Surface Morphology Evolution of Thin Triblock Copolymer Films during Spin Coating

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The surface morphology evolution of thin poly(styrene-*block*-ethylene/butylenes-*block*-styrene) (SEBS) triblock copolymer films as a function of the copolymer concentration was investigated by means of dynamic mode atomic force microscopy. At a relatively low copolymer concentration (0.025% w/v), the periodically orientated stripes were observed. This kind of surface patterning produced in the spin-coating process has not been reported in the literature before. It has been shown by our experiment that a shearing and stretching field can cause flexible polymer coils or aggregates to orientate during the spin coating. At a copolymer concentration of 0.05% w/v, SEBS molecule aggregates form network structures in the whole film. With further increase of the copolymer concentration, a continuous film with a microphase-separated structure was visualized.

Introduction

Spin coating is one of the simplest and the most common techniques for obtaining films over a wide range of thicknesses. For example, the spin-coating technique has been applied to forming photoresist films for defining patterns in microcircuit fabrication, dielectric layers for microcircuit fabrication, magnetic disk coatings, antireflection coatings, and compact disks (DVD, CD, ROM, etc.).[1−3] Many techniques mentioned above depend heavily on the quality and the uniformity of spin-coating layers. The final properties of these layers depend on their morphologies, which are affected largely by the polymer chain orientation and the state of aggregates. Many studies have been directed to predicting final film properties;[2] little attention has been paid to the changes in morphology induced by processing conditions. A better understanding of the effects of the spin-coating conditions on the polymer film morphology is important for making high-quality thin films.

Many authors have studied the process of thin film formation, though different authors sometimes count things differently. There are four distinct stages in the spin-coating process:[4] fluid dispensing, spin-up, stable fluid outflow, and finally evaporation-dominated drying. Usually it is considered that this technique could lead to very uniform films with well-controlled thickness.[5] Meyerhofer[6] presented a model by the description of thin films prepared from solutions by spin coating. In the fluid flow and thinning stage there is a strong inertial force that creates a shearing and stretching field in the fluid. Franke et al.[7] noted that fibers (Almax chopped Al_2O_3 fibers with a length of 0.5 mm and a diameter of 10 μm) in composite

solutions orientated themselves close to the radial direction during spin coating. A result of the Stange et al.[8] study of dilute polystyrene (PS) solutions indicated that for a given combination of a polymer, a solvent, and a substrate, there is a lower limit for the thickness of a continuous film (possibly related to the overlap concentration C^* of the polymer). At an intermediate concentration (a typical value of C^* for the polymer with molecular weight 10^5 is ca. 0.05% w/v), the polymer molecules aggregate to form two-dimensional Voronoi tessellation-like networks. The networks are constructed from particles with size range from those of a single polymer coil to large aggregates. At a concentration of above 0.05 wt %, continuous films have been observed. However, no papers show polymer aggregates form the orientation structure in shearing and stretching gradients when the spin coating of a polymer solution is performed.

The microphase morphology of thin films of ABA triblock copolymers (known as thermoplastic elastomers) has been observed. The surface microdomain morphology of the thin films formed via spin coating depends on processing conditions such as spin speed, spin time, concentration, and so on. In poly(styrene-*block*-ethylene/butylenes-*block*-styrene) (SEBS), the central block, the ethylene/butylene (EB) rubbery sequences, is the major component of the copolymer; the two outer blocks are thermoplastics. Because the components are incompatible, the triblock copolymer is separated on a microscopic scale, into pure rubbery and glassy domains. This type of material with different local mechanical properties constitutes a model system in which a particular contrast on a small scale in the phase images could be obtained. The microphase separation of copolymers with immiscible components has been studied intensively. When the copolymer is near a surface, it self-assembles into an ordered structure with a specific microdomain orientation.[9]

Dynamic mode atomic force microscopy (DFM) is commonly used because of its ability to probe soft and fragile samples, due to the minimization of sample damage

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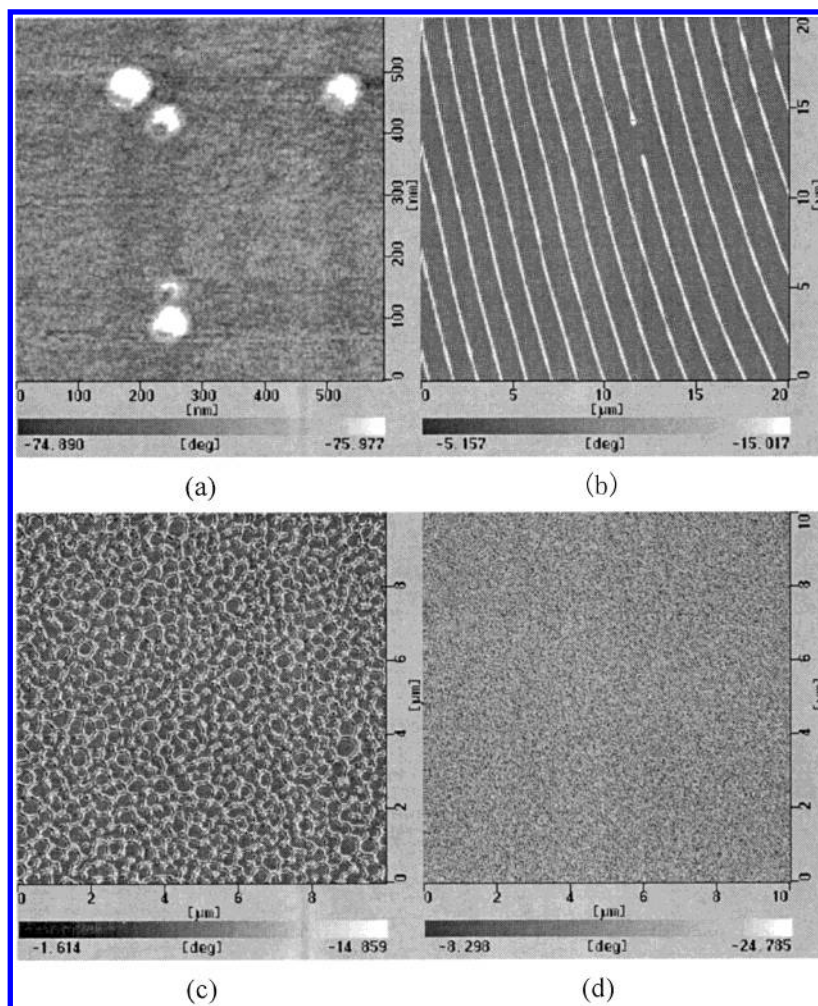(5) Weill, A.; Dechenawx, E. *Polym. Eng. Sci.* **1998,** *28,* 945.
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Figure 1. Phase images of SEBS films at different concentrations: (a) 1×10^{-4}%; (b) 0.025%; (c) 0.05%; (d) 0.25%. The sample of (a) is prepared by solution cast, and samples (b), (c), and (d) are prepared by spin coating. The average height of the strips in (b) and the average height of the nets in (c) are 9.0 and 8.1 nm, respectively. The film thickness of (d) is about 22.0 nm.

during the scans. In one type, the oscillation frequency is fixed and the image records the change of the oscillator phase delay that has a high sensitivity to the variation of the local properties. A number of studies have shown the possibility to extract useful information from the phase images of soft samples, such as blends or copolymers.[10]

In this work, DFM was used to explore the morphology evolution of the spin-coated SEBS triblock copolymer films with the variation of the polymer concentration. In particular, this work aimed at investigating whether a shearing and stretching field in the spin-coating process could cause flexible polymer coils or aggregates to orientate.

Experimental Section

SEBS copolymer is Kraton G1651 (Shell Development Co.) with styrene 33 wt %. It is a clear linear triblock copolymer with two PS end blocks, each with a molecular weight of 29 000 and an ethylene–butylene midblock with a molecular weight of 116 000.[11] The films were prepared with a KW-4A precision spin-coater (Chemat Technology, Inc.) in a glovebox. The spin coating was carried out by dispensing a substantial excess of the SEBS/

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toluene solutions with various concentrations (0.025%, 0.05%, 0.10%, 0.25%, 0.50%, 1.00%, w/v) at room temperature onto a freshly cleft mica substrate (~1 cm²) spun at 4000 rpm for 30 s. The coated substrates were then heated in a vacuum oven at 50 °C for 2 h to remove any remaining solvent.

The DFM measurements in this work were all carried out by the use of SPA300HV with an SPI3800 controller (Seiko Instruments Industry Co., Ltd.) at room temperature. The tip type was SI-DF20, and the cantilever used was fabricated from Si_3N_4 with a spring constant of 15 N/m and a resonance frequency of 141 kHz.
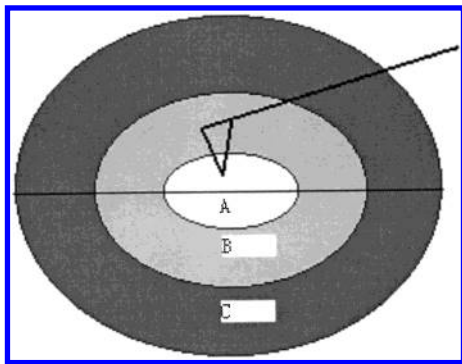
Results

The DFM phase images of the structures formed by spin-coating SEBS onto mica are shown in Figure 1. A gradual transition from the copolymer aggregates at a very lower concentration of 1×10^{-4}% to a continuous film with microphase-separated morphology at a higher concentration of 0.25% can be seen. At a very low concentration of 1×10^{-4}% of the copolymer, the nanosize copolymer aggregates from the cast film are observed (Figure 1a). Some SEBS aggregates are elliptic with an average aspect ratio of 1.5. The average diameter and the average height are 32 and 1.9 nm, respectively. The calculated $2R_g$ is 28.4 nm (R_g is the radius of gyration of the unperturbed chain), which is slightly less than the measured value obtained with atomic force microscopy (AFM). At concentrations 0.025% and 0.05%, one can see from parts b and c of Figure 1 that the substrates are not

Figure 2. The schematic diagram showing three different scanning regions A, B, and C in the radial direction.

covered completely by SEBS molecules, so the continuous films are not formed. The copolymer molecules form ordered stripes at a concentration of 0.025% and network structures at 0.05%. At a higher copolymer concentration (0.25%), a smooth continuous film with microphase-separated morphology (a 2 μm × 2 μm scan is shown in Figure 5b) is formed.

To test the uniformity of the film during the spin coating, the DFM images at different locations from the center of the substrate were obtained. Figure 2 is a schematic diagram showing three different scanning regions, A, B, and C. Figure 3 shows that the morphologies taken from the center part of the rotational axis differ from those of other regions in the radial direction at a concentration of 0.025%. The SEBS networks were observed near the center of the substrate; the orientation structures of elongated SEBS particles in the middle part and a discontinuous orientation structures on the edge of the substrate were observed as well. From the cross-section profile it can be seen that the distance between the two adjacent stripes in the middle part (780 nm) is smaller than that (1450 nm) between the two adjacent ones on the edge of the substrate. But the diameter (300 nm vs 300 nm) and the height (8.8 nm vs 9.1 nm) of each stripe are nearly the same. The morphology is regular and periodic as well and may be useful for novel anisotropic microelectronic device fabrication.

Figure 4 shows the gradually varying morphologies in different regions (A, B, and C) at a concentration of 0.05%. There is a self-similarity in pattern evolution in the radial direction. However, the size of the network grows with the increase of radius from the center to the edge of the substrate.

With increase of the copolymer concentration, the networks were filled in, forming first the polymer films with pinholes and finally a continuous film.[8] It has been noted that the average height of the net (7−10 nm) is equal to the average depth of the holes in the film. It can be deduced that the critical thickness or the smallest thickness forming a smooth continuous film should be equal to the average height of the net. Figure 5 shows the phase images of the continuous SEBS films without pinholes made at different concentrations. Because the cantilever driving amplitude A_0 was fixed and the images were recorded at a high set point value (light tapping), the tip−sample interaction was dominated by attractive forces (e.g., adhesion and capillary forces).[12,13] Therefore the bright parts on the phase images are corresponding to the parts with higher tip−sample attractive forces,[12]

that is, the bright parts correspond to poly(ethylene−butylene) (PEB) domains and the black parts to PS domains. This assignment is consistent with the fact that PS is the minority component in the block copolymer and that it is expected to form isolated microdomains in a continuous PEB matrix phase (Figure 5c). At a concentration of 0.1%, the PEB microdomains were detected, but the domain edge was indistinct. At a concentration of 0.25%, the phase image shows the microphase separation. The small circular and cylindrical PS domains (dark parts) are dispersed in the PEB matrix (bright parts). With further increase of the copolymer concentration, the microphase separation is seen more clearly. At a concentration of 1.0%, phase contrast shows a wormlike structure with black domains in a bright continuous matrix. The specific value of the periodicity in the image obtained is between 30 and 32 nm.

Discussion

To analyze the process of morphology formation at different concentrations, the structure of SEBS in the solutions is considered first. In a solvent, block copolymers undergo microphase separation in accordance with the size of molecules. As a result, micelles form at a low block copolymer concentration by one block aggregating into spherical or cylindrical clusters. When the length of the cylindrical micelles exceeds a characteristic length, the cylindrical micelles may become flexible and behave as giant polymer molecules.[14,15] As for SEBS, the molecules in solutions should adopt a highly stretched conformation due to much stronger repulsive interactions between PS and PEB blocks. This is because toluene is a solvent which is only a little better for PS block chains in solubilization than for PEB block chains. (Solubility parameter of toluene δ = 8.9 cal$^{0.5}$/cm$^{1.5}$, δ_{PS} = 8.7−9.1 cal$^{0.5}$/cm$^{1.5}$, and δ_{PE} = 7.9−8.1 cal$^{0.5}$/cm$^{1.5}$. Data for δ_{PEB} have not been found in the literature.) In our experiment, the concentration of 0.025% should be lower than the overlap concentration C^* of SEBS and the concentration of 0.05% higher than C^*. Although the SEBS concentration used deviated from the conditions under which ordered micellar phases were observed at a low but finite concentration, intermolecular interactions between the block copolymers might induce weak ordering.[16] As the concentration increased during the spin coating, the chains or weak ordering aggregates began to overlap or entangle, forming ordered structures.

During the spin-coating process, it was assumed that the flow had reached a stable condition at the third and the fourth stages, the centrifugal and viscous forces were hence in balance (eq 1), and the fluid flow velocities increased radially outward from the origin (eq 2):[17]

$$-\eta(\partial^2 v/\partial z^2) = \rho\omega^2 r \qquad (1)$$

$$v = (\rho\omega^2 r/\eta)(hz - z^2/2) \qquad (2)$$

The radial and the vertical velocity gradients are expressed, respectively, as follows:

$$\partial v/\partial r = (\rho\omega^2/\eta)(hz - z^2/2) \qquad (3)$$

$$\partial v/\partial z = (\rho\omega^2 r/\eta)(h - z) \qquad (4)$$

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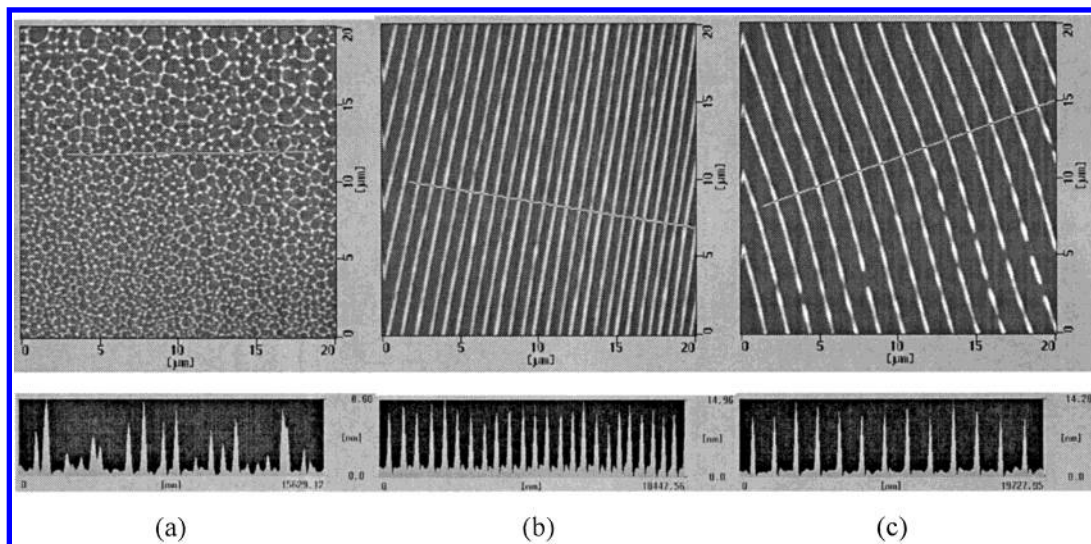
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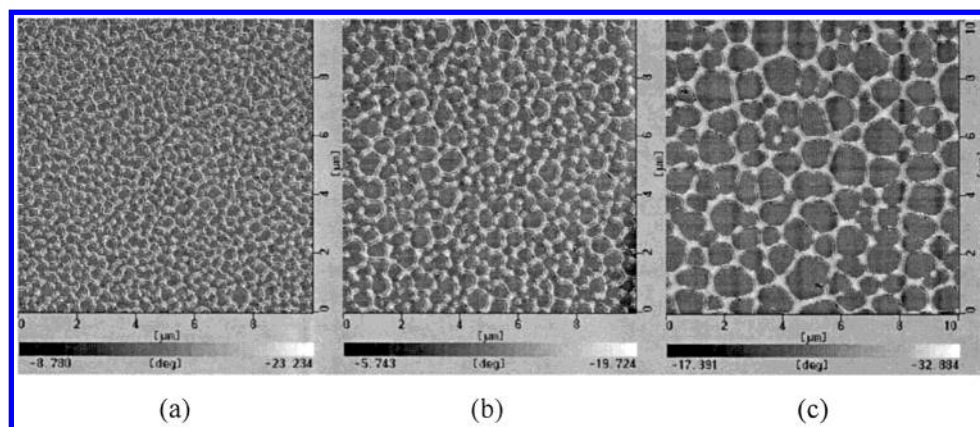(16) Kent, M. S.; Tirrell, M.; Lodge, T. P. *J. Polym. Sci., B: Polym. Phys.* **1994**, *32*, 1927.

Figure 3. Topographical images and sectional view along the line in the AFM images of the SEBS films spin coated at the copolymer concentration of 0.025%, scanned at different regions: (a) region A; (b) region B; (c) region C.

Figure 4. Phase images of SEBS films spin coated at the copolymer concentration of 0.05%, scanned at different regions: (a) region A; (b) region B; (c) region C.
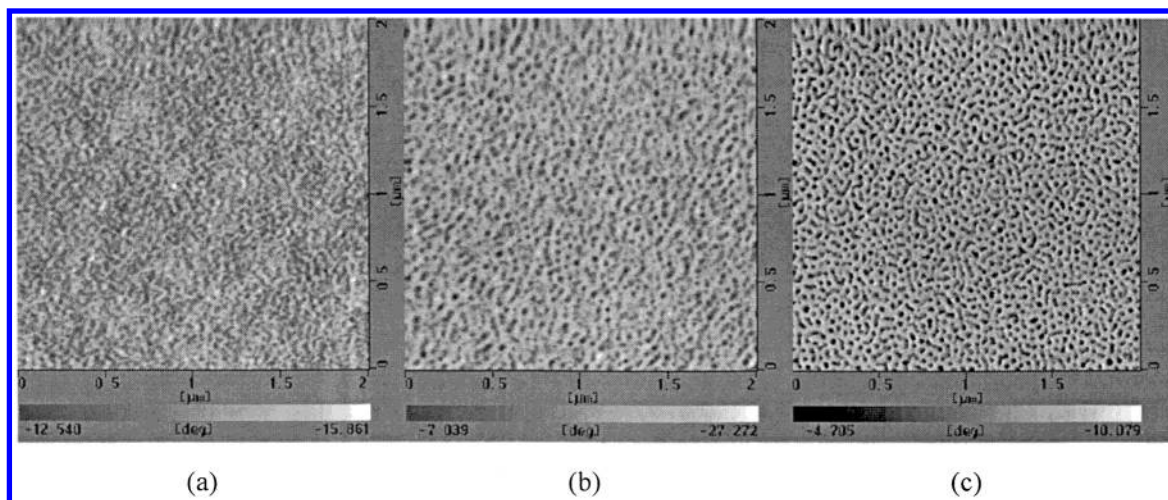
Figure 5. Phase images showing microphase separation of the SEBS films at different copolymer concentrations: (a) 0.10%; (b) 0.25%; (c) 1.0%. Film thicknesses are about (a) 10.5 nm, (b) 22.0 nm, and (c) 118.0 nm.

where z and r define a cylindrical coordinate system aligned with the axis of substrate rotation, v is the fluid velocity in the radial direction, ρ is the fluid density, ω is the rotation rate, η is the viscosity, and z is in the range of from 0 to h at the top of the surface.

(a) Morphology Formation at a Concentration of 0.025%. When the SEBS solution is flowing on the substrate, the vertical velocity gradient (eq 4) makes the solution film thin. As the solution film reaches a critical thickness, the holes of the solvent in the copolymer solution film are nucleated to minimize the elastic energy.[18] Then

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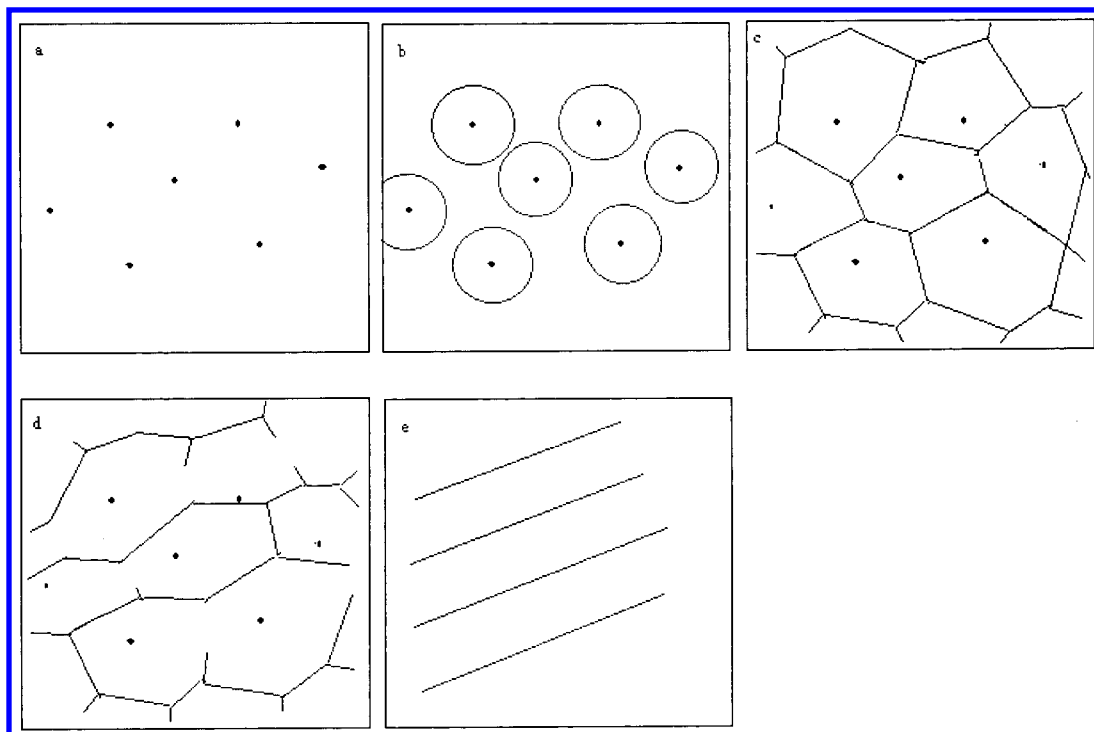
Figure 6. A model for the generation of the orientation structure. Small holes are nucleated on the solution thin film (a) and then grow up (b) to form a transient network (c). The nets are distorted, disconnected, and elongated continually (d) and finally evolved into orientated structure (e).

the holes grow and the solution film retreats. The retreating film runs into another retreating film from the adjacent hole, forming transient nets. The final structures are determined by both the connectivity force of transient nets and the driving force produced by the shearing and stretching field in the spin-coating process. At a concentration of 0.025%, the connectivity force of transient nets is small due to the weak overlapping among the SEBS aggregates. At the center of the substrate, the SEBS networks exist as a result of the low angular velocity of the fluid and the more SEBS molecular aggregates that exist near the center. The smaller driving force (eq 1) cannot make the nets break up and stretch.

When r is extended through to region B, the periodically orientated stripes can be observed. The shear-induced domain elongation in the phase-separated polymer mixtures has been reported.[19-22] The shear flow can elongate the domains and promote the collisions and coalescence between the domains in the flow direction, while in the perpendicular direction the average size of the domains is almost unchanged.[22] The experiments[19,20] have revealed that a strong simple shear flow achieves a stringlike phase-separated structure along the flow direction due to the chain-stretching effect.[21] In region B, the shearing and stretching forces are greater than the attractive forces among SEBS aggregates, the transient nets distort and elongate in the same direction, and the sides of nets break up in the perpendicular direction. The vertical velocity gradient in depth (the fluid contacting the substrate has a velocity of zero and the top layer of the fluid has the greatest velocity) creates a stream to move radially outward[4] and produces an effective rotational force on the SEBS aggregates. The lower end of the deformed SEBS

aggregates experiences smaller radial motion, while the upper end is pushed out more rapidly and makes the SEBS aggregates rotate and elongate in the flow direction further. Meanwhile, the radial velocity gradient also causes the deformed SEBS aggregates to elongate and align in the radial direction. The evolution may be accompanied with the relinking or the joining of SEBS aggregates. The total effect leads to the formation of the parallel orientation structures in the film. When r is increased further, reaching region C, the radial and vertical velocity gradients are big enough to make the SEBS continuous orientation structure break and form a discontinuous structure. The schematic drawings of the evolving of the orientation structures discussed above are shown in Figure 6. One can see from the formation mechanism of the ordered strips discussed above that the ideal distributions of the strips should be in the radial direction. However, it can be deduced that the distributions are not exactly in the radial direction according to the careful analysis of Figure 1b and Figure 3c; a smaller deviation from the radial direction may exist.

(b) Morphology Formation at a Concentration of 0.05%. At a copolymer concentration of 0.05%, the network structures were observed. Stange et al.[8] also observed the network structure when spin coating the PS solutions on a Si wafer and discussed it in terms of a specific mechanism leading to film rupture in the spin-coating process. It was reported that a gel having undergone a volume-shrinking phase transition also formed a bubble-like structure.[23] Network structures could be formed by evaporating solutions of star-shaped polystyrene–polyparaphenylene block copolymers in carbon disulfide under a flow of moist gas.[24] Tanaka[18] thought that the network structures reported in the literature[23-25] were likely induced by the

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same mechanism. Our opinion is that the physical origin of the network structure during the spin coating is similar to that proposed by Tanaka.[18] At the third and the fourth stages during the spin-coating process, the solution film thins gradually dominated by viscous forces and solvent evaporation. When the solution film reaches a critical thickness, the holes of the solvent in the copolymer solution film are nucleated. Then the holes grow and the solution film retreats. The volume of the solution film decreases with time. The retreating film runs into another retreating film from an adjacent hole. Owing to SEBS molecules entangling with one another, the large scission energy of SEBS aggregates, and the driving force under a shearing and stretching field less than the connectivity force of the transient nets in the whole radius range, a network structure is retained. When the viscosity of the remaining solution is high enough, a gelation process takes place and the network structure is frozen in place.

With the increase of the copolymer concentration, the networks are filled in, forming the polymer films containing holes first and finally a continuous film. Because the phase behavior of SEBS triblock copolymer has been studied,[13,26] it is not covered in detail in this paper.

To our knowledge, the orientation structure of flexible polymer molecules has not been found in previous studies in spin coating. Our results also show that the film morphology in a radial direction is different at a low polymer concentration. Although the force field during the spin coating is very complicated, under some conditions, the orientation structure could be formed. The orientation structure might be applied to novel anisotropic microelectronic device fabrication.

Conclusions

The surface morphology evolution of SEBS triblock copolymer films formed in the spin-coating process has been investigated by DFM. The orientation structures and the network structures were observed at the copolymer concentrations of 0.025% and 0.05%, respectively. The formation mechanisms are discussed based on the mechanism of Tanaka,[18] the equations of Emslie et al.,[17] and the shape of the SEBS micelle in solutions. A continuous film with a microphase-separated structure is formed with the increase of the copolymer concentration. The observation of the orientation structure showed that a shearing and stretching field in the spin-coating process could cause flexible polymer coils or aggregates to orientate.

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