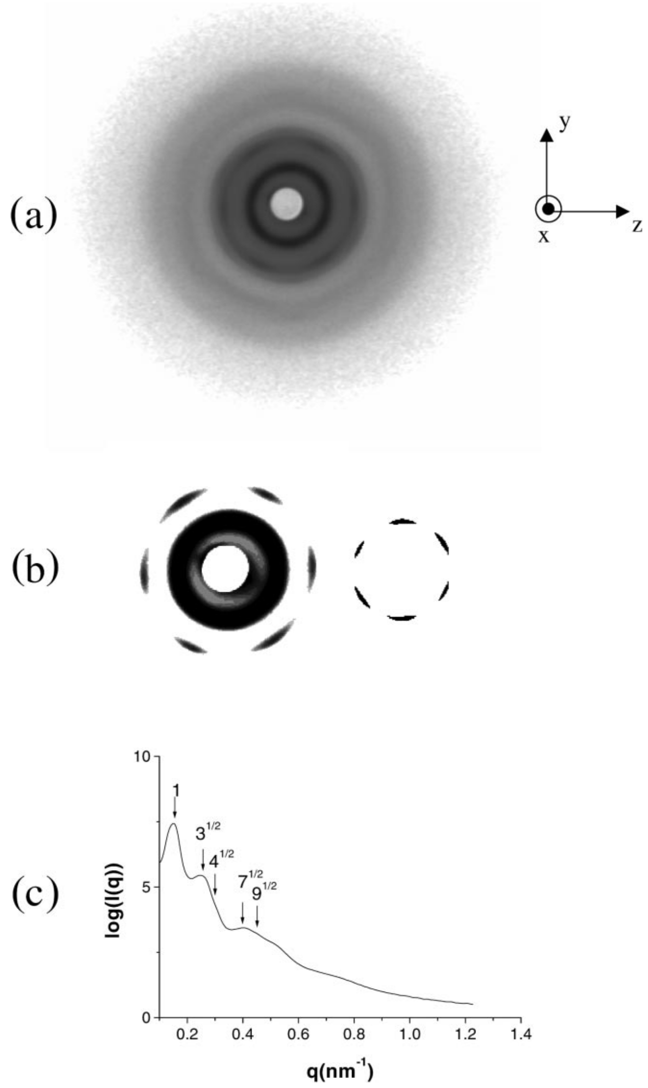


Fig. 2. (a) Two-dimensional SAXS pattern with the incident beam along the flow direction, normal to the *yz*-plane. (b) SAXS patterns with different threshold cut off to emphasize the six-fold symmetry. (c) Azimuthal averaged SAXS profile shows peaks in the ratio of 1.0, $3^{1/2}$, $4^{1/2}$, $7^{1/2}$.

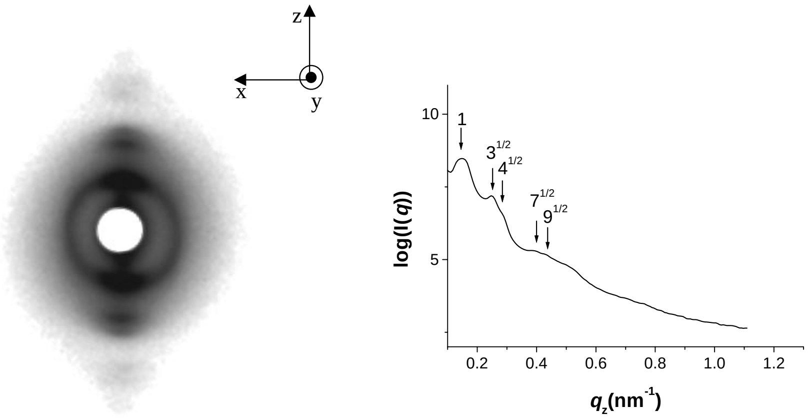
peak (d_{110}) position. Assuming the broad high q peak at $q \sim 0.43\ \mathrm{nm}^{-1}$ arises from the sphere form factor, allows the sphere radius to be estimated as 10 nm. This compares reasonably well to the sphere diameter of 20 nm determined from the TEM image. The small crystals of PE formed during the quenching process apparently do not alter the spherical microdomain structure developed during simple casting and annealing. Bates et al. [43] also showed that quenching a diblock copolymer could result in very fine scale crystallization of the PE block, which does not disrupt the microdomain structure, established by a high temperature annealing treatment.

Figs. 2 and 3 show two-dimensional SAXS patterns of a roll cast film. The coordinate system is chosen so the flow direction corresponds to x, the neutral direction to y and the through thickness direction to z. When the incident beam is parallel to the flow direction, an approximate six-fold symmetric set of intense reflections appear (see Fig. 2(a) and (b)). This indicates that the roll casting process has induced a well oriented, highly ordered structure. The azimuthal averaged intensity scan is shown in Fig. 2(c). The sets of Bragg peaks have approximate q_n/q_1 values of 1.0, $3^{1/2}$, $4^{1/2}$, $7^{1/2}$, $9^{1/2}$ etc. which corresponds well with the hexagonal packing. Fig. 3(a) and (b) shows two-dimensional SAXS patterns with the incident beam perpendicular to the flow direction (parallel to the y direction). The scattering is concentrated along the normal to the flow direction with peaks again in the ratio of 1.0, $3^{1/2}$, $4^{1/2}$, $7^{1/2}$ etc. indicating that the structure is only two-dimensionally ordered as for example, hexagonal packing of cylinders.

TEM micrographs of the RuO_4 stained sections for views along the flow direction and normal to the flow direction (parallel to y direction) are shown in Fig. 4(a) and (b). The magnified inset selected area in Fig. 4(a) shows that the PS domains clearly self-assemble onto a hexagonal lattice during the microphase separation under the applied flow field. Interestingly there are many lattice points in the image without any apparent PS domains. These “PS vacancy” defects shown in the micrograph does not seem to result from misalignment of many small grains because relatively few grain boundaries are apparent, but from a local deficiency of PS implying gaps of the PS cylinders along the flow direction. The three-dimensional structure of the roll cast film becomes plainly evident when examining the view perpendicular to the flow direction. Short cylindrical PS domains and strings of PS spheres are seen to be oriented everywhere along the flow direction. Some spheres are elongated to a prolate ellipsoid shape as is apparent in the magnified inset of Fig. 4(b). The diameters of the spherical and cylindrical shaped PS domains correspond approximately to 22 and 20 nm, respectively.

The morphological examination made for the different directions of the roll cast film demonstrates that the flow field created by the co-rotating cylinders induced a shape transformation from the spherical domain structure of the quiescent film to a cylindrical domain structure during self-assembly of the roll cast film. Since after the roll casting, the films were first annealed for 10 days at 140°C (well above T_g of PS as well as T_m of PE), the roll cast-induced phase transformation is a stable state. To determine whether the transformed cylindrical structure is thermodynamically stable or metastable, an even higher temperature annealing was employed. Two-dimensional SAXS patterns for the sample annealed at 190°C for 48 h are almost the same as those after annealing at 140°C for 10 days (data not shown), implying that the cylindrical structure is an equilibrium state in spite of a low PS volume fraction (13 vol%). Annealing at a higher temperature than 190°C was tried but the sample began to degrade at around 200°C.

The work done by Sakurai et al. [44] confirms our claim of an equilibrium cylindrical microdomain structure at only



(a)

(b)

Fig. 3. (a) Two-dimensional SAXS pattern with the incident beam along the normal to the *xz*-plane. Several strong reflections are shown perpendicular to the flow direction. (b) SAXS profile along the vertical direction of (a) also shows peaks in the ratio of 1.0, $3^{1/2}$, $4^{1/2}$, $7^{1/2}$ etc. confirming the structure is hexagonal packing.

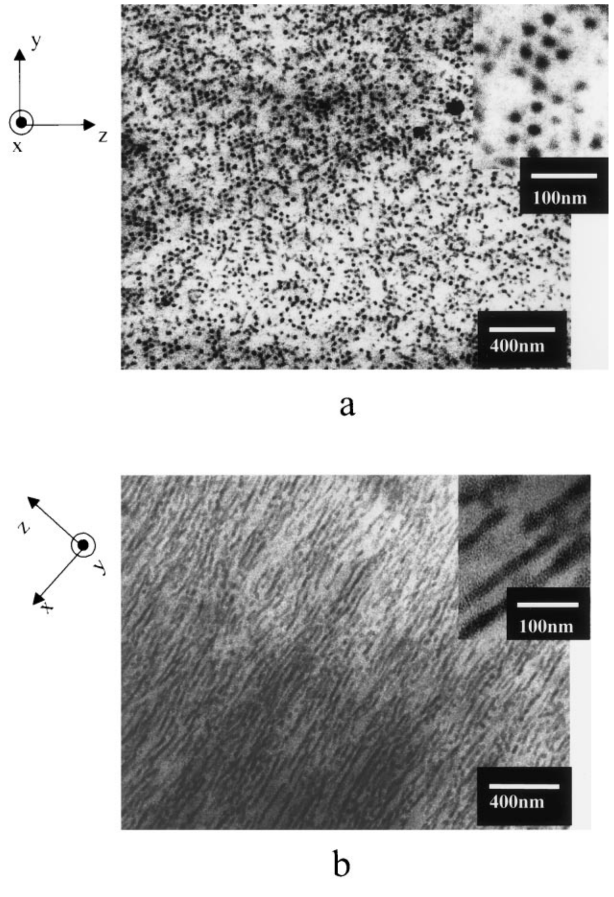


Fig. 4. (a) Bright field TEM micrograph for the roll cast PS/PEP/PE (15/70/15) film: view normal to *yz*. The film was stained with RuO_4. Circular regions of PS are evident. Inset of the selected area magnified from (a) shows a hexagonally ordered structure but with many regions without PS domains. (b) Bright field TEM micrograph for the roll cast PS/PEP/PE (15/70/15) film: view normal to *xz*. Needle shape and prolate spherical PS domains are shown parallel to the roll casting direction. Inset of the selected area magnified from (b) shows an elongated PS domains.

13 vol.% minority component. Sakurai et al. [44] obtained the cylindrical morphology of a PS/PEP block copolymer with a 12.8 vol% polystyrene content by annealing at 300°C. The material they used is quite similar to ours in composition as well as in molecular weight. The only difference is that our material has a small amount of PE component that is completely miscible with PEP above T_m of PE. They explained their results by suggesting that conformational asymmetry between PS segment and PEP segment leads to the shift of the phase boundary toward the PS axis. Thus, we conclude that the spherical PS morphology we obtained by simple casting is a metastable structure and that the cylindrical PS structure developed in the presence of a bias flow field is thermodynamically stable in our material whose degradation temperature does not allow sufficiently high temperature processing to achieve structural equilibrium. In the simple casting process, the microphase separation during evaporation of the solvent first forms a spherical PS microdomains. The subsequent annealing at the experimentally accessible temperature does not provide sufficient energy to overcome the activation energy barrier and transform the metastable sphere structure to the equilibrium cylindrical morphology. However, when energy generated by a strong bias flow field is provided such as in the roll casting process, the sphere morphology becomes unstable under external forces, as predicted by Huang and Muthukumar [35], and at the same time the structure can overcome the activation energy barrier, leading to the equilibrium morphology with cylindrical microdomains. The factors that coalesce the PS spheres along the flow direction, are interfacial energy and viscosity differences. This clustering ultimately leads to the formation of cylinders. The cylinders are aligned in the flow direction as expected, since this orientation represents a minimum in the potential energy when compared with other possible

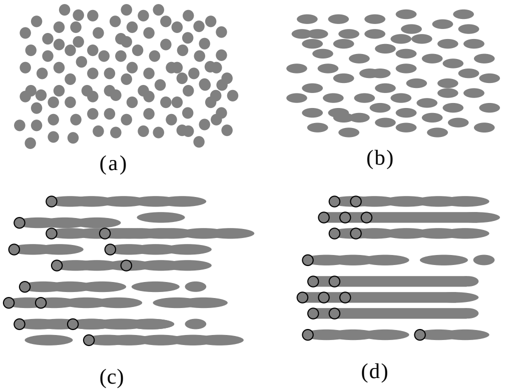


Fig. 5. Schematic diagram of the proposed mechanism of cylinder formation under the flow field with solvent evaporation. (a) Microphase separation is initiated at a certain concentration of polymer solution during the evaporation of solvent in roll casting process. Solvent swollen PS spheres are formed. (b) The PS spheres become prolate and align along the flow direction. (c) The development of needle shaped PS cylinders. (d) PS cylinders arrange to form a hexagonally packed structure.

orientations. A similar phase transformation from spherical micelle to cylinder was observed when a block copolymer/homopolymer/solvent blend was subjected to a strong electrical field [7,8] as well as when surfactant solutions were subjected to an applied flow fields [3,4]. The transformed structures formed in the other systems are, however, all metastable. A schematic diagram of domain formation and transformation by the flow field is shown in Fig. 5(a)–(d).

The imperfect cylinder structure may be due to the lack of time to form long continuous cylindrical domains even with a strongly coupled field due to the dramatic drop in molecular diffusivity resulting from the evaporation of the solvent during roll casting. The resultant domain structure contains, in addition to cylinders, prolate spheres and pearl shaped strings of PS shown in Fig. 4(b).

Since most block copolymers have relatively low degradation temperatures, a metastable spherical microdomain morphology is likely a common occurrence. This may be a reason that the boundary volume fractions between spherical and cylindrical structure predicted by theories are usually lower than those obtained by the experiments [45].

4. Summary

The metastable spherical structure observed in the quiescently formed solvent cast film of PS/PEP/PE terpolymer can be essentially transformed into a thermodynamically equilibrium cylindrical structure under application of a strong external flow field during microphase separation by the roll cast process. Highly ordered six-fold SAXS pattern with the incident beam along the flow direction and TEM micrograph of the same plane shows a well-defined hexagonal arrangement of PS microdomains. Highly ordered SAXS scattering peaks perpendicular to the flow direction when the incident beam is perpendicular to the flow direction and TEM micrographs also confirm that the spherical microdomain structure was converted into cylindrical structure. The high temperature and long time annealing process verified that the flow field induced cylindrical structure is an equilibrium state that is consistent with the work done by Sakurai et al. [44]. The similar observations in some surfactant systems under external forces suggest the mechanism shown in Fig. 5 to explain the phase transformation.

This study illustrates clear experimental evidence of how an equilibrium morphology can be facilitated by an applied field. In addition, it is the first real space study by TEM to investigate the shape transformation from the spherical to cylindrical microdomain structure.

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