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Microstructure of Mixed Cadmium Stearate and Behenate Langmuir-Blodgett Films

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(Dated: Received on July 2, 2006; Accepted on November 28, 2006)

X-ray diffraction (XRD) was used to investigate the microstructure and phase separation of mixed multilayers of cadmium stearate (SA) and behenate (BA) deposited onto hydrophilic glass by the Langmuir-Blodgett technique. No unitary fatty acid diffraction peaks in the XRD spectra of the mixed LB films, which reveals that domains in these samples are small and uniform. The interplanar spacing of the mixed LB films changes with the ratio of BA to SA in a step-shaped curve, which suggests that with the changing of the ratio between BA and SA, only three kinds of ordered structure form in the mixed system, and each microstructure, in particular, the short chains against long chains meshed microstructure can be maintained in a certain ratio range. In addition, for the meshed microstructure, the alkyl chains of both SA and BA stand straight or may have exactly the same small tilted angle from the substrate normal, as is indicated by the symmetric and asymmetric stretching vibration of methylene (CH_2) peaks which are at 2847.80 and 2914.37 cm^{-1} respectively in the Fourier transform infrared (FT-IR) transmission spectra. The mixed system always goes through a longitudinal regularity decreasing process when BA/SA is out of the intermediate ratio range (BA/SA: 1/5-1/1), which is illustrated by the relative XRD intensity changing with the ratio of BA/SA in a "W" shape. These results for the mixed LB films of BA/SA provide meaningful data for choosing the mixture ratio when fabricating composite films with special structure.

Key words: Langmuir-Blodgett (LB) film, Microstructure, X-ray diffraction (XRD), FT-IR transmission spectrum

I. INTRODUCTION

The Langmuir-Blodgett (LB) technique has been shown to be a powerful and convenient method for molecular assembly [1-5], and it provides us the possibility of synthesizing organic molecules, almost without limitations, with a desired structure and functionality. This enables the production of electrically, optically and biologically active components on a nanometer scale since it enables (i) the precise control of the monolayer thickness, (ii) homogeneous deposition of the monolayer over large areas, (iii) the possibility of making multilayer structures with varying layer composition and (iv) deposition of monolayers on almost any kind of solid substrate. Additionally, as models of cellular membranes, LB films have been used to study the microstructure of composite bio-membrane, such as domains and lipid rafts [6-8] which are derived from phase-separation of different ingredients of the mixed systems. Special microstructures formed by bio-molecules with different chain lengths play significant roles not only in performing bio-functions but also in improving mechanical properties of the framework of cellular membranes. On the other hand, composite LB films are widely used as boundary layer lubricants to improve me-

chanical properties (adhesion, friction, wear) and realize special lubrication for microelectromechanical systems (MEMS) [9]. In our former work [10,11], we designed a unique composite LB film based on long chain fatty acids with different chain lengths (stearic acid, arachidic acid) and octodecylamine, which had fine mechanical properties.

It is very important to study the microstructure, molecular conformation and molecular orientation of LB films, since the physical and chemical properties of the LB films are strongly correlated to the film microstructure. It has already been fully confirmed by atomic force microscopy (AFM) that phase-separation is ubiquitous in mixed Langmuir films (even for long chain fatty acids with different chain length) in which the same molecules aggregate together to form abundant domains [11-16]. Such phase-separated monolayers are transferred layer by layer onto the solid substrate and form longitudinal ordered layered multilayers, i.e. so-called LB films. Therefore the mixed Langmuir monolayers act as a "template", and their configuration of phase-separation directly determines the structure of LB multilayers. Many thin film analysis techniques have been widely used in characterization of the LB film, among which are Fourier transform infrared (FT-IR) spectroscopy, Raman spectroscopy, ultraviolet visible absorption spectra and fluorescence spectra, as well as XRD [17-26]. These promising nondestructive and quantitative characterization techniques, are believed to be able to offer large quantities of informa-

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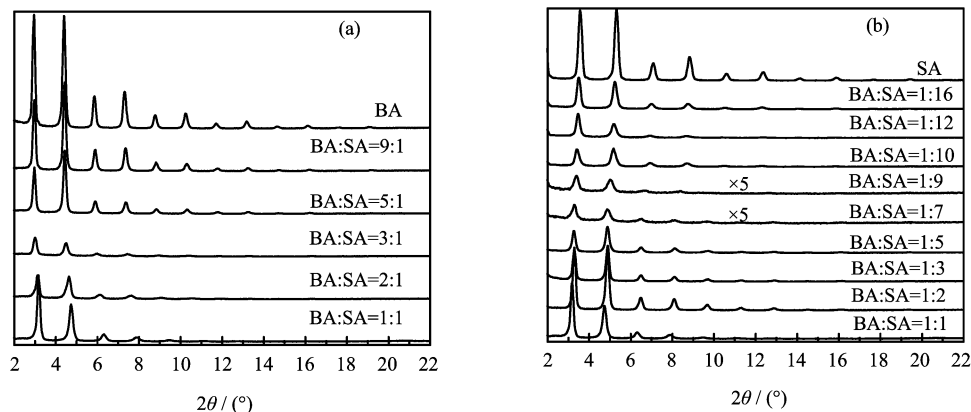


FIG. 1 The XRD spectra of the mixed BA (a) and SA (b) LB films (21 L) (intensity of BA/SA=1/7 and 1/9 shown in the profile is fivefold of the actual intensity)

tion directly correlated to the molecular structure and interactions, surface and interface roughness. In this work, we have studied the phase-separation, microstructure, molecular orientation and surface morphologies of mixed LB films of SA and BA in a large ratio range by XRD, FT-IR transmission spectra and AFM.

II. EXPERIMENTS

Materials: Stearic acid and behenic acid were purchased from Tokyo Kasei, $\text{CdC}_{12} \cdot 2.5\text{H}_2\text{O}$ and chloroform used in the experiment was analytic grade without further treatment.

LB films preparation: The Y-type LB multi-layers (21 layers) were deposited on an LB-105 trough (France). Monolayers of pure and mixed cadmium stearate (SA) and behenate (BA) were prepared on water subphase (containing 0.3 mmol/L cadmium chloride; pH=6.3; surface pressure, 73 mN/m) by spreading a corresponding acid solution with a concentration of 1 mmol/L in chloroform. The monolayers were transferred to hydrophilic glasses, CaF_2 substrates ($n=1.42$) and newly cleaved mica surfaces at speed, surface pressure and temperature of 4 mm/min, 38 mN/m and 20 °C, respectively. Glass and CaF_2 substrates were made hydrophilic by treatment with chromic acid, sonicated in chloroform, acetone, alcohol and deionized water in that order, then kept in deionized water until they were dipped into subphase. The transfer ratio was nearly uniform.

XRD measurements of LB films on glass substrates: XRD was measured with a sealed tube diffractometer system, parallel beam optics (X'Pert pro, Philips) using nickel filtered $\text{Cu K}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). XRD measurements were performed by keeping the incidence angle α equal to the exit angle β ($\alpha=\beta=\theta$), $DS=0.5^\circ$, $RS=0.2 \text{ mm}$, tube voltage 40 kV, tube current 40 mA, angular range $0.6^\circ \leq 2\theta \leq 22^\circ$, and scan speed $0.02^\circ/\text{s}$.

Fourier Transform Infrared transmission spectra mea-

surements of LB films on CaF_2 substrates were carried out on an FT-IR 360. The scanning resolution was 0.01 cm^{-1} and the detector used was TCD.

AFM measurements were carried out on an SII-SPA400 AFM (Japan) in contact mode under air environment at room temperature. The scanner size was $20 \mu\text{m} \times 20 \mu\text{m}$, and Si_3N_4 tips (Nanosensor Co) were used.

III. RESULTS AND DISCUSSION

A. XRD measurements

The XRD spectra are all shown in Fig.1 of the mixed cadmium stearate and behenate LB films in the ratios of BA/SA=9/1, 5/1, 3/1, 2/1, 1/1, 1/2, 1/3, 1/5, 1/7, 1/9, 1/10, 1/12, 1/16 and the unitary samples, i.e. BA and SA. Twelve Bragg diffraction peaks and the so-called "odd-even intensity oscillation" phenomenon, as may be expected [27], have been observed for unitary SA and BA, indicating strong periodicity in the direction normal to the substrate and clear interfaces between the neighboring layers of the LB films.

LB multilayers are obtained by transferring the Langmuir films from the air-water interface layer by layer and the periodic XRD peaks come from the longitudinal layer-layer diffraction. So the structure of multilayer LB films and their XRD spectra are determined by the configuration of monolayers at the air-water interface. For mixed Langmuir films of BA and SA, the same molecules will aggregate together to form abundant domains with different heights. Obviously, the configuration of the monolayer pattern will change with the ratio of BA/SA and simultaneously determine the structure of the multilayer LB films. Therefore the phase-separation information of mixed Langmuir films will be manifested by the XRD spectra of their multilayers both in peak position and intensity.

In order to study the microstructure of the mixed LB

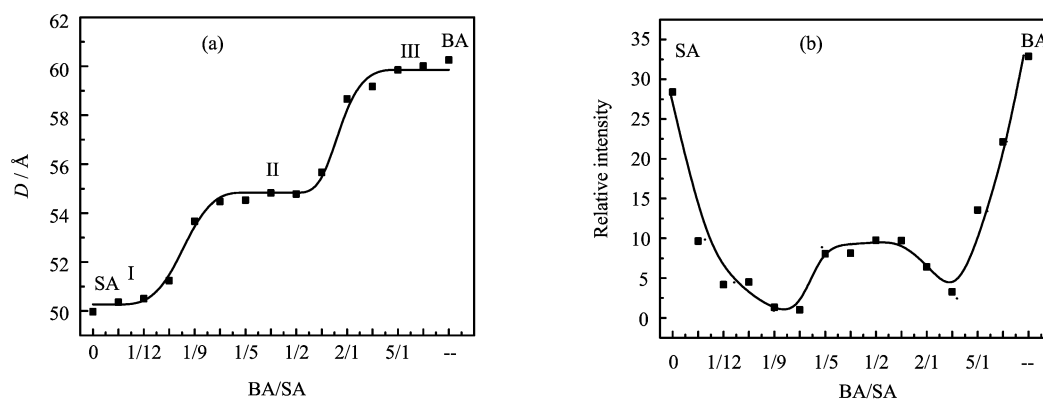


FIG. 2 The interplanar spacing D values (a) and relative X-ray diffraction intensity (b) vs. the ratio of BA/SA.

films in detail, we first calculated the interplanar spacing d_{00l} by formula: $2d_{00l}\sin\theta=n\lambda$, where $n=1$ and λ is the excitation wavelength of X-ray. For layer-by-layer structure such as LB films, if two or more kinds of ordered structures coexist in a sample, two or more sets of parallel peaks will show up in its XRD spectrum accordingly. However, there are no parallel peaks coexisting in all XRD spectra (Fig.1), which suggests that there is only one kind of ordered structure in the sample and domains in the mixed LB films are small and uniform. Such a result is different from what was reported by He *et al.*: X-ray diffraction peaks for the unitary BA and SA molecules and the special structure (which has formed in the mixed LB films) coexist in the XRD spectra of the mixed LB films with special molar ratio [28]. In a sense, the mixed LB films we fabricated here were homogeneous on a nanometer scale.

The interplanar spacing D value of mixed LB films changes with the ratio of BA/SA in a step-shaped curve (Fig.2(a)). Three steps are clearly found, and they stand for three kinds of ordered structures respectively. For step I (from BA/SA=1/9 to 1/16), the interplanar spacing D value is 50.51 Å, near to that of pure SA, which suggests that BA clusters in the mixed films are tilted, or BA molecules in the film are so few that they cannot affect the interplanar spacing enough (see Fig.3I). For step II (BA/SA: 1/7-1/1) the D value is 54.86 Å, about the average of the D value of BA and SA, and this special D value is retainable in a considerably large range of the ratio between BA and SA. For step III (BA/SA: 3/1-9/1) the D value is 59.87 Å, close to that of unitary BA, which indicates that long chain domains against long chain domains microstructure has formed in their growth direction. At the same time, for the difference in height between BA and SA domains, some “holes” have formed in the mixed films of this special ratio range (Fig.3 III). In fact, these “holes” played a significant role in fabricating special functional nanostructures in our former work [11,12]. From Fig.2(a), we also can see that the film microstructure changes with the ratio of BA/SA asymmetrically, which suggests that

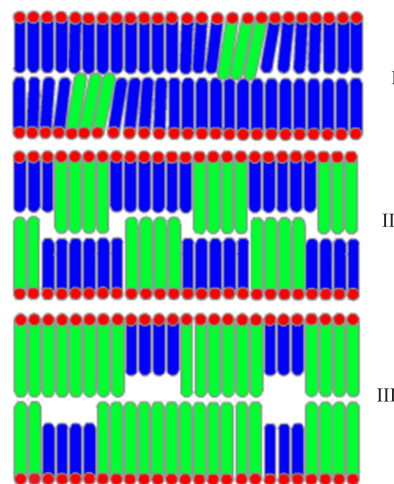


FIG. 3 Schematic diagrams of the three kinds of microstructures in the mixed LB films of cadmium stearate and behenate based on XRD and FTIR transmission spectra. Cadmium fatty acid is denoted by a rod linked with a ball, with the ball denoting the headgroup Cd^{2+} and carboxyl, and short and long rods denote the alkyl chain of the stearate and behenate.

BA is much more effective than SA in modulation of the mixed LB films' microstructure.

For step II, there are two possibilities which may result in the interplanar spacing 54.86 Å, which is the average of that of BA and SA. (1) As the consequence of equilibrium effect of multiple interactions, long alkyl chains of BA molecules in the mixed films are tilted more than SA from the substrate normal to a certain extent; (2) In the direction normal to the substrate, the superstructure of long chain (BA) domains against short chain (SA) domains have formed in the mixed system.

In the LB investigations, a consensus is extensively accepted that the long alkyl chains determine the arrangement of molecules and the degree of organization of the LB films. In FT-IR spectroscopy, the vibration

of methylene (CH_2) is presented as the symmetric (at $\sim 2851\text{ cm}^{-1}$) and asymmetric (at $\sim 2923\text{ cm}^{-1}$) stretching vibration peaks, and deformation vibration peak at $\sim 1468\text{ cm}^{-1}$. Compared with the stretching vibration peaks, the deformation vibration peak intensity is much smaller, the stretching vibration of CH_2 signal peak positions (sensitive to the packing of the alkyl chains) are usually used to determine the molecular orientation and conformation in organic LB films. In principle, broad bands at higher wavenumbers indicate poorly ordered chains having many large defects, while sharp bands at relatively low wavenumbers indicate highly ordered chains having predominantly trans-zigzag conformations. Typically, for amphiphilic acids (e.g. stearic acid, arachidic acid and behenic acid) which are the most widely investigated molecular system, a considerable amount of work has demonstrated that the densely packing of alkyl chains (even crystallization) could be produced by LB method. Most of the LB films we fabricated in this paper have good periodicity along the growth orientation which has been clearly discussed above by XRD data. However, the exact molecular orientation in the mixed LB films is not known.

In order to confirm what kind of microstructure formed in the mixed LB films of cadmium stearate and behenate (from 7/1 to 1/1), 21-layer LB films of cadmium stearate, cadmium behenate, and cadmium stearate/behenate (2/1) deposited on amphiphilic CaF_2 substrates were measured with FT-IR spectra in the region from 2000 cm^{-1} to 3600 cm^{-1} (Fig.4). The FT-IR transmission spectra are exactly the same for unitary and mixed LB films of cadmium stearate and behenate. The peaks at 2847.80 and 2914.37 cm^{-1} have been attributed to CH_2 symmetric and asymmetric stretch, and both shift to the lower wavenumbers compared with the IR peaks at about 2851 and 2923 cm^{-1} , reported by Huo [31]. Thus it is reasonable to infer that the alkyl chains of the cadmium stearate and behenate are more orderly and densely packed in the LB films than what has been reported and have predominant trans zigzag conformations. What's more, all the alkyl chains of unitary and mixed LB films of cadmium stearate and behenate have the same tilted angle from the substrate's normal, or are all perpendicular to the substrate plane [31-37]. Thus, the first possibility is excluded and the interplanar spacing 54.86 \AA should be ascribed to forming long chain domains against short chain domains (meshed) microstructure in the direction normal to the substrate. It is worth noting here that, in reference [37], Wu *et al.* got the conclusion that the two characteristic bands became increasingly sharper and shift to lower wavenumbers with increasing length for 2-alkyl benzimidazoles with various chain lengths (from C5 to C15). In contrast, for the LB films of cadmium stearate and behenate fabricated in this work, it is not the case that the two typical vibration peaks shifted to lower wavenumber with alkyl chain lengths (from C18 to C22). The explanation for these FT-IR data is, as the consequence

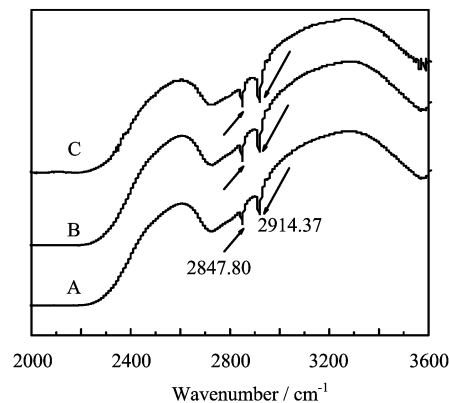


FIG. 4 FTIR spectra of 21-layers cadmium stearate (A), cadmium behenate (B), cadmium stearate and behenate (2:1) (C) deposited on amphiphilic CaF_2 substrate at $\text{pH}=6.3$. All the data positions in the FT-IR spectra were collected simultaneously without tuning of the central infrared wavenumbers and each sample was scanned several times with the same curve.

of equilibrium effect of multiple interactions, long alkyl chains of SA (C18) molecules have stood straight and so do the BA (C22) molecules. That is to say, the alkyl chain length has little influence on the tilted angle of alkyl chain axis when the number of carbon atom $n \geq 18$ with the given experimental parameters in this work.

The relative XRD intensity of the third peak of the mixed multilayers is presented as a function of the ratio of BA/SA in Fig.2(b), which exhibits a W-shaped curve. Other progression diffraction peaks have the same pattern. Clearly, a step appears in the ratio range of 1/5-1/1 in Fig.2(b), which indicates that the longitudinal regularity of the mixed LB films is maintained well in this large ratio range. As discussed in the above paragraph, in this ratio range, the microstructure of long chain-against-short chain has formed along the longitudinal direction. (LB films of this kind microstructure may have fine mechanical properties.) It is easy to understand that the relative X-ray diffraction intensity is stronger for the mixed multilayers of large BA/SA ratio, in which the mixed multilayer microstructures are gradually closer to that of the unitary BA or SA. Note that the XRD intensity varies with BA/SA ratio in a W shape not "U" or "V" shape. This implies that the XRD intensity must go through a decreasing process once the ratio of BA/SA is out of the intermediate range (1/5-1/1) in either direction. We also note that the XRD intensity of the mixed multilayers of BA/SA=1/7 is much weaker than that of 1/5, though its longitudinal microstructure is still long chain domains against short ones (see Fig.2(a) II region). These suggest that the multilayers in intermediate ratio range (BA/SA: 1/5-1/1) have better longitudinal regularity and phase stability.

As what we have discussed above, for the mixed multilayer LB films, the XRD spectra are actually a re-

flection of the phase-separation in their monolayers. In constructing the mixed multilayer LB films, the internal layers act as a “template” for the outermost layer, and the unit cell of the “template”, i.e. mixed monolayers, consists of domains (BA and SA) with different height. Because of the rough “template” surface, it is only when the ratio between BA and SA is appropriate that ordered and stable structure can form, in which the longer and shorter domains are exactly suitable for each other. The plateaus presented in Fig.2(a) denote that the longitudinal periodic structures of the multilayer-LB films are extremely tendentious instead of uniform as the mixed ratio changes from pure SA to pure BA, and the plateaus presented in Fig.2(b) further confirms that only the mixed multilayers fabricated in intermediate ratio range (BA/SA: 1/5-1/1) are ordered and stable. It is noticeable that the so-called “ordered and stable” region only exists when shorter chain molecules (SA) are in the majority (i.e. BA/SA=1/5-1/1), which is somewhat like that of bio-membranes.

The schematic diagrams of the three tendentious microstructures of the mixed LB films of BA and SA can be illustrated in Fig.4. It is clear that, for region II, i.e. BA/SA=1/5-1/1, the mixed multilayers can form a structure in which the longer and shorter chain domains mesh with each other in hydrophobic layers. The “meshed structures” are quite ordered and stable, therefore they may have fine mechanical properties. For region III, in which longer domains (BA) are major, small holes with longitudinal size of only 0.5-1 nm can form. So this structure can be used to fabricate special nanostructures. On the other hand, the results also suggest that for a mixed system of molecules with different chain lengths such as BA and SA, it is not just the mixture ratios that can fabricate very stable and ordered structures, and the optimization of organic materials in semiconductor devices or as electrical conductors in devices is closely related to the optimization of electroactive molecular structures [38,39].

B. The possibility of forming “meshed structures”

As discussed above, the simple schematic diagrams of the three kinds of microstructures in the mixed LB films of cadmium stearate and behenate shown in Fig.4 are very consistent with XRD results. On the other hand, if the “meshed structure” shown in Fig.3 II really have formed in the mixed films with the ratio of BA/SA=1/1-1/7, the film must have undergone a process of reorganization in the outmost layer of the mixed LB films, and then the longer and shorter chain domains mesh with each other in hydrophobic layers. However, we cannot expect that every longer and shorter chain domain will have the chance to mesh with each other without reorganization. Now the question is whether it is possible to have such molecular reorganization at such high surface pressure (38 mN/m).

During every “downstroke” in which the LB films

are in the subphase, two asymmetric (mismatched) monolayers are present tail-to-tail. In the subphase, molecules in the outmost layer of the mixed LB films have a larger degree of freedom than at the air-water interface, and a certain displacement may take place, then come to the thermodynamic (or the lower energy) equilibrium structure—“meshed structure”, even at such a high surface pressure as 38 mN/m. In order to clarify the microstructure and test the quality of the multilayer LB films, AFM images of cadmium stearate and behenate 21-layer-LB films deposited on freshly cleaved mica surface at pH=6.3 are shown in Fig.5. Their morphologies are similar and all in bulk phase. Films with holes were observed, and the outermost layers of the multilayer LB films are disordered while the inner layers are compact and crystallized. If molecular reorganization had not happened in the mixed LB films, there would be more large holes in the morphologies of the mixed films, and surface roughness would increase greatly compared with the unitary sample. However, that is inconsistent with what we see in Fig.5(c) (take the morphology of mixed LB film of cadmium stearate and behenate (2/1) as an example). Of course, the most important consequence of non-reorganization is that good periodicity in the direction normal to the substrate and clear interfaces between neighbouring layer would be destroyed which may lead to much lower X-ray diffraction intensity or even no diffraction peaks. As shown in Fig.1 and Fig.2, the facts are not so: reorganization in the mixed films at high surface pressure is not only possible, but required.

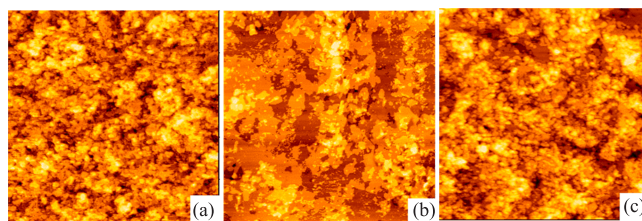


FIG. 5 AFM images of cadmium stearate and behenate 21-layer-LB films deposited on newly cleaved mica surface at pH=6.3 (A) cadmium behenate LB film, $10\ \mu\text{m} \times 10\ \mu\text{m}$, 32 nm in z scale; (B) cadmium stearate LB film, $10\ \mu\text{m} \times 10\ \mu\text{m}$, 32 nm in z scale; (C) Mixed LB films of cadmium stearate and behenate (BA/SA=1/2), $10\ \mu\text{m} \times 10\ \mu\text{m}$, 38 nm in z scale.

IV. CONCLUSION

In this paper, we found an interesting phenomenon in the mixed 21-layer LB films of cadmium stearate and behenate. Phase-separated domains in the multilayer LB films are small and uniform. The interplanar spacing D values and relative X-ray diffraction intensity of the mixed LB films change with the ratio of BA/SA in a step- and W-shaped curve respectively, which in-

icates that only three kinds of longitudinal periodic structures can form in the mixed multilayer LB films of all ratios and each microstructure can be maintained in a certain ratio range. Furthermore, the mixed system always goes through a process of the longitudinal regularity decreasing when the ratio of BA/SA is out of the intermediate ratio range (BA/SA: 1/5-1/1). More tilted BA clusters are embedded in SA when the ratio of BA/SA is below 1/9. Longer and shorter chain domains mesh with each other when BA/SA=1/7-1/1, and the alkyl chains of both SA and BA stand straight or have the same tilted angle, especially when BA/SA=1/5-1/1. These "meshed structures" are much ordered and stable, therefore they may have fine mechanical properties. When BA/SA=3/1-9/1, long chain-against-long chain domains are in the majority, and some hydrophobic "holes" (caused by the difference in height between BA and SA) formed in the alkyl layers which can be used to fabricate special functional nanostructures. Those results may be meaningful for us to determine mixture ratio when fabricating composite films with special structures.

V. ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (No.90306010 and No.20371015) and Youth Foundation of Henan University of Science and Technology (2004QN037)

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