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Direct Observation of Phase Separation in LB Film Composed of Polyamic Acid Long Alkyl Amine Salts by Using Friction Force Microscope (FFM)

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The surface of a LB film of polyamic acid long alkyl amine salts, consisted of a mixture of aromatic and aliphatic polyamic acids, was observed by means of friction force microscopy (FFM). The LB film having 11 layers gave no significant pattern by atomic force microscopy (AFM), whereas clearly phase separated morphology was observed by using FFM.

Scanning probe microscopy has been accepted as a superior method for surface observation of organic thin films. Especially, atomic force microscopy (AFM) does not require special properties such as conductivity for a sample to observe the surface roughness in nano-scale. Friction force microscope (FFM), which is a optional technique of AFM, offers a particular information even if a surface is obviously flat. This was demonstrated by Fujihira et al. in the LB films of fatty acids consisted of a mixture of alkyl and perfluoro-alkyl chains.[1,2] They obtained an image of clearly phase separated structure between the two different kinds of fatty acids.

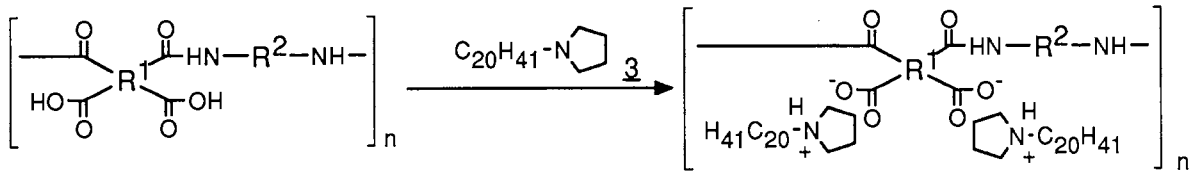
In the study of the preparation of polyimide LB films,[3,4] we have prepared the LB films of polyamic acid long alkyl amine salts 2 as the precursor LB films for polyimides. As shown in eq.1, amphiphilic polymers 2 were obtained by simply mixing polyamic acids 1 with long chain alkyl amine 3. In this comunication, we report direct observation of the surface of the LB film of 2 composed of a mixture of the aromatic and aliphatic polyamic acids.

The chemical structures of aromatic polyamic acid 1a and aliphatic polyamic acid 1b are shown in eq.1. These polyamic acids were dissolved in a mixture of N,N-dimethylacetamide (DMAc) and benzene (1:1) at a concentration of 1.00 mM. After the same amounts of the solutions of 1a and 1b were mixed, double amount of the solution of alkyl amine 3 diluted to the same concentration in the same solvent for the solution of 1 was combined with the mixed solution of 1. The resulting mixture was subjected to the LB method. The deposition of the L film was carried out at 20 mN/m onto a silicon wafer starting upward deposition, and was performed by Y type deposition. The measurements of AFM and FFM were carried out with a Seiko Denshi SPI-3700 at room temperature under air atmosphere.

Figure 1 shows the surface image of the LB film of 2 with 11 layers observed by AFM and FFM. In the case of AFM (Fig. 1a), no significant image was observed. On the other hand, FFM afforded clearly phase separated image as shown in Fig. 1b, where the diameter of the island was approximately 1 μm. It is impossible to determine the correlation between the island and sea in the photograph and aromatic and aliphatic parts in the mixed polymer at this stage.

This is the first report of the direct observation of the two dimensional phase separated morphology in a

mixture of two polymers. Since the polymeric LB films are more reliable than the LB films of monomeric compounds, studies of the observation of phase separation behavior in the polymeric system would bring about significant progress in the surface technology.

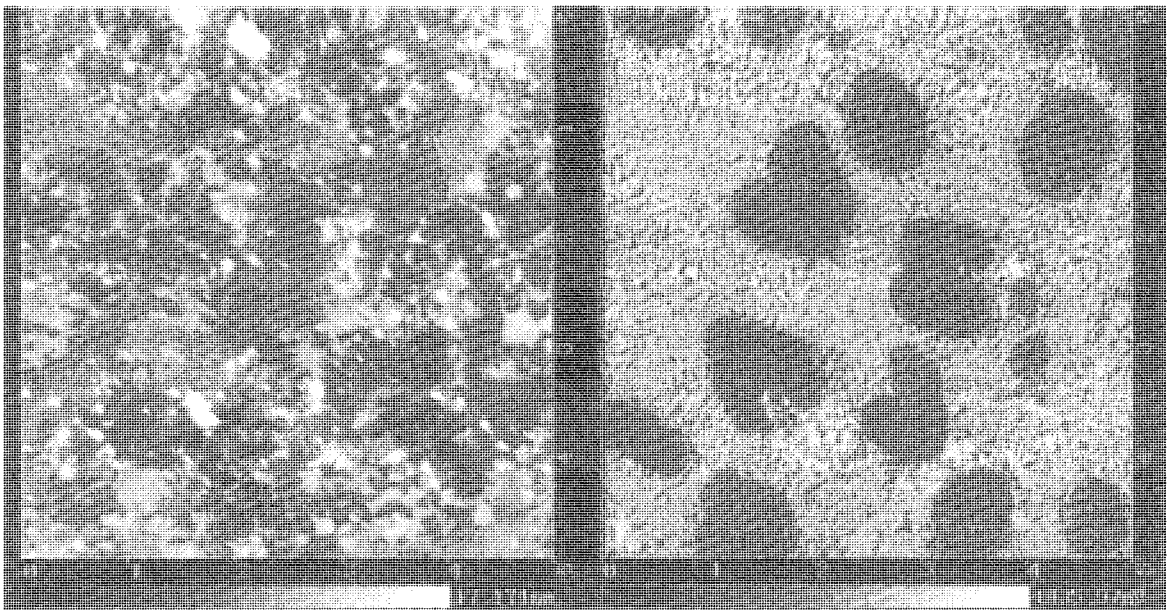


(1)

1 2

a: R^1: R^2:

b: R^1: R^2: $-(CH_2)_6-$



a) b)

Fig. 1. Surface image of LB film of mixture of 2a and 2b. a): observed by AFM, b): observed by FFM. Both views are the exactly same area with 5 μm squre.

References

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