

A highly ordered polymeric Langmuir-Blodgett film

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Summary

A new type of polymeric LB film named "Reversed Duckweed" type LB film was fabricated by use of a new kind of amphiphilic polymer which was composed of a flexible hydrophilic epichlorohydrin-ethylene diamine crosslinking microgels and several hydrophobic stearic chains. It had highly ordered structure, including a well ordered layer structure and highly oriented hydrophobic alkyl chains in each layer, which was confirmed by low angle X-ray diffraction and polarized FTIR-ATR experiment.

Introduction

Langmuir-Blodgett (LB) films have been extensively investigated in recent years because of their potential applications in micro-electronic and optoelectronic devices(1). However, LB films prepared from organic low molecular weight materials are lack of long term stability and thermal stability, which devalue their future application and development. Therefore, polymers have been used to fabricate LB films, and these polymeric LB films may offer much more perspectives for the application because of their structural stability. How to develop polymeric LB films combining structural stability and high ordered structure is an important topic.

The rearrangement and orientation of hydrophobic chains of prepolymerized amphiphiles at the air/water interface are interfered by polymer main chains, resulting in low order of the polymeric LB films. Ringsdorf and his co-workers (2-4) have put forward an approach to decouple the interaction between the polymer main chains and side groups by introducing "spacer group" into the prepolymerized amphiphiles, in this way the order of polymeric LB films is enhanced to some extent. In the previous work of our group, we introduced a flexible network into the amphiphilic polymer in order to enhance the order of the polymeric LB films. In view of this point, the new types of polymeric LB films, "Duckweed" and "Reversed Duckweed" type LB films, were developed (5-8). The so-called Duckweed type of LB film means that the hydrophobic networks are floating onto the air-water interface and the hydrophilic grafting chains are projected into the water, vice versa the Reversed Duckweed type LB film means that the hydrophilic networks extend into water and the hydrophobic grafting chains are upward packing away from the surface of water. The network is a slightly cross-linked microgel, and thus it is flexible enough to reform its configuration(9). In this paper, we report

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the fabrication of a new type of Reversed Duckweed polymeric LB film which has a highly ordered structure.

Experimental

Synthesis and characterization of the amphiphilic polymer

The amphiphilic polymer (for simplicity we term it as ES) was synthesized according to the approach showed in Fig. 1, stearic acid was reacted with a large excess of ethylene diamine under melting condition to produce the monoamide, then it was purified by recrystallization from ethanol. The subsequent polymerization can be proceeded by following steps: 12.1g monoamide and 0.9g ethylene diamine were mixed under melting condition and heated to 100°C, then 6.8ml epichlorohydrin (0.08mol) dissolved in DMF was added dropwise to the well-stirred reaction mixture over a period of 20 minutes, the reaction mixture was stirred for 1hr, and then cooled to the room temperature to produce a white solid precipitation, it was purified by two times of precipitation of hot ethanol solution into ether to ensure the removal of all unpolymerized substance; the final product (white powder) was dried in vacuum for 24h at 40°C.

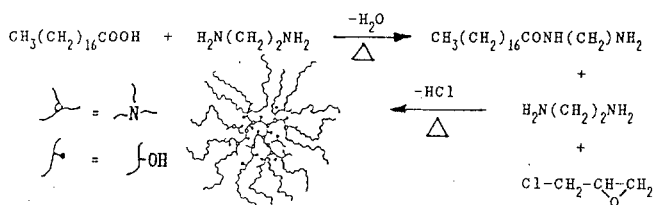


Fig. 1 Approach for synthesizing the amphiphilic polymer

IR(KBr): 3301 cm^{-1} (OH), 2955 cm^{-1} (CH₃), 2848, 2919 cm^{-1} (CH₂), 1689 cm^{-1} , 1637 cm^{-1} (C=O, in amide). Compared with the IR spectra of the starting materials, the N-H stretching bands disappeared in polymer, indicating the formation of the hydrophilic networks linked by >N-.

Its number average molecular weight is 7840, determined by means of membrane osmometer (KUAUER Model), the content of alkyl chains was determined by weighing the amount of stearic acid obtained from thoroughly hydrolysis of 0.5g polymer in HCl solution, the stearic acid was washed with water and dried in vacuum for 24hr at 50°C. The result was: the content of alkyl chains was 75.8%, indicating one molecule contained 20.8 stearic chains on average.

Spreading experiments, LB transfer and characterization of LB films

Monolayer experiment was performed on a computer-controlled KSV-5000 instrument with a Whilhelmy plate system. The film was spread from chloroform/ethanol mixed solution in the concentration of 1mg/ml on pure Milli-Q water (15MΩ). Compression rate was 20mm/min.

Y-type LB films were deposited on a thoroughly cleaned single crystal silica slide for X-ray diffraction and Si-ATR plate for FTIR-ATR measurement while the surface pressure was maintained at 30 mN/m, the dipping speed of 2mm/min and an upper delay of 10 min. for drying.

FTIR-ATR spectra was measured with a Bruker IFS-66V FTIR spectrometer equipped with a MCT detector at 25°C. 51 reflections of the IR beam were allowed for the Si-ATR plate. X-ray diffraction was carried out in D/max γ A diffractometer, Cu α target.

Results and discussion

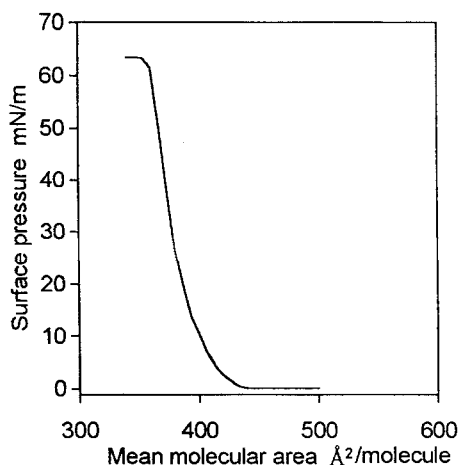


Fig.2 The π -A isotherm of amphiphilic polymer ES, at 20° C

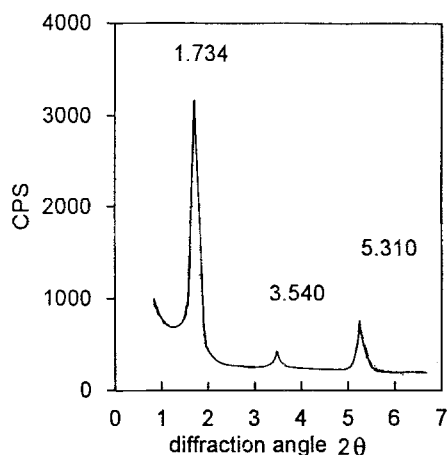


Fig.3 Low angle X-ray diffraction of pattern of LB film polymer ES (49 layers, Y type)

Fig.2 was the π -A isotherm of the polymer ES, indicating that the self-organizing ability of this amphiphilic polymer ES at the air-water interface. As seen from the π -A isotherm, ES can form a stable monolayer and had high collapse pressure up to 60 mN/m. The monolayer of ES showed a typical condensed phase, and the limiting area was 410 $\text{\AA}^2/\text{molecule}$. Based on the suggested "Reversed Duckweed" model that hydrophobic alkyl chains are upward packing away from the surface of water, we could get the area of every alkyl chain occupied was 20 \AA^2 on average, which was almost consistent with the limiting area of a stearic acid monolayer, this data suggested that alkyl chains were closed packed. Moreover, the monolayer exhibited very little area-losing even at the pressure of 50 mN/m for several hours, and thus it demonstrated a very high stability. Such a high stability should be ascribed to nothing but the ordered structure of the monolayer.

The monolayer can be readily transferred onto solid substrate with a transfer ratio of unity. Low angle X-ray diffraction was adopted to study the layer structure. As we know, the structural requirements for observing many orders of X-ray reflections are much stringent, since only a few interruptions in the layer structure, although leaving most of the structure intact, may cause serious loss of phase coherence and X-ray intensity. Thus, in low angle X-ray diffraction experiment, more than one diffraction peaks were seldom observed for polymeric LB multilayers due to its relative low order(10). To our knowledge, only few examples had been reported that more than one diffraction peaks could be observed in low angle X-ray diffraction for polymeric LB film(11). Here, we observed three orders of diffraction for polymeric LB films of ES(Fig.3), and peaks' intensities showed odd-even alternation. Higher orders of diffraction, sharpness of the diffraction peaks, odd-even alternation of the peaks' intensities and large intensity of the first order diffraction provided ample evidences that this kind of Reversed-Duckweed type LB film had a well ordered layer structure. A layer spacing 50 \AA could be easily calculated according to the Bragg equation.

Polarized FTIR-ATR technique was adopted to study the orientation of alkyl chain in multilayers. The dichroic ratio which is the key parameter used in determining the molecular orientation, is defined:

$$D(\theta, \gamma) = \frac{As}{Ap}, \text{ where } D(\theta, \gamma) \text{ is the dichroic ratio, } \theta \text{ is the angle of the transition moment with the}$$

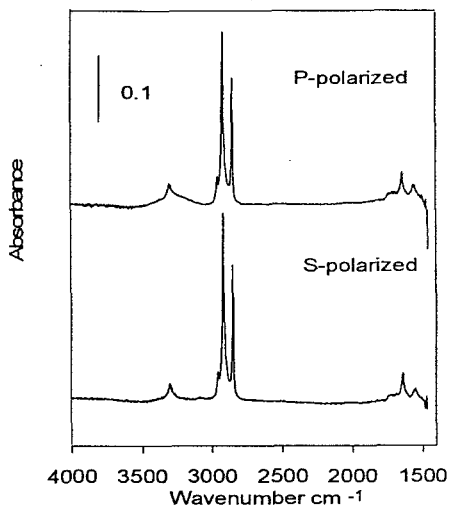


Fig.4 Polarized FTIR-ATR spectrum of the Reversed Duckweed LB film(15 layers, Y-type)

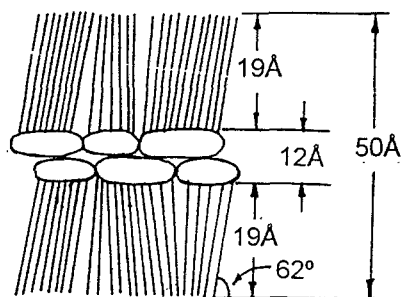


Fig.5 The schematic structural model of Reversed Duckweed LB film

c axis; γ is the tilt angle of the molecular chain axis (c axis) from the film surface normal; A_s is the absorbance intensity of S-polarized light, A_p the absorbance intensity of P-polarized light. 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, we can derive the $D(\theta, \gamma)$ as follows:

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

where E_x^2 , E_y^2 , E_z^2 are electric field intensities(12). The polarized FTIR-ATR spectra of Reversed Duckweed LB film of ES were shown in Fig.4. According to the equation(*), we obtain an average tilt angle of the alkyl chain axes $\gamma = 28^\circ$. The result supported the model of Reversed-Duckweed LB films.

According to the results mentioned above, an assumed model of our Reversed-Duckweed LB film can be schematically depicted in Fig.5. The total length of the alkyl chain with 17 carbon atoms was about 22 Å, considering the average tilt angle of alkyl chains is 28° , so the vertical length of alkyl chains was about 19 Å. Assuming there was no gap between layers, the thickness of one layer of hydrophilic network was about 6 Å, the area of the hydrophilic network was 410 \AA^2 (with radius of 12 Å). In this case, the network might be imagined as thin flat-shaped configuration.

Based on above results and previous reported results, we think that the following two factors are responsible for the high ordered structure of this polymeric LB film: one is a delicate balance between the hydrophilic part and hydrophobic part, and the other is a flexibility of the network. The balance between the hydrophilic part and hydrophobic part played an important role in the process of self-organization at the air-water interface(13). Too much hydrophobic part will result in relatively low collapse pressure for its monolayer. On the other hand, an amphiphilic polymer with too much hydrophilic part cannot form a stable and condensed monolayer. According to above results, we considered that the balance between the hydrophilic part and hydrophobic part could have been reached for this amphiphilic polymer ES we used here. As we reported, we could adjust the ratio of the hydrophilic and hydrophobic part and obtained another sample (ES-1) of this kind of polymer with

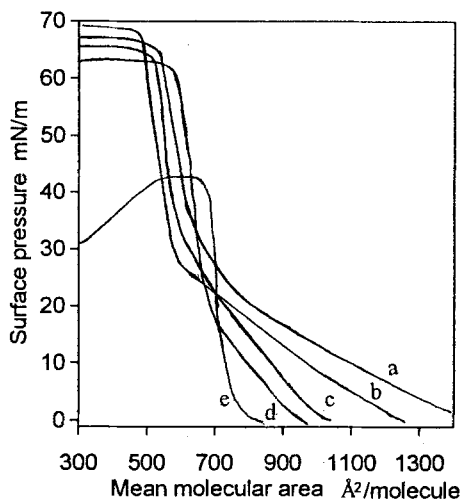


Fig. 6 π -A isotherms of amphiphilic polymer ES-1 with alkyl chains content of 48.5% and its C_{60} complex monolayer. Mole ratios: C_{60} :ES-1=0:1 (a), 0.5:1(b), 1:1(c), 2:1(d) and 4:1(e)

low content of alkyl chains, e.g. 48.5%. Its number molecular weight is 12100, and each molecule contained 20.6 alkyl chains on average. From Fig. 6 we could see that this sample (ES-1) with low content of alkyl chains could only form a liquid analogue monolayer with poor stability due to its stronger hydrophilicity. When some amounts of hydrophobic C_{60} were introduced into the amphiphilic polymer ES-1 to balance the hydrophilicity and hydrophobicity, a stable and ordered complex monolayer could be formed and transferred as LB multilayer, which indicated that the balance between the hydrophilic part and hydrophobic part was recovered(14). We considered that the flexible hydrophilic network act as a kind of special spacer group, because it could reform its configuration to decouple the interference between the hydrophobic chains and the hydrophilic network during the process of self-organization at the air-water interface. However, if the network is highly crosslinked or rigid, the amphiphilic polymer would have ball-shaped configuration rather than the "Reversed Duckweed" structure and couldn't take the function as spacer group. For the amphiphilic polymer we used here, the hydrophilic network was flexible enough and could reform its configuration to be a thin flat-shaped configuration on which hydrophobic alkyl chains close packed with high orientation, and herein the flexible network acted as special spacer group.

Therefore, we could take the conclusion that this Reversed Duckweed LB film had highly ordered structure: including a well-ordered layer structure and high orientation of the hydrophobic alkyl chains in each layer. As our published results and the undertaking work, this new polymer can be used as a good matrix for assembling functional ultrathin films, and in this way this amphiphilic polymer may have a great interest both in theory and in application.

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References

1. Ulman A., (1991) An Introduction to Ultrathin Organic Films. Academic Press, INC
2. Elbert R., Laschewsky A., Ringsdorf H., (1985), *J. Am. Chem. Soc.*, 107: 4134
3. Ringsdorf H., Laschewsky A., Schmidt G, Schneider J., (1987), *J. Am. Chem. Soc.*, 109:778
4. Laschewsky A., Ringsdorf H., *Angew. Makrolol. Chemie.*, (1986), 145: 1
5. Yin R., Cha X., Zhang X., Shen J. C., (1990), *Macromolecules*, 23: 5185
6. Cha X., Yin R., Zhang X., Shen J. C., (1991), *Macromolecules*, 24: 4985
7. Shen J. C., Zhang X., Zhang R. F., (1992), *Thin Solid Films*, 210/211: 624
8. Zhang R. F., Zhang X., Shen J. C., (1994), *Langmuir*, 10: 2727
9. Li J. B., Yin R., Fu G., Ma R. J., Shen J. C., (1993), *Acta Polymeric Sinica*, 2: 201

10. Young M. C. J., Jones, R., Tredgold R. H., Lu W. X., Ali-Adib Z., (1989), *Thin Solid Films*, 182: 319
11. Hirano K., Sato M., Fukuda H. (1992), *Langmuir*, 8: 3040
12. Dong J. A., Elias I. F., (1992), *J. Phy. Chem.*, 96: 9952
13. Zhu J. Y., Eisenberg A., Bruce L. R., (1991), *J. Am. Chem. Soc.* 113: 5583
14. Zhang X., Zhang R. F., Shen J. C., Zou G. T., (1994), *Makromol. Rapid Commun.*, 15: 373