Formation of Microscopic Ordering and Macroscopic Patterns in Solid Polyacrylate−Tetraoctylammonium Bromide Films

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Received December 1, 2005; Revised Manuscript Received February 11, 2006

ABSTRACT: Previously, we observed the rather unusual macroscopic patterns that formed in the solid films cast from organic solutions containing a surfactant tetraoctylammonium bromide (TOAB) and a chromophore-containing polymer, and we proposed that the patterns resulted from the phase separation between the polymer-rich amorphous structures and the surfactant-rich mesomorphous structures (*Macromolecules* **2005**, *38*, 9266). In this study, it was found that the mesomorphous structure and macroscopic patterns could also form in the solid films cast from a mixture of toluene, TOAB, and polyacrylates with common polar groups like hydroxyl or carboxyl. It was also found that the higher polymer chain mobility as well as the balanced interactions between the three components in the system are crucial to the formation of mesomorphous structure and the macroscopic patterns. The patterns and the ordered mesomorphous structures were found to be destroyed at the elevated temperatures, further proving that the pattern formation needs the participation of solvent. The small-angle X-ray scattering (SAXS) investigations shows that different polar groups in the polymer chains cannot make any difference in SAXS profile in terms of peak position ratios, suggesting that the resultant mesomorphous structures do not change with the type of the polar groups in the polymer chains. These results prove that the ordered supramolecular structures can also be formed in the polymer−surfactant-organic solvent system, and the weak van der Waals interactions can lead to the formation of mesomorphous structures and macroscopic patterns.

Introduction

Self-assembly is the spontaneous intermolecular association via noncovalent bonds, and these noncovalent bonds usually include electrostatic interactions, hydrogen bonds, or hydrophobic interactions,[1] and the supramolecular structures resulting from the self-assembly have attracted much attention due to their enhanced materials properties.[1−6] The supramolecular structures formed by polymer and surfactants often exhibit unique mechanical, optical, electrical, and biological properties,[1,2,7−11] and these structures can form a novel class of functional materials which have aroused great interest in recent years due to their simple preparation approaches and interesting properties; on the other hand, the interactions between the polymers and surfactants have been extensively studied because of their fundamental importance and their numerous technological applications.[12−17] In the solid polyelectrolyte−surfactant systems prepared from water or highly polar solvents, the strong interactions between them such as electrostatic interaction or hydrogen bonding often result in highly ordered mesomorphous structures, such as cubic, hexagonal, lamellar, etc.[8,9,18−22] However, for polymer−surfactant system in low-polar or nonpolar solvents, few reports have been found involving the investigation of the mesomorphous structure formation.

Previously, we observed rather unusual patterns formation by dissolving tetraoctylammonium bromide (TOAB) and a chromophore-containing random copolymer into some low-polar solvents like toluene and then casting the solution on the glass substrate and drying the solution in the air. We found that during the evaporation of the solvent, water-wave-like macroscopic patterns composed of concentric rings were formed on the substrate.[23] We also found that the concentric rings, with their diameters being up to centimeters, consist of convex ridges and concave valleys, with the former being amorphous phase and the latter being ordered mesophase. We supposed that the formation process of the macroscopic patterns was as follows: first the mesomorpous structure was formed by surfactant molecules and polymer chains during the solvent evaporation, then phase separation occurred between the surfactant-rich mesophases and the polymer-rich amorphous phases, and finally, the interfacial tension “pushed” the polymer-rich amorphous phase to form the concentric rings.[23] The synthesized polymer is a random copolymer prepared by copolymerization of a thiophene-containing acrylate, methyl methacrylate, and ethyl acrylate in organic solvent; we found that no mesomorphous structure and macroscopic pattern could be obtained in the polymer−surfactant system if we removed the thiophene-containing acrylate from the polymer chains,[23] suggesting that the pendant thiophene-containing chromophore groups were critical to the formation of mesomorphous structure.

The mesomorphous structure is the key to the pattern formation, and the driving forces for mesophase formation have yet to be clarified. There is no Coulombic force, hydrogen bond, or other strong interaction in the polymer−surfactant−toluene system, we therefore anticipated that in this system the formation of the mesomorphous structure was probably driven by the weak van der Waals interactions, especially the polar interactions. If this assumption is true, the pendant chromophore group in our previously synthesized polymer[23] should not be the only group that can form mesophases and macroscopic patterns, and there are some polymers with other pendant polar groups that should

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10.1021/ma052577c CCC: $33.50

also be able to form macroscopic patterns with the surfactant TOAB.

The possibility of forming well-organized patterns on a macroscopic scale leads to new approaches for producing polymer-based composite materials with periodic modulations in properties,[24−26] which not only can be applied in the study of phase separations and surface phenomena but also have potential importance in patterning technologies, such as coating technologies, preparation of polymer films, optical elements, etc. Among the investigations on the macroscopic patterns, Whitesides[24] and co-workers studied macroscopic patterning in poly(dimethylsiloxane) through a hierarchy of interactions in self-assembly. Sharma[25] reported self-organized polymer patterns resulting from the evaporation of an organic solvent drop on a soluble layer of polymer. Kumacheva[26] generated periodic patterns by buoyancy-driven convection in the monomeric fluid methacryloxypropyl-terminated dimethylsiloxane and preserved the patterns by controlled photopolymerization.

In the present work, to gain better understanding of the mesophase and pattern formation in the polymer−surfactant−organic solvent system, we try to further investigate the driving force for the macroscopic pattern formation and to verify that the polar groups in the polymer side chains are critical to the formation of the mesophase structure and eventually the macroscopic pattern. Thus, we substituted the thiophene-containing polar groups with the common polar groups such as carboxyl and hydroxyl groups, prepared a series of random copolymers of acrylates with pendant carboxyl or hydroxyl groups, and studied the pattern formation of the solid-state systems consisting of these polyacrylates and the surfactant TOAB. It is found that, under proper conditions, the pendant polar groups in the polymer chain, such as hydroxyl or carboxyl, can also lead to the formation of mesomorphous structure and macroscopic pattern; the properties of the synthesized polymers are very important for the pattern formation, but only with the right combination of the amount of polar groups, the molecular weight of the polymer, and the rigidity of the polymer chain can the mesomorphous structure and macroscopic pattern be obtained in the solid films.

Experimental Section

Materials. Acrylic acid (AA), 2-hydroxyethyl acrylate (HEA), methyl methacrylate (MMA), ethyl acrylate (EA), tetraoctylammonium bromide (TOAB), tetrabutylammonium bromide (TBAB), tetradodecylammonium bromide (TDAB), 1-dodecanethiol, and *tert*-butylhydroquinone were purchased from Aldrich Chemicals. Acrylic acid, 2-hydroxyethyl acrylate, methyl methacrylate and ethyl acrylate were distilled before use. N, N-dimethylformamide (DMF), toluene, tetrahydrofuran (THF) and methanol were analytically pure solvents, and they were distilled before use.

Polymerization. Acrylic acid (for carboxyl-containing polyacrylate, CPA) or 2-hydroxyethyl acrylate (for hydroxy-containg polyacrylate, HPA), methyl methacrylate, and ethyl acrylate were dissolved in dry dimethylformamide. The polymerization was carried out in the presence of azobis(isobutyronitrile) (AIBN) as an initiator. For each reaction, the weight percentage of monomers and initiator in the reaction system was around 20 wt %. The polymerization medium was outgassed twice before heating and stirring at 70 °C for 18 h under nitrogen. Then the polymerization mixture was poured into cold methanol. The isolated copolymer was redissolved in THF and precipitated in cold methanol, filtered, washed with deionized water, and finally dried under vacuum at 60 °C for 72 h.

Conversion Rate Determination. The conversion rate for the polymerizations was determined via gravimetry. Right after the polymerization, by evaporating off the solvent, residual monomer, and any other volatile components and by weighing of the remaining polymer solid, the amount of the residual monomer can thus be calculated from the knowledge of the recipe. In this study, after 18 h of polymerization, 10 g of solution was taken out and then a given amount of *tert*-butylhydroquinone was added to inhibit the polymerization of residual monomers; then the sample was dried under vacuum at 100 °C for conversion rate determination.

Film Preparation. The polymer−surfactant films were prepared as follows: the surfactant and the polymer at a certain ratio were dissolved in toluene to form a solution with the concentration of 6 wt %, a clear solution resulted, and then the solution was filtered through a 0.50 μm Teflon filter and cast on 2.5 cm × 4 cm glass substrates. Then a culture dish was covered over the glass substrate. Afterward the films were allowed to dry in a thermostat at a constant temperature.

Characterization. Molecular weight and molecular weight distribution was determined by Waters Gel Permeation Chromatography with the 2410 RI detector, polystyrenes were used as standard. ^{1}H NMR spectra were recorded on a Varian Unity Inova 500 MHz NMR spectrometer. Polarizing micrographs were taken on a Zeiss Axiolab Polarizing microscope. Small-angle X-ray scattering (SAXS) measurements were performed on Philips X'Pert PRO X-ray diffractometer (Cu Kα) (scattering vector $q = (4\pi/\lambda) \times \sin\theta$; 2θ is the angle between the incident light and the scattered light).

Results and Discussion

Preparation of Acrylate Copolymers. To investigate the effects of polymer properties on the pattern formation, we prepared a series of acrylate copolymers with hydroxyl or carboxyl groups. By adjustment of the feed of the carboxyl-containing or hydroxyl-containing monomers, the polyacrylates with different amounts of pendant carboxyl groups (the carboxyl-containing polyacrylate was designated as CPA) or hydroxyl groups (the hydroxyl-containing polyacrylate was designated as HPA) were obtained. The monomer feed for polymerization, the molecular weight, and the glass transition temperature (T_g) of the resultant polyacrylates are listed in Table 1.

Macroscopic Patterns Formed by Surfactant and Copolymers with Hydroxyl or Carboxyl Group. The polymer and the surfactant TOAB were dissolved in toluene with an appropriate polymer-to-surfactant ratio, a colorless and transparent solution was obtained, and then the solution was cast on glass substrate and was allowed to dry in a thermostat at a certain temperature. Under appropriate conditions, the macroscopic pattern composed of millimeter-to-centimeter-scale concentric rings appeared during the solvent evaporation. The photographs of the macroscopic patterns formed in the CPA-TOAB and HPA-TOAB solid films are shown in Figure 1. The successful formation of macroscopic patterns by using copolymers with some common polar groups indicates that our previously synthesized thiophene-containing polymer[23] is not the only polymer that can form macroscopic patterns with TOAB. This kind of pattern formation is a rather general phenomenon, as some other polymers with common polar groups can also form macroscopic patterns with TOAB under favorable conditions, and it is highly possible that the polar interaction is one of the major driving force for the pattern formation.

Effects of Polymer Properties on Pattern Formation. The polymer properties, such as the polar group (hydroxyl or carboxyl) contents in the polymer and the molecular weight as well as the glass transition temperature of the polymers, were all found to affect the formation of macroscopic pattern, as shown in Table 2.

The acrylic acid and three acrylates in this study are widely used monomers for copolymerizations, and the reactivity ratios

Table 1. Monomer Feed, Molecular Weight and T_g of the Synthesized Polyacrylates

polymer name	AIBN (wt %)[a]	AA (mol %)[d]	HEA (mol %)[d]	MMA (mol %)[d]	EA (mol %)[d]	T_g (°C)	M_w	PD[b]
Polyacrylate with Pendant Carboxyl Groups (CPA)								
CPA-1	5	6.8	0	83.4	9.8	85	5.2×10^4	1.85
CPA-2	5	9.5	0	80.8	9.7	85	4.6×10^4	2.05
CPA-3	5	13.4	0	77	9.6	86	5.8×10^4	2.02
CPA-4	5	19.7	0	70.9	9.4	85	5.5×10^4	1.95
CPA-4-R	5	19.7	0	80. 3	0	106	4.7×10^4	2.13
CPA-4-H1	1.2	19.7	0	70.9	9.4	86	1.16×10^5	1.82
CPA-4-H2	0.5	19.7	0	70.9	9.4	87	1.89×10^5	1.76
CPA-4-SH[c]	0.5	19.7	0	70.9	9.4	85	3.5×10^4	1.93
Polyacrylate with Pendant Hydroxyl Groups (HPA)								
HPA-1	5	0	6.8	83.1	10.1	86	4.3×10^4	1.78
HPA-2	5	0	9.5	80.2	10.3	87	6.8×10^4	1.96
HPA-3	5	0	13.4	76.4	10.2	87	4.6×10^4	2.24
HPA-4	5	0	19.7	70.0	10.3	86	5.8×10^4	2.06
HPA-4-R	5	0	19.7	80.3	0	103	5.5×10^4	2.29
HPA-4-H	0.5	0	19.7	70.0	10.3	89	1.95×10^5	2.05

[a] The amount of AIBN was based on the total weight of the monomers. [b] PD: polydispersity. [c] 1-dodecanethiol (1.5 wt %) was added and the amount of the chain transfer agent was based on the total weight of the monomers. [d] The mole percentage of a monomer based on the total amount of all the monomers.

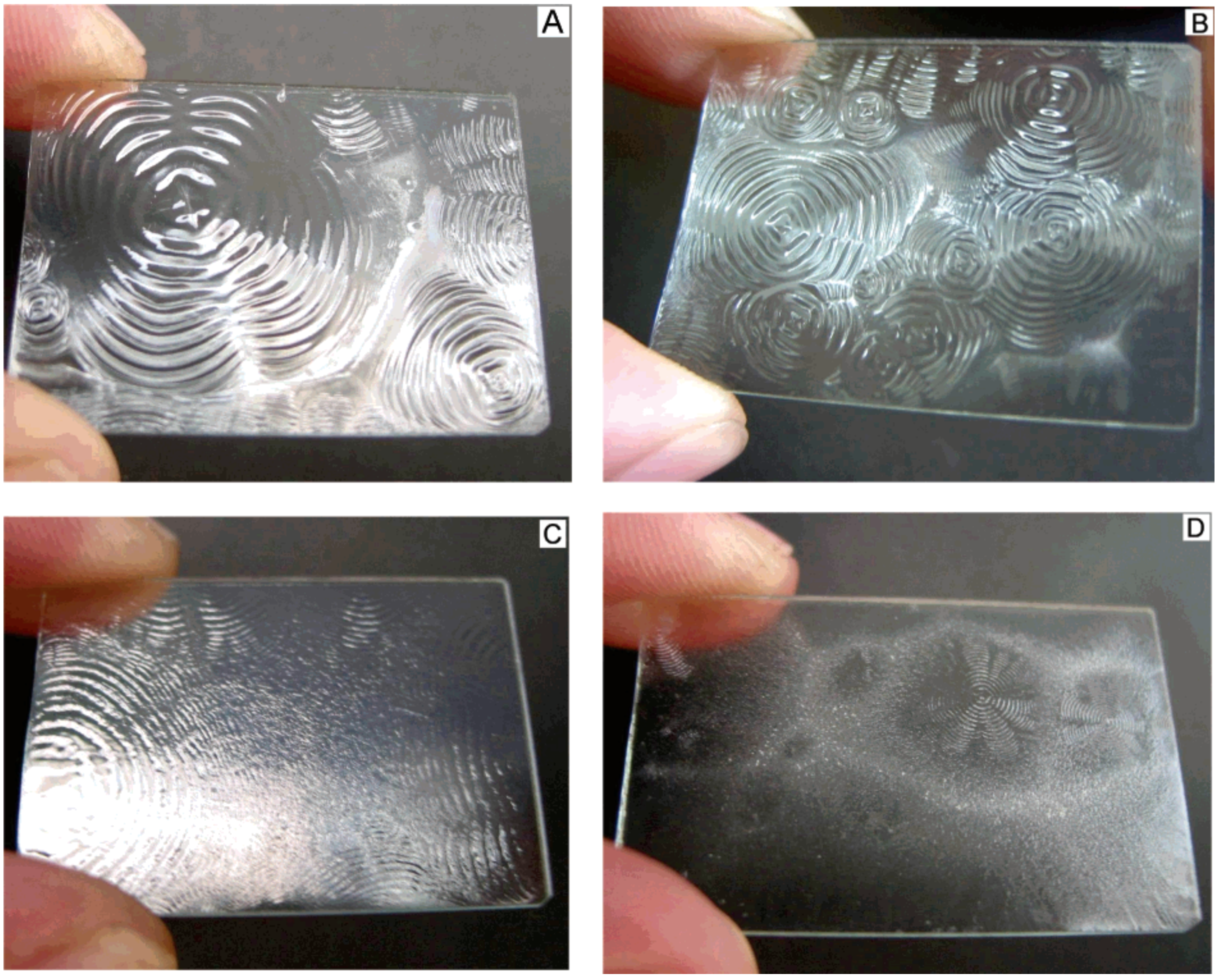

Figure 1. Photographs of the macroscopic patterns formed on 4.0 cm × 2.5 cm glass plates by polymer and surfactant TOAB from toluene solution at 25 °C and the amount of the polymer/TOAB solution cast on the glass was the same. Key: (A) well-formed pattern by using CPA-4 with a polymer content of 40 wt %; (B) well-formed pattern by using HPA-4 with a polymer content of 50 wt %; (C) poorly formed pattern by using CPA-3 with a polymer content of 30 wt %; (D) poorly formed pattern by using HPA-4 with a polymer content of 40 wt %.

between them are all in moderate range,[27] for example, for the copolymerization of AA and EA, the reactivity ratios r_1 and r_2 are 0.91 and 1.02, respectively, while the reactivity ratios r_1 and r_2 for copolymerization of HEA and EA are 0.97 and 0.5, respectively.[27] So in this study, these monomers can easily form copolymers. On the other hand, we found that for all the copolymerizations, the conversion rates for the monomers exceeded 99% upon 18 h of solution polymerization. Thus, in this study, the monomer contents in the polymers are close to the monomer feeds, and we roughly take the monomer feeds as the monomer contents in the polymers, as seen in Table 2.

From Table 2 we can see that, first, the amount of polar groups in the polymers is critical to the formation of macroscopic pattern. As for the polyacrylates with pendant carboxyl

Table 2. Effects on the Formation of the Macroscopic Pattern[a]

polymer	T_g	mol wt	AA or HEA feed (mol %)[b]	polymer content in solid film wt %)	pattern formation
CPA-1	85	5.2×10^4	6.8	10−90	○
CPA-2	85	4.6×10^4	9.5	10−30, 50−90	○
CPA-2	85	4.6×10^4	9.5	40	⊙
CPA-3	86	5.8×10^4	13.4	10, 20, 60−90	○
CPA-3	86	5.8×10^4	13.4	40	●
CPA-3	86	5.8×10^4	13.4	30, 50	⊙
CPA-4	85	5.5×10^4	19.7	10, 20, 60−90	○
CPA-4	85	5.5×10^4	19.7	40	●
CPA-4	85	5.5×10^4	19.7	30, 50	⊙
CPA-4-R	106	4.7×10^4	19.7	10−90	○
CPA-4-SH	85	3.5×10^4	19.7	10, 20, 60−90	○
CPA-4-SH	85	3.5×10^4	19.7	40	●
CPA-4-SH	85	3.5×10^4	19.7	30, 50	⊙
CPA-4-H1	86	1.16×10^5	19.7	10−90	○
CPA-4-H2	87	1.89×10^5	19.7	10−90	○
HPA-1	86	4.3×10^4	6.8	10−90	○
HPA-2	87	6.8×10^4	9.5	10−90	○
HPA-3	87	4.6×10^4	13.4	10−30, 50−90	○
HPA-3	87	4.6×10^4	13.4	40	⊙
HPA-4	86	5.8×10^4	19.7	10−30, 70−90	○
HPA-4	86	5.8×10^4	19.7	40, 60	⊙
HPA-4	86	5.8×10^4	19.7	50	●
HPA-4-R	103	5.5×10^4	19.7	10−90	○
HPA-4-H	89	1.95×10^5	19.7	10−90	○

[a] The films were cast at 25 °C, the solvent was toluene and the surfactant was tetraoctylammonium bromide (TOAB); (○) no pattern formed; (⊙) poorly formed macroscopic pattern; (●) well-formed macroscopic pattern. [b] AA: acrylic acid; HEA: 2-hydroxyethyl acrylate. The AA or HEA feed is roughly regarded as the AA or HEA content in polymers.

groups (CPA), when the amount of polar carboxyl groups was too low (CPA-1), no macroscopic patterns can be obtained, no matter what the polymer content in the solid film was; the macroscopic patterns can only be obtained with the polymers CPA-2, CPA-3, and CPA-4, while the well-formed macroscopic pattern (see Figure 1) can only be obtained with the polymers CPA-3 and CPA-4. Similarly, for the polyacrylates with pendant hydroxyl groups (HPA), macroscopic patterns can only be obtained with the polymer HPA-3 and HPA-4, and the well-formed macroscopic pattern can only be obtained with the polymer HPA-4. Compared with the polymer CPA, higher amounts of hydroxyl groups are needed to obtain the macroscopic pattern, probably because the carboxyl groups have higher polarity compared with the hydroxyl groups. As we tried to use the polymers with even higher carboxyl content (>25 mol %) for the pattern formation, we could not obtain a well-formed pattern. These results indicate that the polar interaction between the polar groups of the polymer and the surfactant is essential to the formation of macroscopic patterns. For the macroscopic pattern formed by using CPA-4, the sizes of the convex ridges and concave valleys are about 0.8 and 0.6 mm, respectively, and as the amount of the polar groups AA was reduced (CPA-3 or CPA-2), both the circular ring dimension and the inter-ring spacing became smaller. As for the formation of microscopic mesomorphous phases through self-assembly in well-known polyelectrolyte−surfactant complex in water or high-polar solvents, the driving force is the electrostatic interaction, sometimes reinforced by a hydrophobic interaction or a hydrogen bond.[1,2,5] However, in this study, the macroscopic mesomorphous phases were obtained by dissolving polymer and a structurally symmetrical surfactant in the low-polar solvent toluene, hence the above-mentioned three strong interactions do not exist. In this case, the driving force(s) for the formation of microscopic ordering (mesomorphous region) should be the van der Waals interactions between polymer chain and surfactant, including both polar interactions and nonpolar interactions. In a toluene solution of polymer and surfactant, the polar interaction is the stronger one, and the polar interactions between polymer chains and surfactant molecules not only interfered with the crystallization of surfactant molecules during the solvent evaporation but also drove the formation of the mesomorphous structure. When the amount of polar groups in the polymer reaches a certain point, the interactions among the three components may favor the formation of mesophase structure and macroscopic pattern. As the amount of polar groups in the polymer chains was further increased (>25 mol %), the nonpolar interactions in the system became weak, such as the interaction between the molecules of the low-polar solvent and the polymer chains, and the interaction between the nonpolar polymer backbones and the surfactant tails, and as a result, no well-formed patterns could be obtained. We therefore think that both the polar interactions and nonpolar interactions in the system contributed to the pattern formation, and the balanced interactions among the three components are also necessary for the pattern formation.

Second, the molecular weight of polymer was also found to be crucial to the formation of macroscopic pattern. We could not obtain the pattern with the polyacrylates prepared by adopting the commonly used recipes for solution polymerization, until we deliberately reduced the molecular weight by increasing the initiator amount to a relatively high level (5 wt % of the total weight of monomers) or by using chain transfer agent 1-dodecanethiol. As can be seen from Table 2, low molecular weight around $\sim 10^4$ (CPA-4, HPA-4, CPA-4-SH) favors the pattern formation, and no macroscopic patterns could be obtained with polyacrylates (with pendant carboxyl or hydroxyl groups) at higher molecular weights level ($\sim 10^5$). As we mentioned before,[23] the pattern formation is basically a solvent evaporation induced phase separation (or segregation) between the polymer-rich phase and surfactant-rich phase, and the patterns were formed before all of the solvent was evaporated off. In general, the effect of molecular weight of polymer on the phase separation in solution is governed by thermodynamic factors;[28,29] however, in the present work, the phase separation occurs during a solvent-casting process in rather thick films, and the resulting phase-separated morphology may be far from thermodynamic equilibrium, and the relaxation toward the equilibrium is hindered by kinetic barriers. Thus, we believe the mobility of polymer chains during the solvent evaporation plays an important role in the phase separation process. In this study, the original concentration for polymer/surfactant solution was 6 wt %, a concentration at which the polymer chain entanglement exists. With the evaporation of solvent (toluene), the concentration of the solution gradually increased and the solution turned into concentrated solution, leading to enhanced entanglement among polymer chains; on the other hand, with the solvent evaporation, the phase separation occurred between the polymer-rich amorphous phase and the surfactant-rich mesophase, thus the pattern formation was probably governed by the interplay between two processes: phase separation (segregation) and chain entanglement. In a low polar solvent like toluene, the polyacrylates with higher molecular weight should have a greater extent of chain entanglement than those with lower molecular weights. Therefore, as the polymer/surfactant solution was cast on the glass substrate, the total composition of the solution changes during the solvent evaporation, and at some specific composition of the mixture, the bionodal region in the phase diagram was passed and the phase separation was about to take place; for the polyacrylates with lower molecular weight, they were capable of undergoing phase separation before their chains were frozen during the solvent evaporation, while those with higher molecular weight could not undergo phase separation due to their lower chain mobility caused by the higher extent of chain entanglement.

Third, the glass transition temperature of polymer chain is also a decisive factor for the pattern formation. By copolymerizing the carboxyl or hydroxyl-containing monomer with methyl methacrylate (without ethyl acrylate), the polyacrylates CPA-4-R and HPA-4-R were obtained. The glass transition temperatures for the two polymers are remarkably higher than those polymers containing the repeat unit of ethyl acrylate. No macroscopic pattern formation could be obtained with CPA-4-R and HPA-4-R even if the polar group content was at a higher level. We suppose, this glass temperature dependence of pattern formation is also due to the different mobility of the polymer chains for different samples during the solvent evaporation. As the solutions are cast on the substrate at a certain temperature, the solvent evaporates and the composition for the mixture changes; at a specific composition of the mixture, thermodynamically the phase separation can take place. However, only the chain segments for the polymer with lower T_g can actually move and eventually undergo phase separation in a mixture of surfactant, polymer, and residual solvent, while those with higher T_g cannot undergo phase separation because the motion of the polymer chain segments are greatly limited at this film-forming temperature. Actually, the patterns were formed under a temperature which is much lower than the T_g for all polymers, we think the residual solvent in the mixture can increase the polymer chain mobility to some extent, but not enough to help the polymers with higher T_g to form patterns with the surfactant TOAB. We also found that, at higher film-forming temperatures such as 40, 50, and 60 °C, the polymers with higher T_g (CPA-4-R and HPA-4-R) could not form a pattern with the surfactant, we suppose, the higher temperature may enhance the chain motion for these polymers, but at higher temperature, the solvent evaporates even faster and the polymer chains have no enough time to undergo phase separation before they are frozen during the solvent evaporation.

Other Effects on Pattern Formation. The weight ratio of polymer to surfactant in the solution is also critical to the pattern formation. For the polymer CPA-4, as the weight percentage of the polymer was too low or to high, no macroscopic pattern appeared in the solid polymer−surfactant film as the solvent evaporated. As for the effect of surfactant, only the symmetrical surfactant with eight-carbon (C_8) tails (TOAB) can form macroscopic patterns, and the increase in the polar interaction by using surfactant tetrabutylammonium bromide (TBAB, with four C_4 alkyl tails) or the increase in the nonpolar interaction by using surfactant tetradodecylammonium bromide (TDAB, with four C_{12} alkyl tails) cannot lead to the formation of the macroscopic pattern. These experimental phenomena are similar to what we have observed in our previous study.[23]

In summary, since the pattern formation in the polymer−surfactant−solvent mixture is the result of the interplay of the solvent, the polymer and the surfactant, the condition for the pattern formation is rather complex. First, the polymer properties like the molecular weight and glass transition temperature can greatly influence the formation of macroscopic patterns, and the balanced interactions between the solvent, polymer, and the surfactant is also necessary for the pattern formation.

Polarizing Optical Micrographs. The morphologies of the macroscopic patterns were studied by using the polarizing optical microscope with some small rings in the pattern. Figure 2 shows the morphology for a same part of a pattern under parallel-polarized light and perpendicular-polarized light, respectively. With the comparison of Figure 2A and Figure 2B, it can be found that each brighter stripe in Figure 2A correspond

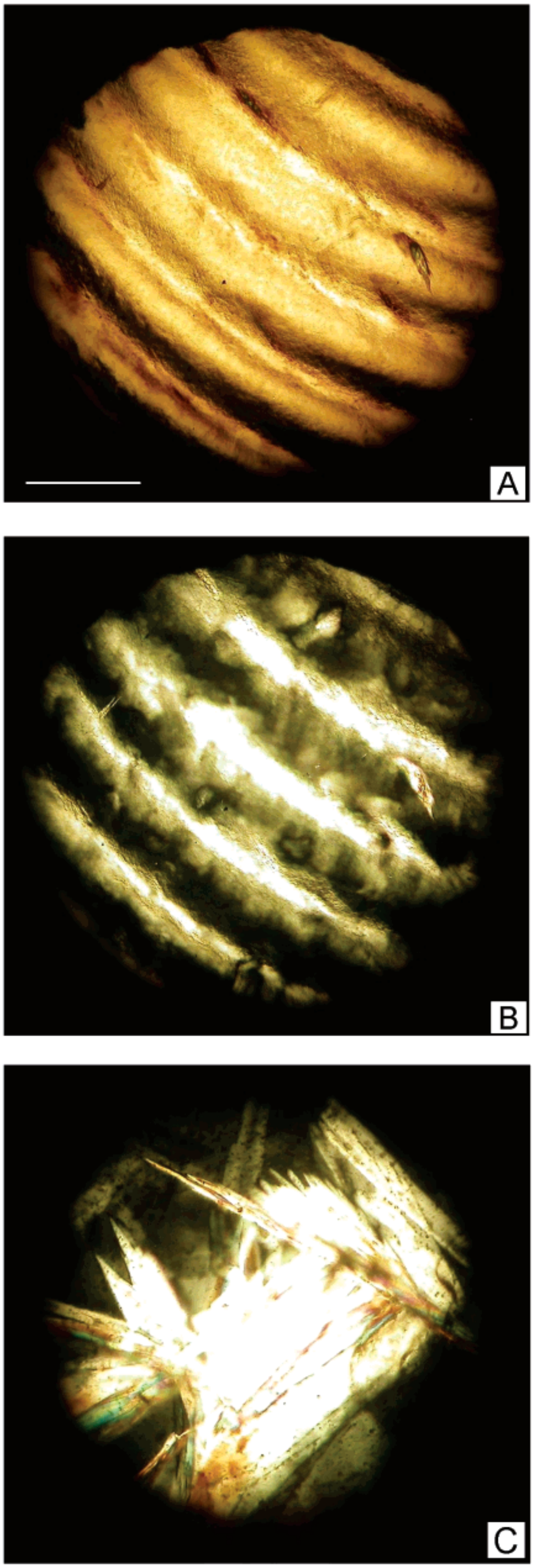

Figure 2. Photographs for films observed on polarizing optical microscope. Key: (A) part of a pattern under parallel-polarized light, scale bar = 0.5 mm; (B) same part of the pattern as that in Figure 2A under perpendicular-polarized light; (C) part of the film formed by toluene solution of pure TOAB under perpendicular-polarized light.

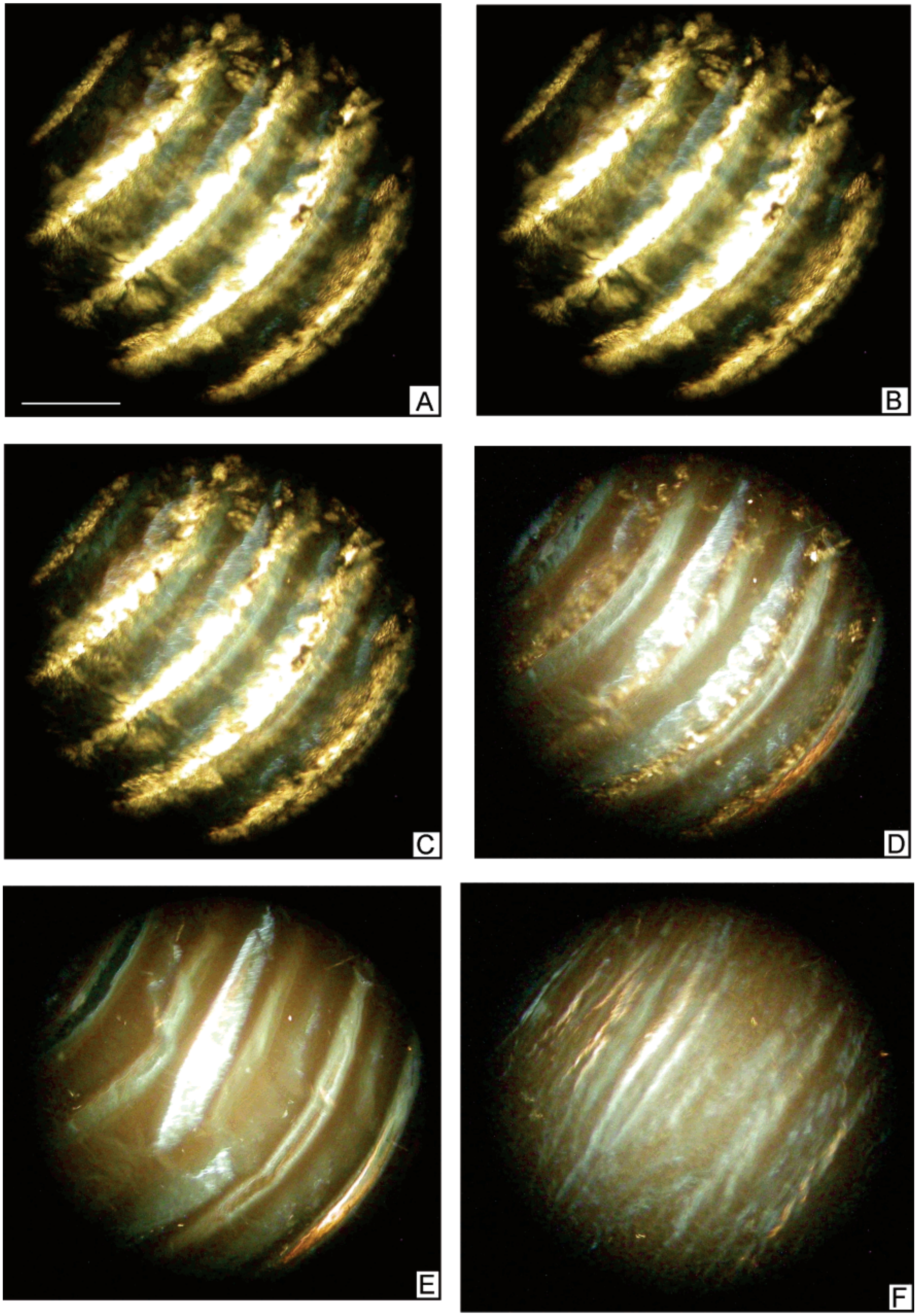

Figure 3. Photograph of a part of the pattern under perpendicular-polarized light after being annealed under different temperatures for 20 min, scale bar = 0.5 mm. (the CPA-4 and TOAB film obtained from toluene solution with the polymer content of 40 wt %). Key: (A) 25 °C; (B) 70 °C; (C) 80 °C; (D) 85 °C; (E) 90 °C; (F) 95 °C.

to one bright stripe in Figure 2B, and that the convex ridges mostly contain the isotropic (amorphous) structure, while the concave valleys mainly comprise the ordered anisotropic structure, similar to what we have observed in our previous study.[23] The center of the rings also consists of the ordered structure (Figure S5), and with the rotation of polarizers, the concave regions in a pattern always correspond to the bright stripes, and the convex regions correspond to the dark stripes (Figure S6), further confirming that the dark stripes (the convex ridges) represent the amorphous structure, while the bright stripes (the concave valleys) represent the ordered anisotropic structure.

For comparison, the photograph for a film cast from toluene solution of pure surfactant TOAB is shown in Figure 2C, under the perpendicular-polarized light, the highly crystalline structure of the surfactant is very much different from the mesomorphous structure in polymer/TOAB films.

The morphologies of the macroscopic pattern upon annealing under various temperatures were also studied on the polarizing optical microscope. We first put the sample on the hot stage of the microscope, increased the temperature to a certain value, annealed the sample for 20 min and let the sample to cool to room temperature (~25 °C), and then observed the morphology of the sample under perpendicular-polarized light. Afterward, we repeated this process at several higher temperatures, and the results are shown in Figure 3.

In Figure 3, the sample was observed under perpendicular-polarized light, thus the bright stripes represent the anisotropic structures (concave valleys in the patterns). As the annealing temperature was below 70 °C, no obvious change in the morphology could be observed. When the annealing temperature was increased to 80 °C, slight change could be observed for the samples under perpendicular-polarized light. As the annealing temperature was increased to 85 °C, which is close to the glass transition temperature of the polymer, the bright stripes (anisotropic regions) began to disappear. As we further increased the annealing temperature, the bright stripes completely disappeared under perpendicularly polarized light; and observed with naked eyes, the boundaries between the concave valley and the convex ridge in the pattern gradually blurred out and finally became invisible. We believe that, since the glass transition temperature is the macroscopic index of the onset of cooperative segmental motion of the polymer,[30] at the temperatures above T_g of the polymer, the mobility of the polymer chain segments will be remarkably enhanced in the solid film of the polymer−surfactant system, and the motion of the polymer chains can damage the ordered structures formed by the surfactant and polymer. Microscopically, the increase in annealing temperature not only led to higher mobility of the polymer chains inside the polymer-rich amorphous convex regions, but also the destruction of the polymer−surfactant anisotropic structure in the concave regions; these two factors contributed to the disappearance of the macroscopic pattern. On the other hand, as the temperature was reduced to the film-forming temperature (~25 °C), no anisotropic structure was reformed, thus no bright stripes could be observed under microscope. This result further proves that the pattern formation is a solvent evaporation induced process and the solvent is necessary for the formation of anisotropic structure as well as the macroscopic patterns; without the help of the solvent, the mixture of polymer and surfactant cannot restore the anisotropic structures and macroscopic patterns.

Small-Angle X-ray Scattering Profiles. The investigations on ordered structures in the macroscopic pattern with small-angle X-ray scattering (SAXS) measurement are illustrated in Figure 4, in which the scattering intensities are given as a function of the scattering vector q (nm^{-1}). The SAXS measurements were conducted for both the convex region and the concave region, and the size of the focal spot of the X-ray beam (less than 0.5 mm^2 in this study) can be slightly less than that of the convex regions or concave regions.

The information on the morphology can be obtained from the relative positions of SAXS peaks.[1] It can be seen that for the pure surfactant, there are three sharp peaks in the SAXS profile. The positions of these peaks are 3.32, 6.65, and 9.97 nm^{-1}, and this relative position of peaks is close to that of the lamella structure,[2,5,31−34] with d (the thickness of each repeat layer) of 1.9 nm. For both the CPA-4 and the HPA-4 polymer systems, with the addition of small amount of polymer (10 wt %) into the surfactant, there were still three peaks in the SAXS profile with the peak positions similar to those of the pure surfactant, the relative intensity of the latter two peaks substantially decreased, and no new peak emerged, proving that small amount of polymer cannot form any new structure with the surfactant. For the convex region in this samples, no peaks can be observed in the SAXS profile, indicating that the convex ridge in the macroscopic pattern mainly contains the amorphous region. As the amount of polymer was increased to 40 wt % for the TOAB/CPA-4 system, for the material in a concave region, there were 6 peaks in the SAXS profile with their peak positions of 3.00, 3.33, 6.05, 6.69, 9.08, and 10.03 nm^{-1}, indicating that a new structure was formed, and the scattering is generated by a superposition of two different lamellar systems, the old one with a period of around 1.9 nm, and the new one with a period of around 2.1 nm. We suppose that the old lamellar system was formed by surfactant molecules themselves, and the new one was probably formed by the insertion of polymer

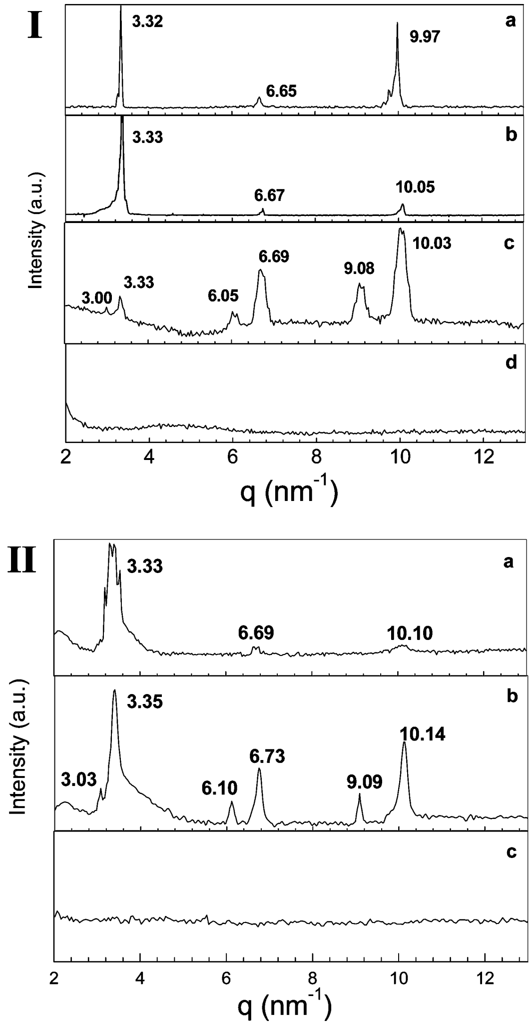

Figure 4. SAXS profiles. (I) The CPA-4 and TOAB systems: (a) pure surfactant TOAB cast from toluene; (b) CPA-4/TOAB system cast from toluene with a polymer content of 10 wt %; (c) concave region from the CPA-4/TOAB system with a polymer content of 40 wt %; (d) convex region from the CPA-4/TOAB system with a polymer content of 40 wt %. (II) The HPA-4 and TOAB systems: (a) HPA-4/TOAB system cast from toluene with a polymer content of 10 wt %; (b) concave region from the HPA-4/TOAB system with a polymer content of 50 wt %; (c) convex region from the HPA-4/TOAB system with a polymer content of 50 wt %.

chains into the original surfactant lamellar structures. The TOAB/HPA-4 system shows the same behavior, as shown in Figure 4(II). It can also be seen that further increase in polymer content to 90 wt % led to the disappearance of all scattering peaks.

The small-angle X-ray scattering investigations further prove that the ordered structure observed on the polarizing optical microscope is the mesomorphous phase formed by the surfactant chain packing in the polymer−surfactant system, and the different polar groups (thiophene-containing chromphore in our previous study;[23] hydroxyl and carboxyl in the present study) in the polymer chains cannot make any difference in the peak position ratios in the SAXS profiles for the mesomorphous structures formed by the surfactant and the polymer. We therefore can say that similar mesomorphous structures were formed by TOAB and polymers with different polar groups during the solvent evaporation.

Conclusions

The microscopic structure and macroscopic pattern can also be obtained with tetraoctylammonium bromide (TOAB) and the polyacrylates with common polar groups like carboxyl or hydroxyl, and the pattern formed from a ternary mixture of low-polar solvent, TOAB, and polar group containing polymer is a rather general phenomenon if conditions are favorable, and the driving forces for the structure formation are weak van der Waals interactions. The formation of the microscopic ordering requires the relatively high mobility of the polymer chains as well as the delicate balance of the polar interactions and nonpolar interactions among the three components in the system. By adjusting the amount of polar groups in the polymer, the molecular weight and the glass transition temperature of the polymer, microscopic ordering and eventually macroscopic pattern can be obtained from the ternary system. However, further investigations are needed to give a clear picture for the precise structures formed by TOAB and the polymers from the organic solvent.

Acknowledgment. This work was supported by the NSFC (Projects Nos. 50473035 and 50573023), the NSFG (No. 04020043), and the NCET.

Supporting Information Available: Figures showing FTIR spectra,^{1}H NMR spectra, photograph of the center of a concentric ring under perpendicular-polarized light, and photographs of a part of the pattern on polarizing optical microscope as the polarizers are rotated. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA052577C