

Well-Ordered Structure and Phase Transition Behaviors of a Reversed Duckweed Polymeric Langmuir–Blodgett Film Studied by Fourier Transform Infrared Spectroscopy and Small-Angle X-ray Diffraction

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A Reversed Duckweed polymeric Langmuir–Blodgett (LB) film was characterized by Fourier transform infrared (FTIR) spectroscopy. It has a well-ordered structure which is similar to that of the monomer–octadecylacrylamide–LB film, which provides proof that the flexible hydrophilic network does not interfere the side-chain alignment. The phase transition behavior was studied by using temperature dependent FTIR and small-angle X-ray diffraction. The LB film shows a unique thermal transition behavior, which undergoes a three-phase transition processes: from a highly ordered structure transition into a melted disordered state through two Langmuir–Blodgett “liquid crystal” states.

Introduction

Polymeric Langmuir–Blodgett (LB) films can offer superior mechanical properties, higher damage thresholds, and improved stability compared with properties offered by low molecular weight molecules, and they have been extensively investigated in recent years because of their potential applications in microelectronic and optoelectronic devices.¹ Thus attention has been directed to the fabrication of polymeric ultrathin films with a highly ordered molecular array and controlled thickness. Since Tredgold first successfully fabricated the polymeric LB film, many groups have been involved in this research.² Ringsdorf et al. introduced spacer groups into preformed polymers in order to decouple the side-chain ordering from the polymer backbone structure that resulted in close packed ordered polymeric monolayer and multilayer films.^{2b,c} Wegner et al. developed a kind of “hair-rod” polymeric LB film^{2d} and Eisenberg developed a so-called polymeric surface micelle monolayer.^{2e} Our group has also focused on this research for several years. We developed a new kind of polymeric LB film, namely, “Duckweed” and “Reversed Duckweed” polymeric LB films.³ This kind of polymeric LB film is fabricated by using a new kind of the amphiphilic polymer composed of hydrophobic microgel cores and hydrophilic chains, or vice versa, using the amphiphilic polymer which was composed of hydrophobic long alkyl chains and hydrophilic lightly cross-linked networks. This kind of amphiphilic polymer

can self-rearrange at the air/water interface and is readily transferable as so-called “Duckweed” or “Reversed Duckweed” polymeric Langmuir–Blodgett (LB) films onto solid substrates. “Duckweed” means that the hydrophobic microgels are floating onto the surface of water, and the hydrophilic grafting chains are projected into the water; “Reversed Duckweed” means that the hydrophilic networks extend downward into water and the hydrophobic grafting chains are upward packing away from the surface of water. Their unique feature is the combination of order and stability.

The phase transition behavior in polymeric LB films is also a matter of keen interest, because the phase transition behavior may provide much valuable information of the two-dimensional phase transition and thermal stability of LB films, which is quite important for the application of LB films, and further the studies of phase transition are helpful in understanding the nature of phase transitions of biologically relevant molecules.⁴

In spite of the importance of this aspect, studies of the phase transition behaviors of polymeric LB films by using IR spectra have been scarcely reported. Since the first study of the order–disorder transition of a LB film of cadmium arachidate by using temperature dependent infrared spectroscopy,^{5a} several groups have carried out the studies of the order–disorder transition behaviors, but most of the studies are concentrated on small molecules, such as cadmium arachidate and dye containing long alkyl chains.⁵ As far as we know, there is one publication concerned with the phase transition behaviors

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(1) (a) Ulman, A. *Introduction to Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991. (b) Fuchs, H.; Ohst, H.; Prass, W. *Adv. Mater.* **1991**, *3*, 10.

(2) (a) Tredgold, R. H.; Winter, C. S. *J. Phys. D: Appl. Phys.* **1982**, *15*, L55. (b) Ringsdorf, H.; Laschewsky, A.; Schmidt, G.; Schneider, J. *J. Am. Chem. Soc.* **1987**, *109*, 778. (c) Laschewsky, A.; Ringsdorf, H. *Angew. Makromol. Chem.* **1986**, *145*, 1. (d) Schaub, M.; Wenz, G.; Wegner, G.; Stein, A.; Lemm, D. *Adv. Mater.* **1993**, *5*, 919. (e) Zhu, J.; Eisenberg, A.; Lennox, R. B. *J. Am. Chem. Soc.* **1991**, *113*, 5583.

(3) (a) Yin, R.; Cha, X.; Zhang X.; Shen, J. C. *Macromolecules* **1990**, *23*, 5158. (b) Cha, X.; Yin, R.; Zhang, X.; Shen, J. C. *Macromolecules* **1991**, *24*, 4985. (c) Shen, J. C.; Zhang, X.; Zhang, R. F. *Thin Solid Films* **1992**, *210/211*, 628. (d) Zhang R. F., Zhang X., Shen J. C. *Langmuir* **1994**, *10*, 2727.

(4) (a) Roberts, G. G., Ed. *Langmuir–Blodgett Films*; New York, 1990. (b) Ulman, A. *Adv. Mater.* **1991**, *3*, 298. (c) Tieke, B. *Adv. Mater.* **1990**, *2*, 222. (d) Embs, F.; Funhoff, D.; Laschewsky, A.; Licht, U.; Ohst, H.; Prass, W.; Ringsdorf, H.; Wegner, G.; Wehrmann, R. *Adv. Mater.* **1991**, *3*, 46.

(5) (a) Naselli, C.; Rabe, J. P.; Rabolt, J. F.; Swalen, J. D. *J. Chem. Phys.* **1985**, *82*, 2136. (b) Naselli, C.; Rabe, J. P.; Rabolt, J. F.; Swalen, J. D. *Thin Solid Films* **1985**, *134*, 173. (c) Cohen, S. R.; Naaman, R.; Sagiv, J. *J. Phys. Chem.* **1986**, *90*, 3054. (d) Kobayashi, K.; Takaoka, K.; Ochiai, S. *Thin Solid Films* **1989**, *178*, 453. (e) Hasegawa, T.; Kamata, T.; Umemura, J.; Takenaka, T. *Chem. Lett.* **1990**, 1543. (f) Katayama, N.; Enomoto, S.; Sato, T.; Ozaki, Y.; Kuramoto, N. *J. Phys. Chem.* **1993**, *97*, 6880.

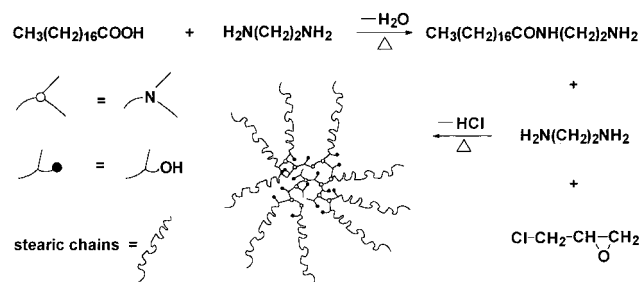


Figure 1. Schematic chemical structure of amphiphilic polymer ES-3.

of poly(diacetylene) derivative by using temperature dependent infrared spectroscopy.⁶

Temperature dependent X-ray diffraction is another useful tool in the study of LB film.⁷ X-ray diffraction can give us much useful information about the layer structure of LB films; combining the X-ray diffraction and temperature dependent IR may provide deep insight into the thermal stability of the polymeric LB films.

In our recent work, we synthesized a new amphiphilic polymer which was composed of a hydrophilic epichlorohydrin-ethylenediamine slightly cross-linked microgel and hydrophobic stearyl grafting chains (denoted as ES).⁸ We have found that one of this type of amphiphilic polymer, whose hydrophilicity and hydrophobicity had been well balanced, can form a Reversed Duckweed polymeric LB film which was well ordered.^{8a} This sample also exhibited thermotropic liquid crystalline behaviors though it does not bear mesogenic groups.^{8b} Furthermore, it has been found that it is a very good matrix for functional assembly. This amphiphilic polymer has shown some perspective for applications.^{8c} Here, we report the phase transition behaviors of the Reversed Duckweed polymeric LB films by using temperature dependent FTIR and X-ray diffraction.

Experimental Section

Materials. The amphiphilic polymer (ES-3) was composed of hydrophilic ethyldiamine-epichlorohydrin slightly cross-linking networks and hydrophobic stearyl chains. Its schematic chemical structure is shown in Figure 1, and its synthesis was described in detail in our previous paper.^{8a} Its M_n is 7840 and its alkyl chains content is 75.8%. The amphiphilic polymer was slightly cross-linked; the cross-linking degree was defined as the content of =N- of the hydrophilic part and was determined as 25%.

Procedures. The preparation of polymeric LB film was reported previously.^{8a} The LB films were deposited on Si for X-ray diffraction measurement, CaF₂ plates for infrared transmission measurements, and Ag-evaporated glass slides for grazing angle reflection (GAR) measurements. All of the FTIR spectra were measured on a Bruker IFS-66V spectrometer. The spectra were taken at a 2 cm⁻¹ resolution. The FTIR temperature controller is homemade and gives a temperature stability of better than 0.1 K when the sample is heated to the desired temperature (20 min wait for equilibration). The method for determining FTIR band half-width and peak position is a second derivative method attached program of the Bruker IFS66V FTIR instrument. Small-angle X-ray diffraction was carried out on Rigaku X-ray diffractometer (D/max γ A, using copper K α radiation of wavelength 1.542 Å), the temperature controller was homemade and gives a temperature stability of better than 0.2 K when the

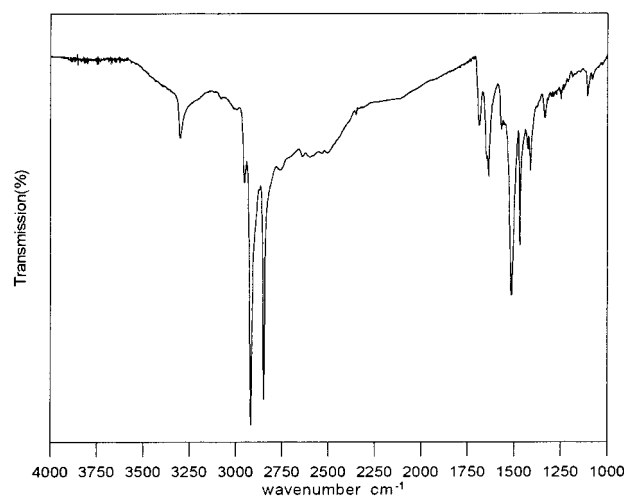


Figure 2. Transmission infrared spectrum of ES-3 at room temperature.

Table 1

wavenumber/ cm ⁻¹	assignment	wavenumber/ cm ⁻¹	assignment
3301	$\nu(\text{N-H})$	1648	$\nu(\text{C=O})$
2955	$\nu_{\text{as}}(\text{CH}_3)$	1552	$\delta(\text{NH})$
2918	$\nu_{\text{as}}(\text{CH}_2)$	1467	CH_2 scissor
2850	$\nu_{\text{s}}(\text{CH}_2)$		

sample is heated to the desired temperature (10 min wait for equilibration).

Results and Discussion

In the previous paper, we have shown that the amphiphilic polymer ES-3 can form stable condensed mono-layer and be transferred as a well-ordered "Reversed Duckweed" LB multilayer.^{8a} In this paper we give some more detailed FTIR evidence to further prove the existence of the well-ordered structure.

The spectrum of amphiphilic polymer ES-3 at room temperature is shown in Figure 2 (in KBr pellet). Using the published IR data and considering the molecular structure, we list the band assignments shown in Table 1.

The transmission spectra and GAR (the grazing angle reflection) spectra of the ES-3 LB film are shown in Figure 3. The two spectra are quite different from each other. The N-H stretching (3301 cm⁻¹), C=O stretching (1648 cm⁻¹), and CH₂ scissoring (1467 cm⁻¹) absorption are not observed in GAR in which the electric field vector is perpendicular to the Ag surface, while those absorption bands are very strong in the transmission spectra. This indicates that the transition moments of these groups are parallel to the surface of solid supports, which means that the N-H and C=O are highly oriented parallel to the surface and the long alkyl chains are standing up from the surface of LB multilayers. If the long alkyl chain is completely perpendicular to the surface, the absorption of CH₂ asymmetric stretching (2918 cm⁻¹) should not be observed in GAR. However, the CH₂ asymmetric stretching (2918 cm⁻¹) absorption and $\delta(\text{NH})$ adsorption are observed in GAR. Considering this fact and the relative intensity ratio of CH₂/CH₃, we can conclude that the long alkyl chains are tilted regularly.

Furthermore, a polarized FTIR-ATR (attenuated total reflectance) technique was adopted to study the orientation of alkyl chain in the multilayer. The dichroic ratio (D), which is the key parameter used in determining the molecular orientation, is defined as the ratio of the

(6) Mino, N.; Tamura, H.; Ogawa, K. *Langmuir* **1991**, 7, 2336.

(7) (a) Ringsdorf, H.; Schlarb, B.; Venzmer, J. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 114. (b) Sasanuma, Y.; Kitano, Y.; Ishitani, A.; Nakahara, H.; Fukuda, K. *Thin Solid Films* **1991**, 199, 359.

(8) (a) Zhang, X.; Zhang, R. F.; Li, H. B.; Zhao, B.; Shen, J. C. *Polym. Bull.* **1996**, 36, 227. (b) Li, H. B.; Zhang, X.; Zhang, R. F.; Shen, J. C.; Zhao, B.; Xu, W. Q. *Macromolecules* **1995**, 28, 8178. (c) Zhang, X.; Zhang, R. F.; Shen, J. C.; Zou, G. T. *Makromol. Rapid Commun.* **1994**, 15, 373.

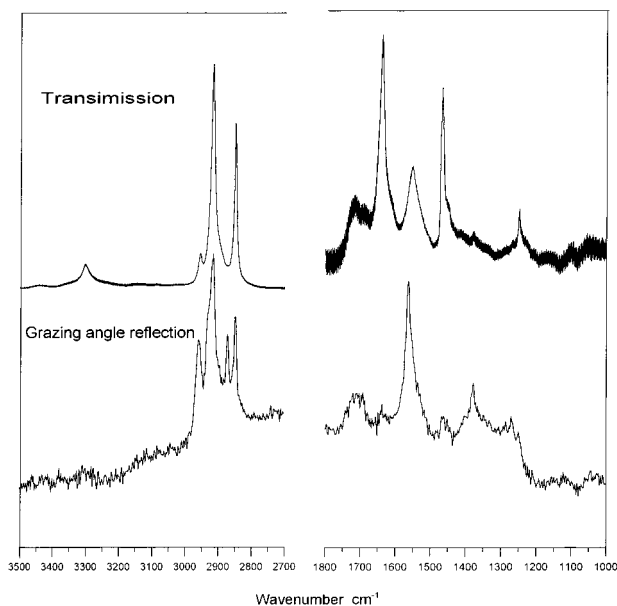


Figure 3. Transmission and GAR (grazing angle reflection) spectra of ES-3 LB films (20 layers).

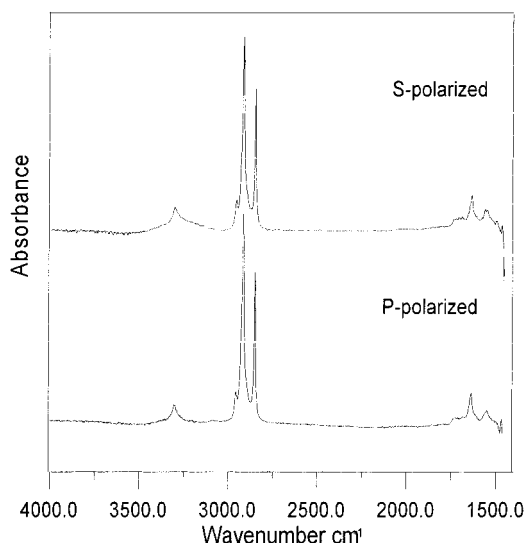


Figure 4. Polarized ATR-FTIR spectra of ES-3 polymeric LB film (10 layers).

absorbance intensity of s-polarized light to that of p-polarized light.⁹

$$D(\gamma, \theta=90^\circ) = \frac{E_y^2 (2 - \sin^2 \gamma)}{E_x^2 (2 - \sin^2 \gamma) + 2E_z^2 \sin^2 \gamma}$$

The polar angles are defined as follows: γ is the tilt angle of the molecular chain axis from the film surface normal; θ is the angle of the transition moment with the molecular chain axis. The refractive index of the film is 1.5. The polarized FTIR-ATR spectrum of the CH_2 groups is shown in Figure 4. Using the uniaxial orientation modes (which means all molecular chain axes are uniaxially oriented around the film surface normal) and the transition moment of CH_2 group stretching vibration perpendicular to the alkyl chain axis,⁹ we obtain an average tilt angle of the alkyl chains axis $\gamma = 28^\circ$.

From the results above we can propose the schematic structural model of Reversed Duckweed polymer LB films shown in Figure 5.

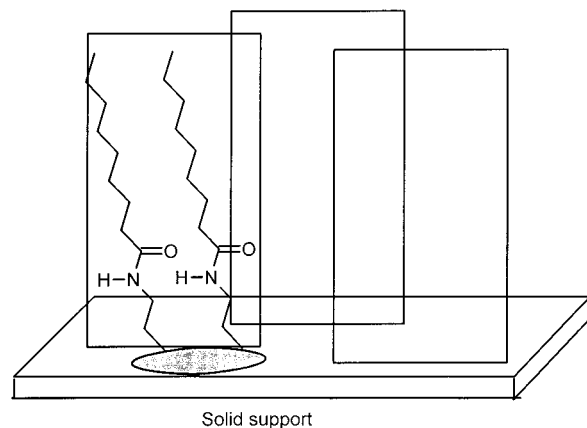


Figure 5. Schematic structural model of ES-3 polymeric LB film.

Miyashita has reported the highly ordered structure about *N*-octadecylacrylamide (ODA) Langmuir–Blodgett films,¹⁰ the alkyl chains have a high biaxial orientation and in each layer the N–H and C=O groups are oriented parallel to the surface of the substrate and alkyl chains are tilted regularly. ODA could be considered as the monomer of polymer ES-3. Comparing Miyashita's results with our results reported here, we find that the structure of the alkyl chains is very similar; namely, the well-ordered structure in the monomer ODA was maintained in the polymeric ES-3 Langmuir–Blodgett film, which indicates that the polymer backbone did not interfere with the orientation of the alkyl chains in this case. From the above results, we infer that the flexible hydrophilic network really has a similar effect of the spacer group, which strongly supports our assumptions previously.^{8a}

Temperature dependent infrared transmission spectroscopy is an useful tool to study the phase transition behaviors of LB films. We found that the bands 3301, 2918, and 2850 cm^{-1} of ES-3 polymeric LB film change greatly with increasing temperature.

It is well-known that the frequencies and bandwidths of CH_2 antisymmetric and symmetric stretching bands are sensitive to the conformation and mobility of the alkyl chains, respectively.¹¹ If the alkyl chains are highly ordered (all trans conformation), the bands appear near 2918 and 2850 cm^{-1} , the alkyl chains are highly disordered, and the frequencies may shift upward up to near 2927 and 2856 cm^{-1} . So, the frequencies and widths of CH_2 antisymmetric and symmetric stretching bands can be used as practical indicators of the phase transition process of alkyl chains. While infrared spectroscopy cannot be used to absolutely identify a certain phase, it does permit the precise monitoring of subtle changes in the absorption bands characteristic of specific functional groups.¹² Figure 6 shows the temperature dependent behavior of CH_2 stretching bands. Figure 7 illustrates the temperature dependence of the frequencies and widths of CH_2 stretching bands. We can see that frequencies and widths show remarkable changes around 340, 370, and 410 K, which indicate that near 340, 370, and 410 K three transition processes may occur. At room temperature, the polymeric ES-3 LB film is in a highly ordered state (frequencies of CH_2 are at about 2916 and 2854 cm^{-1} , respectively) and the LB film is in a highly disordered state when it is heated

(10) Miyaashita, T.; Suwa, T. *Langmuir* **1994**, *10*, 3387.

(11) Mantsch, H. H.; Martin, A.; Cameron, D. G. *Biochemistry* **1981**, *20*, 3139.

(12) Sapper, H.; Cameron, D. G.; Mantsch, H. H. *Can. J. Chem.* **1981**, *59*, 2543.

(9) Ahn, D. J.; Franes, E. I. *J. Phys. Chem.* **1992**, *96*, 9952.

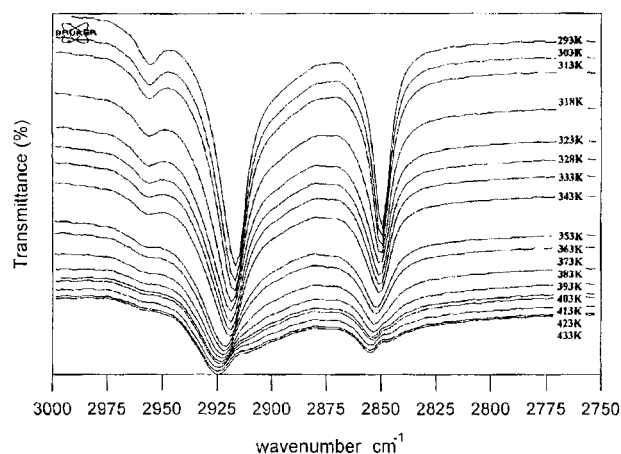


Figure 6. Temperature dependent behavior of the symmetric and asymmetric CH_2 stretching band of ES-3 polymeric LB film.

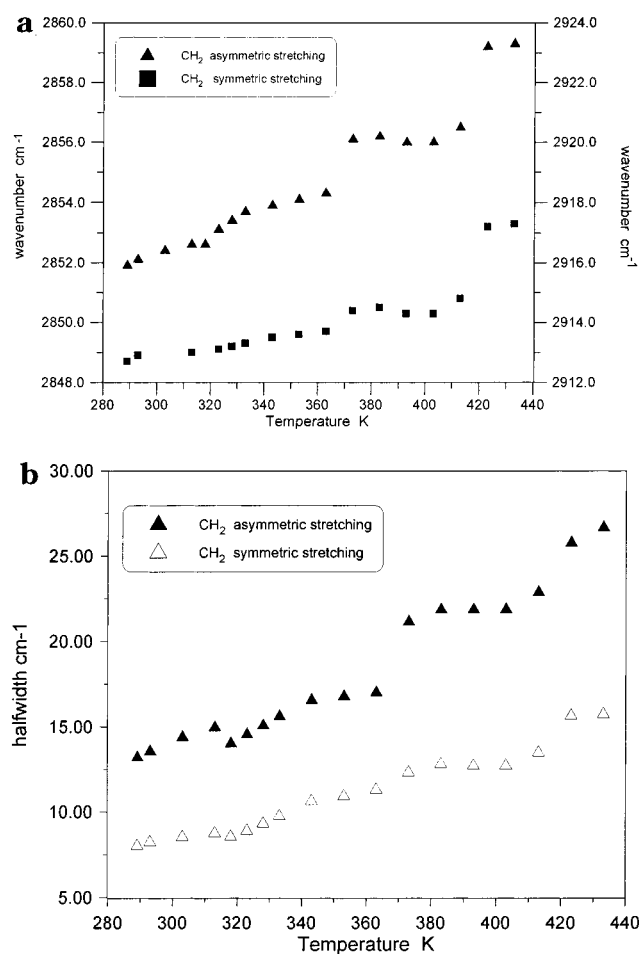


Figure 7. Temperature dependent behaviors of (a) frequencies and (b) bandwidths of symmetric and asymmetric stretching bands of CH_2 .

above 420 K. As seen, the ES-3 LB film undergoes three transition processes from a highly ordered state into a melted disordered state through two meso-states from room temperature to 420 K.

Figure 8 shows the temperature dependent behaviors of the N–H stretching. The N–H bond also shows three corresponding thermal transition processes: the N–H stretching shows sharpening as well as increasing of the intensity at first and then shows broadening and decrease in intensity as well as higher frequency shift. However,

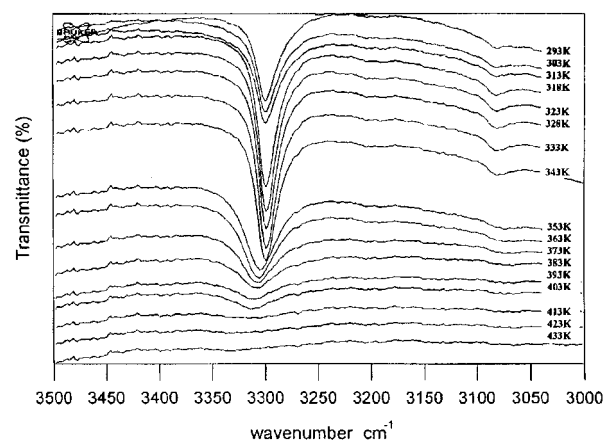


Figure 8. Temperature dependent behavior of N–H stretching bands.

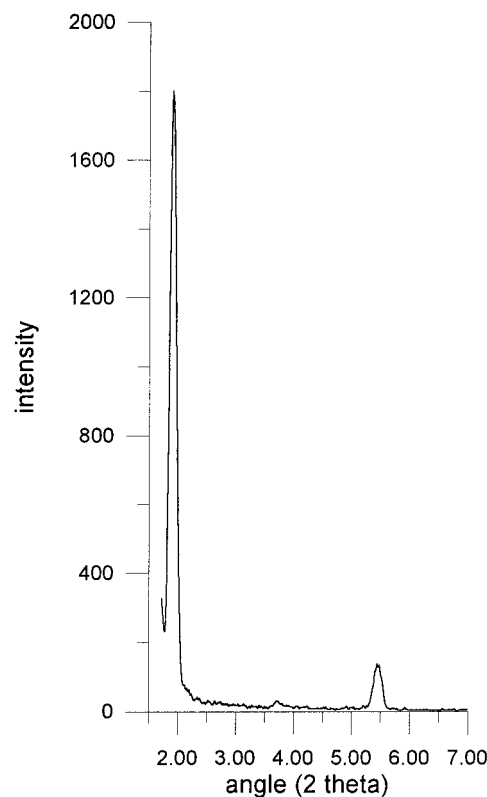


Figure 9. Small-angle X-ray diffraction patterns of ES-3 polymeric LB film.

we cannot understand the detailed information given by the temperature dependent behaviors of the N–H group at present.

As mentioned before, all of the results of FTIR provide us with information about the change of short-range order, but small-angle X-ray diffraction can give us information about the layer structure. The X-ray diffraction patterns are shown in Figure 9. At room temperature, it is clearly seen that there exist three diffraction peaks for a multilayer LB film (20 layers in total). Higher orders of diffraction, sharpness and large intensity of the first diffraction peak, and odd–even alternation of the peak intensities provide ample evidence that this kind of Reversed Duckweed polymeric LB film had a well-ordered layer structure. Figure 10 is the temperature-dependent X-ray diffraction pattern of ES-3 LB film. The temperature dependent behaviors of the intensity and line width of X-ray diffractions are shown in Figure 11. The phase

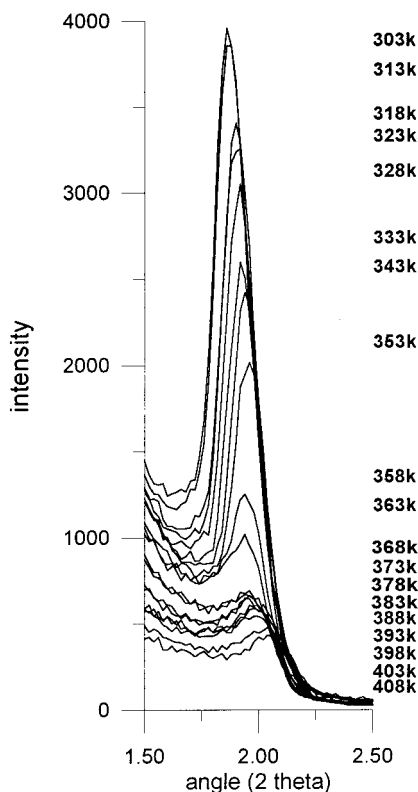


Figure 10. Temperature dependent small-angle X-ray diffraction patterns of ES-3 polymeric LB film.

transitions can be easily seen, which are consistent with the data from FTIR. We can see that below 353 K, with the increase of the temperature the intensities of the diffraction peaks decreased gradually and the diffraction peaks shift to bigger angle, which indicates that the d -spacing becomes smaller as the temperature increase. It may be result from reorientation of the alkyl chains with increase of temperature, which is consistent with the results of temperature dependent FTIR. When the film is heated to around 363 K, the intensities of diffraction peaks decrease gradually, but the diffraction peak shifted to a small angle. When the film is heated above 363 K, the diffraction peak shifted to a bigger angle, the intensity decreased tremendously, and the shape of the peaks became not so sharp. When the film is heated beyond 403 K, the intensities of diffraction peaks decrease much more significantly and become halos. The first transition is corresponding to the orientation change of the long alkyl chains, and the second transition is caused by conformational change of long alkyl chains, corresponding to the order-disorder transition. Above 398 K, the LB film melted into isotropic liquids; the layer structure is destroyed. Combining the results of FTIR and low-angle X-ray diffraction, we can correlate that the transition detected by X-ray diffraction at around 353 K corresponds to the phase transition at 340 K detected by FTIR, 363 K corresponds to 370 K, and 398 K corresponds to 410 K.

Now, combining the results of X-ray diffraction with that of FTIR, we can see that the mobility of polymeric LB film increased and the molecular order decreased during the first two transition processes, but the layer structure still existed; during the third transition process, the layer structure is destroyed, allowing a tremendous increase of the mobility and decrease of the order.

As to phase transition behaviors of the LB films, Naselli^{5a} observed a two-step melting process in a LB film of cadmium arachidate: The first step is a pretransitional

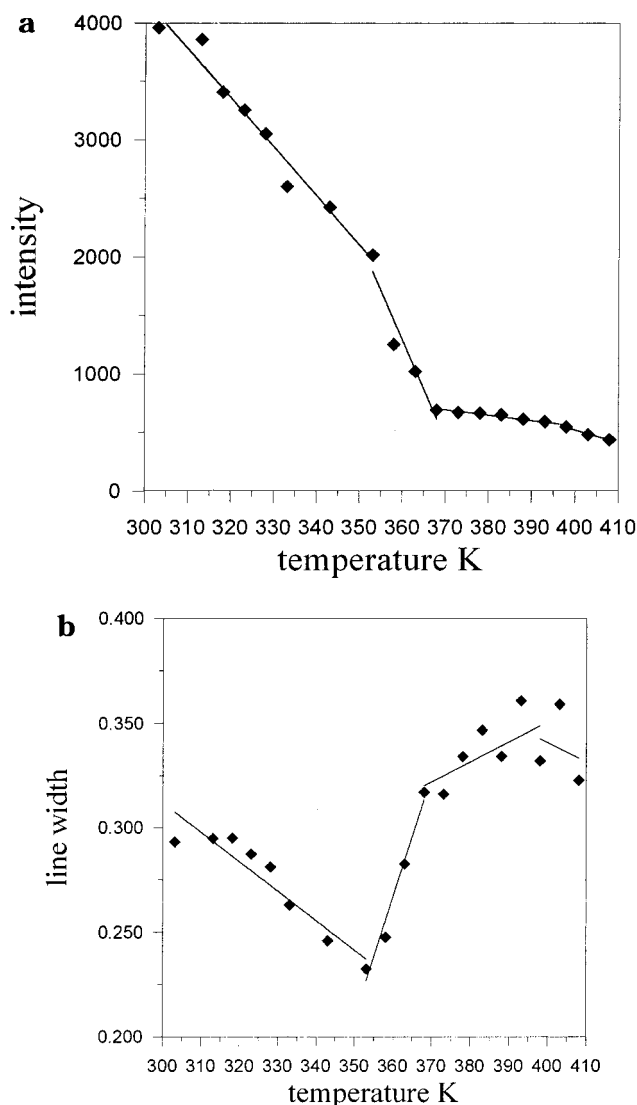


Figure 11. Temperature dependent behaviors of (a) intensity and (b) line width of X-ray diffraction.

disordering of the alkyl chains below melting points (order-disorder transition) followed by the second process of irreversible breakup of the head group above the melting point. In other cases, only an order-disorder transition process can be observed. In common polymeric LB films, the phase transition behavior is just like that of small molecules. However, the ES-3 polymeric LB film undergoes a three-transition process from a highly ordered state into a melted state. From the discussion above, we have seen that the last transition process is a process of disappearance of layer structure.

In our previous work, we have demonstrated that due to the strong collective interaction of the pendant long alkyl chains, some semirigid rods are formed which have the similar effects to the rod mesogens in usual liquid crystals, so the amphiphilic polymer ES-3 without mesogen can exhibit thermotropic liquid crystalline behavior. ES-3 exhibits a three-phase transition process: the amphiphilic polymer starts melting at 362.1 K, undergoes two smectic phases in the ranges 362.1–381.9 K and 381.9–403.9 K, and then melts at 403.9 K as an isotropic liquid, which has been identified by differential scanning calorimetry, X-ray diffraction, and FTIR measurement.^{8b} Compared the phase transition temperatures of the LB film with that those of the bulk materials determined by FTIR, we find that the corresponding transition temperatures of

LB films are almost the same as those of the bulk materials, respectively. So, it is highly possible that the transition behaviors of LB films are very similar to the transition behaviors of the bulk crystal to liquid crystal. Following Penner and Ringsdorf,¹³ we think that the two meso states of the LB films can be regarded as two "Langmuir–Blodgett liquid crystals" states with different order.

Conclusion

The Reversed Duckweed polymeric LB film has a well-ordered structure which is similar to that of the monomer octadecylacrylamide LB film, which indicate that the

flexible hydrophilic network has the effect of a spacer group. From the discussion above, we may also draw the following conclusion: The thermal transition of the Reversed Duckweed polymeric LB film may be considered as a Langmuir–Blodgett crystal to two "Langmuir–Blodgett liquid crystals" to a melted isotropic state phase transition due to the very similarity of the phase transition behaviors of the LB film and the bulk material.

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(13) Penner, T. L.; Schildkraut, J. S.; Ringsdorf, H.; Schuster, A. *Macromolecules* **1991**, *24*, 1041.