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Atomic force microscopic (AFM) study on a self-organizing polymer film

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Summary

The structure of a self-organized polymer film prepared by slow evaporation of organic solvents is studied by atomic force microscopy, and compared with that of polymer film prepared by natural evaporation of organic solvents. AFM studies clearly indicates that there exists a self-organizing process of alkyl chains resulting in the partial interdigitated layer structure under the condition of slow evaporation of organic solvents.

Introduction

Self-organization of amphiphilic molecules in solution and at interfaces has always received much attention because of its relevance to technical and biological applications. Among these molecules, self-assembling and self-organization of polymers have arouse much interest of scientists and some significant advances have been achieved recently(1). Due to different interactions of segments in the polymer chain, such as hydrophobic and hydrophilic effect, hydrogen bonding, coulombic interaction and Van der Waals interaction, polymer can self-organize to materials with different structural order(2).

Amphiphilic polymers' organization behaviors in solutions and at the air-water interface have been studied intensively. By adjusting the ratio of hydrophilic and hydrophobic part of diblock copolymer, the structure of the polymers can be manipulated, which could help the self-organization of polymers to form an ordered two dimensional array(3). Dropping the polymer solution onto a solid substrate and evaporate the solvent, some polymers can build up ordered layer structure(4). The rate of evaporation has a strong influence on the self-organization of polymers and it can be used to fabricate ordered polymer films with special morphology and order(3b, 4).

In previous work(4), we have used an amphiphilic polymer composed of hydrophilic ethyl diamine-epichlorohydrin slightly crosslinking networks bearing hydrophobic stearoyl side chains (chemical structure shown in Fig. 1) with appropriate hydrophobic/hydrophilic ratio to succeed in fabricating an ordered self-organized polymer cast film with partial interdigitated structure by slow evaporation of organic solvents.

Atomic force microscopy (AFM) is a valuable tool for investigating the surface morphology and structure with atomic or molecular resolution and has been used to characterize the surfaces of a variety of materials, especially to soft, organic materials, such as molecular

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adsorbates, Langmuir-Blodgett films and self-assembled amphiphilies(5). In this contribution, we will adopt the atomic force spectroscopy (AFM) to study the structure of this self-organizing film.

Experimental part

Materials

An amphiphilic polymer composed of hydrophilic ethyl diamine-epichlorohydrin slightly crosslinking networks bearing hydrophobic stearoyl side chains (chemical structure shown in Fig. 1) was synthesized as described in detail in our previous paper(7). This polymer has an Mn 7840 and an alkyl chain content of 75.8%, one molecule contains 20.8 stearoyl side chains on average.

The amphiphilic polymer was slightly crosslinked, its crosslinking degree as defined as the content of tertiaryamine (=N-) unit in the polymer's hydrophilic part is 25%.

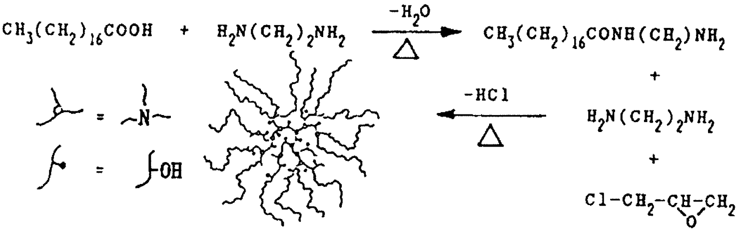

Fig. 1 Schematic chemical structure of the amphiphilic polymer

Preparation of self-organizing polymer film

The polymer was dissolved in $CHCl_3/C_2H_5OH$ (volume ratio 7:3) at a concentration of 2mg/ml, and cast onto a clean Si wafer or newly cleaved mica substrate (for AFM experiments). Under saturated vapor pressure of CHCl3 at room temperature for more than 48 hours the solvent was slowly evaporated, producing the self-organized polymer films on these substrates, then dried under vacuum at room temperature to remove residual solvents.

AFM imaging

AFM experiment was conducted on a commercially available scanning force microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) under ambient condition. The AFM was operated in the tapping mode for low magnification and in contact mode for high resolution using microfabricated Si_3N_4- and Si- cantilevers, respectively. The pyramidal shaped Si_3N_4-tips for the contact mode has a spring constant of 0.032 N/m (Topometrix™) while the Si-cantilevers used in the tapping mode has a spring constant of 30-52 N/m and a resonance frequency ranging from 306 to 365 kHz (Nanosensors™).

Results and discussion

Fig. 2 shows the typical large scale AFM image of a self-organizing polymer film by slow evaporation of the solvent. The multilayered structure of the self-organizing polymer films with flat terraces separated by steps are clearly resolved. The cross section profile along the line A-A' of this image shows heights of steps are equally around 3.6nm, which is in good agreement with the layer spacing 3.66nm of this self-organizing film determined by X-ray diffraction. The high resolution image of the film is shown in Fig. 3 (raw data), it indicates that the alkyl chains are packed in a hexagonal lattice with the lattice parameters of a=b=0.67 nm and a tilt of 49.5° in the direction of the nearest neighbors.

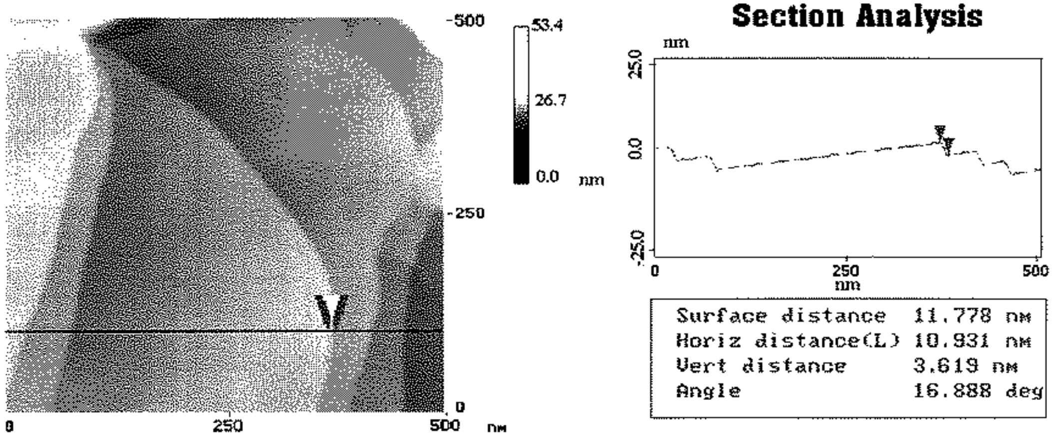

Fig. 2 AFM image of self-organizing polymer film prepared by slow evaporation of organic solvents (left) and section analysis profile along line A-A' (right)

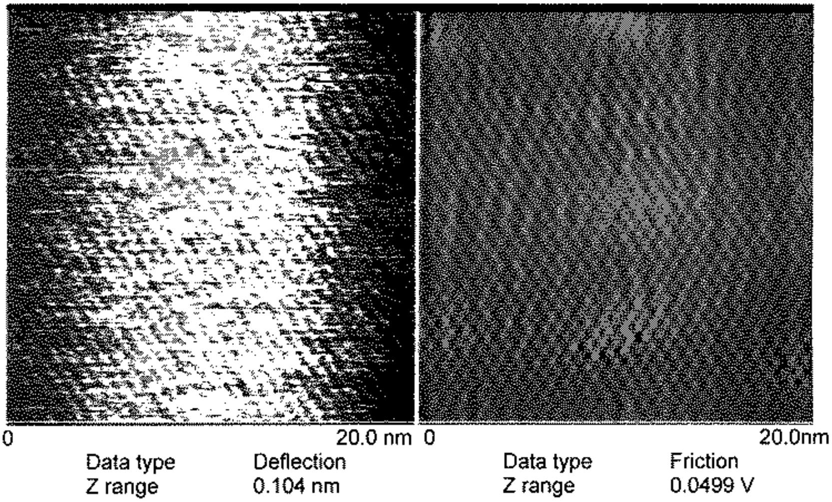

Fig. 3 High resolution image of self-organizing polymer film

In the previous work(4a), we have observed that the evaporation rate of the organic solvents has a great influence on the formation of self-organizing film. By natural evaporation of solvents, the resulting film has almost the same structure as that of polymer bulk crystal whose long spacing is 5.1nm and 4.9nm. AFM image (as shown in Fig. 4) of the sample prepared by natural evaporation of solvents shows the multilayered structure and the steps. The heights of all the steps are around 5nm which is completely different from that of self-organizing film, but is in good agreement with the results of X-ray diffraction of the bulk crystal. This finding further confirms that there exists a self-organizing process of hydrophobic alkyl chains which results in the formation of interdigitated layer structure under the condition of slow evaporation of organic solvents.

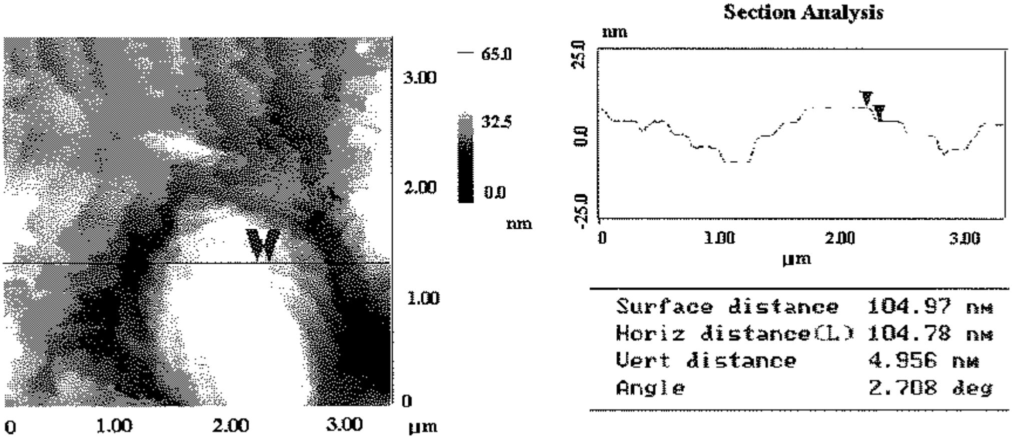

Fig. 4 AFM image of polymer film prepared by natural evaporation of organic solvents

And we also found that the films prepared by natural evaporation are much softer than those prepared by slow evaporation. In opposite to the self-organizing film, it is very difficult to get a high resolution image on the terraces in this case since this film is easily damaged by the AFM tip.

Since the discovery of the interdigitated state in phospholipid bilayer structure, there are only few paper described the formation of the interdigitated structure in LB film and lipid bilayer(6), this kind of partial interdigitated layer structure is very unique for a self organized polymer system.

Based on the present AFM studies, we can see that there really exists a self-organizing process which resulting in the partial interdigitation. We can see that the film growth process is a step-by-step process for both of the films fabricated by slow and natural evaporation of solvents. Namely, one terrace grows on top of the beneath one, and the next one grows on top of it, and so on. Just by slowing the evaporation rate of the solvents, the hydrophobic alkyl chains undergoes a self-organization process and results in a partial interdigitation, the heights of steps decrease from 5nm to 3.6nm.

All of the terraces are hydrophobic alkyl chains. Actually, what we saw in the high resolution image for self-organized film is the part of uninterdigitated alkyl chains. So, why can we observe the high resolution image for the film by slow evaporation and cannot for the film by natural evaporation film? We think that this is closely related to the force between adjacent layers. We find that one layer will be scratched away and leave a hole if we increase the imaging force. The depth of the hole is 3.6nm for self-organized film and 5nm for the film by natural evaporation. We couldn’t find a step and make a hole whose height is half of 3.6nm or 5nm. This indicates that the force between the two hydrophilic networks is much stronger than that between two hydrophobic layer. As seen from the ideal model (Fig. 5), the force between the two adjacent hydrophobic surfaces in polymer film prepared by natural evaporation is only the weak Van der Waals interaction. So that the sample could be easily scratched away and it is difficult to get a high resolution image. On the contrary, for the self-organizing polymer film by slow evaporation, the collective interaction between the hydrophobic interfaces due to the partial interdigitation is stronger than the Van der Waals’s interaction, thus the polymer layer is somehow immobilized by the beneath layer and can stand high imaging force. The surface of terraces in the self-organizing film is more stable than the surface of polymer film by natural evaporation.

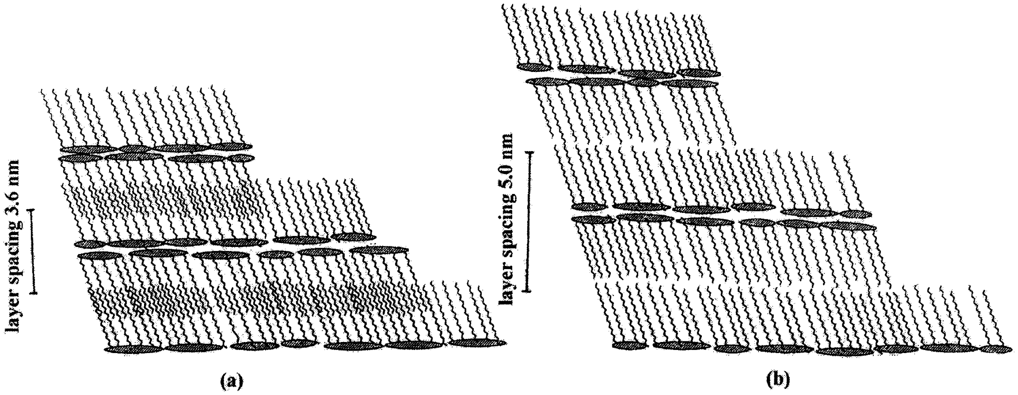

Fig. 5 Comparison of structural model of self-organized polymer film prepared slow evaporation of organic solvents (a) and polymer film prepared by natural evaporation of organic solvents

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