Polyamide monomolecular films prepared by polycondensation at air–water interface

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Novel polyamide films were prepared at the air–water interface by condensation between the dichloride of (2R,3R)-ditetradecanoyl tartaric acid and diamine. A stable monolayer was obtained, which could be transferred onto a substrate. Formation of polyamide monomolecular films was confirmed by i.r. spectroscopy and measurement of film thickness.

(Keywords: polycondensation; polyamide; monomolecular film)

Introduction

Highly ordered molecular films prepared by the Langmuir–Blodgett (LB) technique have aroused widespread interest with regard to molecular architecture and potential applications in various fields, such as non-linear optics and microelectronics. From the viewpoint of practical use, polymeric LB films have advantages in their mechanical strength and thermal stability. Polymeric LB films can be prepared with amphiphilic monomers, which are subsequently polymerized, or with preformed amphiphilic polymers. These methods have led to the development of new polymers[1–4]. Recently, much attention has been paid to monolayers at the air–water interface, as a result of the development of advanced techniques[5–8] by which the scope of monomolecular layers has been revealed. The monolayer may provide unique reaction systems enabling the observation of reaction processes in detail and the preparation of new polymers. Unique thin polymeric films were prepared using the monolayer system[9,10]. Regarding formation of polyamides at the interface, interfacial polymerization[11] has been established as an elegant and convenient method. Polycondensation reaction between acid and amine at the air–water interface can be considered essentially the same as interfacial polymerization. However, it has not been investigated at the molecular level. The LB technique seems to be suitable for this purpose and we can expect the direct preparation of polymeric monomolecular films. In this work, we investigated a reaction system consisting of the dichloride of tartaric acid with long alkyl chains (I) and water-soluble diamine, and revealed the monolayer-forming property of the resulting films.

Experimental

(2R,3R)-Ditetradecanoyl tartaric acid (I, TAC_{14}) was prepared from d-tartaric acid according to ref. 12. The dichloride of TAC_{14} was obtained by refluxing TAC_{14} in thionylchloride for 4 h. After evaporation of excess thionylchloride under reduced pressure, the residue was washed with dry benzene, giving white crystals. The melting point of TAC_{14} dichloride was 65°C. Hexamethylene was distilled before use and *p*-phenylenediamine was purchased from Tokyo Kasei and used without further purification.

Measurement of surface pressure–area curves and polycondensation at the air-water interface was carried out using a Lauda film balance (MGW) at 20–22°C. The samples were dissolved in chloroform at a concentration of 10^{-3} M. For measurement of the surface pressure–area curve, pure water, obtained by double distillation of water using a quartz distiller, was used as the subphase. For polycondensation, pure water subphase containing diamine at a concentration of 10^{-3} M was employed. The monolayer was transferred onto a quartz plate or a CaF_2 plate by the LB method under a surface pressure of 25–30 dyn cm^{-1} (1 dyn$=10^{-5}$ N). The molecular weight of the product from TAC_{14} dichloride and *p*-phenylenediamine was estimated by gel permeation chromatography (Shimadzu LC-5A) using tetrahydrofuran as eluent. The thickness of LB films was measured with an Alpha Step 300 (Tencor Instrument).

Results and discussion

In order to carry out a condensation reaction at the air–water interface, it is important to check the stability of TAC_{14} dichloride on the water surface and its monolayer-forming property. For this purpose, the surface pressure–area curve for TAC_{14} dichloride was measured and is shown in *Figure 1b*, with that of TAC_{14} (*Figure 1a*) for comparison. *Figure 1b* shows the surface pressure–area curve of first compression of TAC_{14} dichloride. For TAC_{14}, the condensed phase was observed and its molecular area, obtained by extrapolation of surface pressure zero, was 48 Å^2. In the case of TAC_{14} dichloride, the curve was rather expanded, and on repeating the measurement it gradually changed and became similar to that of TAC_{14}. This observation indicates that TAC_{14} dichloride is gradually hydrolysed into TAC_{14} as a result of its contact with water.

When the same amount of TAC_{14} dichloride was spread onto the water surface of the subphase, which contained hexamethylenediamine, surface pressure was detected, within a few minutes after spreading, at the molecular area of 80–90 Å^2, where surface pressure was not observed in the case of the water subphase. This suggests that TAC_{14} dichloride reacted promptly with

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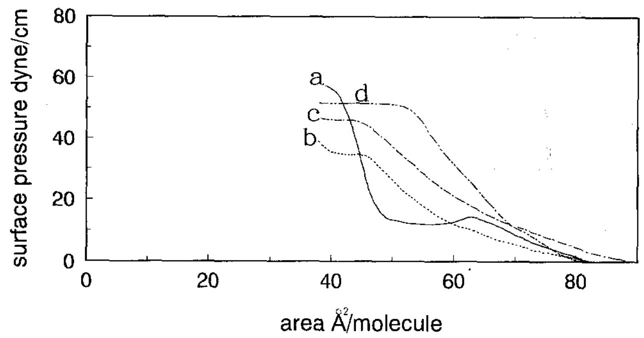
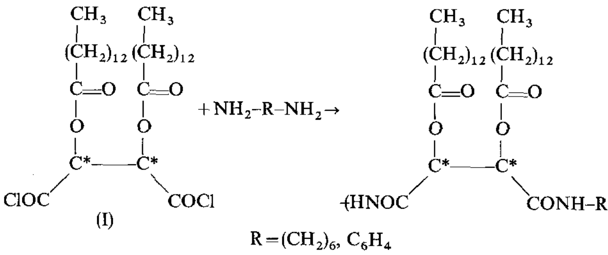


Figure 1 Surface pressure *versus* area curves: (a) TAC_{14} (subphase, pure water); (b) TAC_{14} dichloride (subphase, pure water); (c) product from TAC_{14} dichloride and hexamethylenediamine (subphase, aqueous hexamethylenediamine); (d) product from TAC_{14} and *p*-phenylenediamine (subphase, aqueous *p*-phenylenediamine)

hexamethylenediamine at the water surface. After 15 min, surface pressure became constant and the reaction seemed to be complete. The surface pressure–area curve thus obtained is shown in *Figure 1c*. Compared with that of the water subphase (*Figure 1b*), a remarkable increase of surface pressure was observed in this case and surface pressure reached as high as 50 dyn cm^{-1} by compression. This is considered to be due to the formation of the product from TAC_{14} dichloride and hexamethylenediamine at the water surface. In order to confirm the product formation, the surface film was collected by sweeping the water surface carefully with a barrier, and its i.r. spectrum was examined. The i.r. spectrum of the collected film product showed the disappearance of acid dichloride peaks (1760, 1810 cm^{-1}) and free amine (3330 cm^{-1}) and the appearance of amide I (1660 cm^{-1}) and amide II (1569 cm^{-1}), which indicated the formation of amide bonds in the product, as shown below.



(I)

$R = (CH_2)_6, C_6H_4$

Repeated measurement of the surface pressure–area curve by compression afforded reproducible results. This implies that the surface film obtained by this procedure has a good monolayer-forming property. The monolayer could be transferred onto a quartz plate under a surface pressure of 25–30 dyn cm^{-1}, forming a Z-type film. The i.r. spectrum of the LB films on a CaF_2 plate showed the characteristic peaks of amide I and amide II.

In the case of *p*-phenylenediamine, surface pressure appeared at a smaller molecular area than hexamethylenediamine and it increased more remarkably by compression, as shown in *Figure 1d*. This monolayer could be transferred onto a quartz plate forming a Z-type film. The product collected from the water surface showed the characteristic peaks of amide bonds in the i.r. spectrum and its molecular weight, estimated by gel permeation chromatography, was about 5000, indicating the formation of polyamide.

LB films of 20–30 layers were measured and the average thickness of a monolayer was 15 Å for films prepared using both hexamethylenediamine and *p*-phenylenediamine. This value is reasonable considering the thickness (17.5 Å) estimated from the molecular model, and suggests that alkyl chains are arranged standing upright in the layer.

In conclusion, the polycondensation reaction between TAC_{14} dichloride and diamine at the water surface successfully provided new polyamide monomolecular films. Further investigation, for example of the morphological changes in the monolayers during polymerization with different stereoisomers, is in progress.

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