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Langmuir-Blodgett (LB) films of an amphiphilic diacetylene (DA) complexed with polyallyamine (PAA) were fabricated. Textural structures were observed in the AFM images, while the surface was covered with small grains after the heat treatment at temperatures higher than 100°C. The polymerization of DA proceeded by the irradiation with UV light before the heat treatment whereas only a small fraction of DA polymerized after the heat treatment. The LB films of polymerized DA complexed with PAA showed better stability against heat treatment than the ones without PAA.

Keywords: diacetylene; Langmuir-Blodgett films; heat effect; AFM

INTRODUCTION

Langmuir-Blodgett (LB) technique has been used to fabricate ultrathin films with well-defined structures. Amphiphilic diacetylenes have been reported to polymerize in the LB films owing to the ordered arrangement of the molecules[1]. The polymerization of diacetylenes is affected strongly by the distance and the relative orientation of the adjacent molecules. In this respect, the polyion complex method is interesting since it allows for the modification of the LB film structures[2,3]. In this paper, we will report on the effect of heat treatment on the morphology and polymerization of the LB films of an

amphiphilic diacetylene complexed with polyallylamine.

EXPERIMENTAL

10,12-Pentacosadiynoic acid (DA) was dissolved in chloroform and spread on a $1x10^{-4}$ M polyallylamine (PAA) aqueous subphase or an aqueous subphase containing $4x10^{-4}$ M $CdCl_2$ and $5x10^{-5}$ M $KHCO_3$. The monolayers was transferred at 25 mNm^{-1} using the vertical dipping method. A low-pressure mercury lamp was used as the UV light source for the polymerization of DA. Polymerized form of DA is referred to as PDA. DA and PDA complexed with PAA are referred to as DA/PAA and PDA/PAA, respectively. A Seiko SPA-300 atomic force microscopy (AFM), operating in non-contact mode, was employed to image the LB films. The heating time was 45 min, and the films were cooled down to room temperature before the characterization.

RESULTS AND DISCUSSION

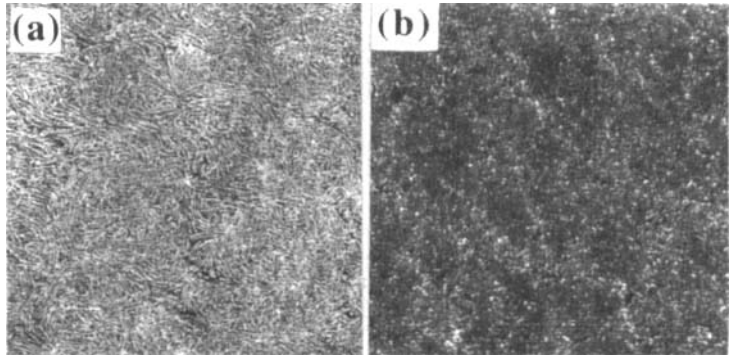

FIGURE 1 AFM images of DA/PAA LB films: (a) before the heat treatment; (b) after the heat treatment at 150°C.

First, we investigated the morphological change of single-layer LB films of DA/PAA by heat treatment. Figure 1 shows AFM images before and after the heat treatment at 150°C. Before the heat treatment, the LB film has a textural structure in which nanofibers with a width of 35 nm cover almost all the surface. Instead of these nanofibers, small grains are seen after the heat treatment. This morphological change

occurred when the film was heated at temperatures higher than 100 °C. This shows that the melting of the film during the heat treatment gives rise to the reorganization of the film structures.

Next, the effect of the heat treatment on the polymerization of DA in the LB films was studied. Figure 2 shows spectral changes of the DA/PAA LB films on the irradiation with UV light before and after the heat treatment at 100°C. A broad absorption band around 540 nm develops before the heat treatment, while the absorption around 300 nm increases slightly after the heat treatment. Only a small fraction of DA polymerized in the latter film. The critical temperature for this spectral change was 100°C. These results show that the melting of the film destroys the favorable arrangement of the adjacent molecules for the polymerization.

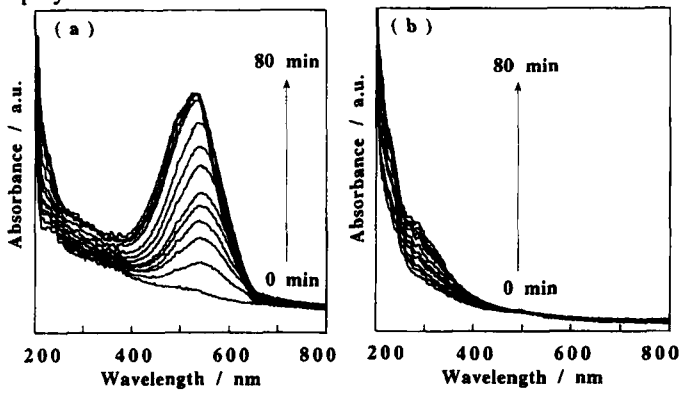

FIGURE 2 Change in UV-vis absorption spectra of DA/PAA LB films on the irradiation with UV light: (a) before the heat treatment; (b) after the heat treatment at 100°C.

Further, we studied the effect of the heat treatment on the electronic state and the morphology of PDA/PAA LB films. Figure 3 shows UV-vis absorption spectra of PDA/PAA LB films after the heat treatment. The heat treatment at 100°C gives rise to another absorption band in the shorter wavelength region. With increasing the heating temperature, the 540-nm band disappears and the new band becomes blue-shifted with a concomitant broadening of the band. No discernible band is seen after the heat treatment at 250°C. These phenomena are probably due to the

distortion of PDA polymer backbones by the reorganization of the films, leading to the shortening of the π-conjugation length.

The morphology of PDA/PAA LB film before the heat treatment was similar to that of DA/PAA LB film, but with a slight increase in the fraction of the void region. This morphology remained essentially unchanged by the heat treatment at the temperature up to 200°C. But, these nanofibers disappeared after the heat treatment at 250°C. The morphology was similar to that shown in Figure 1(b).

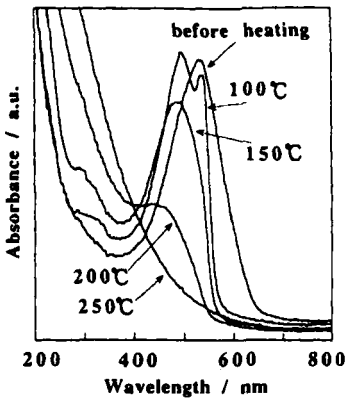

FIGURE 3 UV-vis absorption spectra of PDA/PAA LB films as a function of heating temperature.

Considering that no discernible absorption band was seen after the heat treatment at 250°C, the morphological change may be closely related to the spectral change. It should be noted that the morphology of the LB films of cadmium salt of PDA changed by the heat treatment at 200°C, resulting in a number of concave structures on the film surface. This shows that PAA incorporated into the LB films is responsible for the better stability of the films against the heat treatment.

In summary, we have demonstrated that the heat treatment changes the structures of DA/PAA LB films to a large extent. The role of PAA is shown by the better stability of PDA/PAA LB films against heat treatment compared with the LB films without PAA. This shows that the polyion complex method is useful not only for the control of molecular arrangement in the LB films but also for the modification of physical properties of the films.

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