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PREPARATION OF MONO- AND MULTILAYER FILMS OF AROMATIC POLYIMIDES USING LANGMUIR-BLODGETT TECHNIQUE

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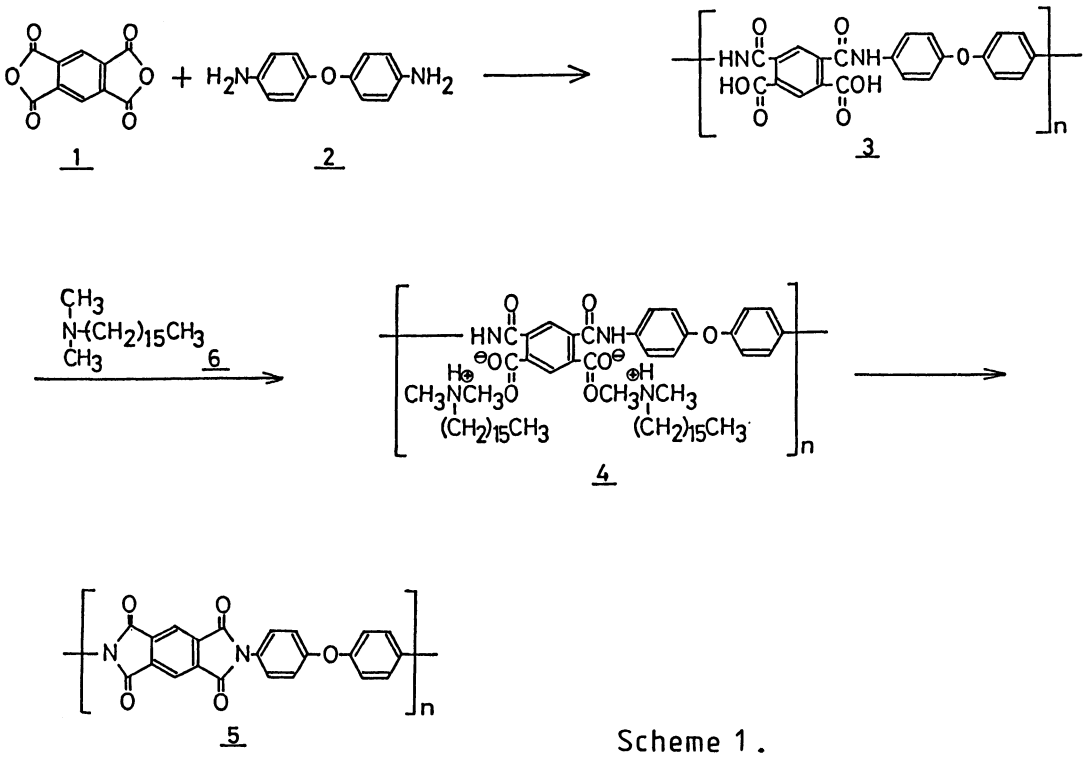
Monolayer film of polyamic acid alkylamine salt at air-water interface was successfully deposited onto appropriate plates. Subsequent treatment of the multilayer film with a mixture of acetic anhydride and pyridine afforded the multilayer film of polyimide. The distance between two layers of the polyimide multilayer film was estimated to be 4 Å.

Wholly aromatic polyimides have been used as high temperature insulating materials in microelectronics[1] and high permselective membranes for gas separation.[2] In such a case, preparation of ultra-thin films of polyimide has been required to obtain higher performance materials. For instance, lower driving voltage as well as higher degree of integration of MIS (metal-insulator-semiconductor) type devices can be achieved by use of thinner insulating layers.[3]

Generally, polyimide 5 is synthesized starting from tetracarboxylic acid dianhydride 1 and diamine 2 via polyamic acid 3 as illustrated in Scheme 1.[4] Because polyimide 5 is quite insoluble in organic solvents and infusible below 500 °C, the fabrication into polyimide films is usually performed at the stage of polyamic acid 3, followed by thermal treatment to 300 °C or by chemical treatment with a mixture of acetic anhydride and pyridine. Minimum thickness of polyimide films cast by spinning coat technique was about 0.1 μm.

Langmuir-Blodgett technique is one of the most promising method for the formation of ultra-thin ordered multilayer films.[5] A number of studies have been reported about the polymerization of amphiphilic monomeric ordered layers.[6,7] These polymeric monolayer films, however, are thermally unstable because of the destructable long alkyl chain.

The formation of monolayer films of polyamic acid alkylamine salts 4 at air-water interface was previously reported.[8] In this paper, we describe the first successful preparation of mono- and multilayer films of polyimide 5 without any



Scheme 1.

pendant long alkyl chain from the corresponding films of polyamic acid salt 4 obtained by Langmuir-Blodgett technique.

Polyimide 5 was prepared as illustrated in Scheme 1. A solution of polyamic acid salt 4 in a mixture of N,N-dimethylacetamide (DMAc) and benzene (1:1) at a concentration of 1 mmol L^{-1} was prepared from polyamic acid 3[9] and N,N-dimethylhexadecylamine 6 in the molar ratio of 1:2, i.e. an equimolar amount of carboxylic function and amine. And it was spread on deionized water. The surface pressure-area relationships for the monolayer film of 4 are shown in Fig. 1 where X-axis is the area of the repeat unit of 4.[10] Extrapolation of the steep rise of the curve to zero pressure gives a surface area of 138 $Å^2$, which is in good agreement with the area of cross section where aromatic rings of polyamic acid lie flat on the water surface.[8]

Deposition of polyamic acid salt 4 was carried out at a surface pressure of 25 dyne cm^{-1} onto quartz plate by drawing down- and up-ward through the liquid-air interface at a rate of 3-5 mm min^{-1} at 20 °C. The multilayer obtained was Z type-film, where the transfer ratio constant was almost 1, only at the up-ward trip. The plots of absorbance at 258 nm in the UV spectra of multilayer films 4 against the number of layers are shown in Fig. 2. The linear relationship obtained suggests that the films have the ordered multilayer structure. On the transmission FT-IR spectrum of film 4 (200 layers) deposited on silicon wafer (Fig. 3), typical absorptions were observed at around 2920 cm^{-1} and 1675 and 1610 cm^{-1} due to long-chain hydrocarbon and carbonyl groups, respectively. The observation of scanning electron microscopy (SEM) showed that no voids and cracks were present on the film surface.

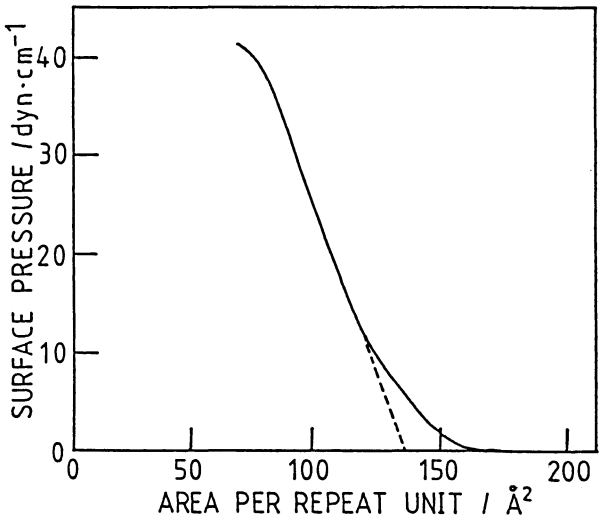


Fig. 1. Surface pressure-area curve of polyamic acid salt 4 apread on deionized water.

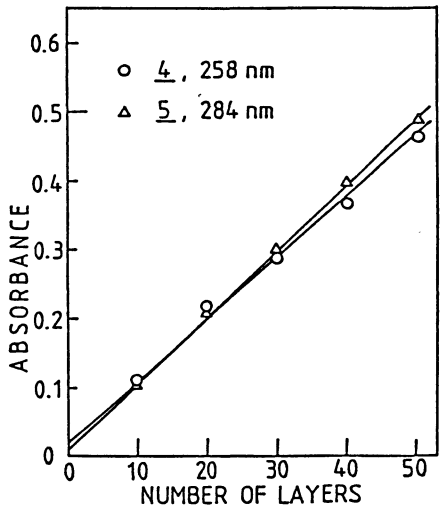


Fig. 2. Plots of UV absorbance against number of layers of polyamic acid salt film 4 at 258 nm, and polyimide film 5 at 284 nm.

Multilayer films 4 on quartz plate thus obtained were immersed overnight in a mixture of acetic anhydride, pyridine, and benzene (1:1:3) to afford polyimide films 5.[4] The plots of absorbance at 284 nm of 5 possessing the corresponding amount of layers to that of 4 are shown in Fig. 2. A linear relationship was again obtained between the number of layers and the absorbance. The absorption due to hydrocarbon group disappeared in the IR spectrum of polyimide 5, and new characteristic absorptions corresponding to carbonyl group appeared at 1780 and 1720 cm^{-1} as shown in Fig. 3. **This suggests that the cyclization of polyamic acid salt 4 to polyimide 5 proceeded almost completely with the removal of long-chain alkylamine 6.** The X-ray interference pattern of polyimide multilayer film 5 (100 layers) as shown in Fig. 4, suggests that the film has uniform thickness of around 400 Å according to Bragg's equation. Furthermore, the thickness of the same film was measured directly to be 420 Å using mechanical stylus probe (Talystep). Fig. 5 shows the reciprocal capacitance against the number of layers for polyimide 5. If 4 Å of monolayer thickness is assumed, the dielectric constant of 5 gives a

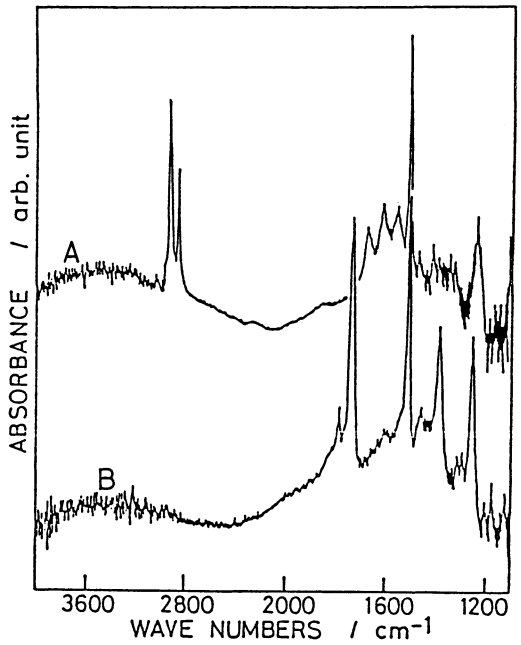


Fig. 3. IR spectra of polyamic acid salt film 4 (A) and polyimide film 5 (B), deposited 200 layers.

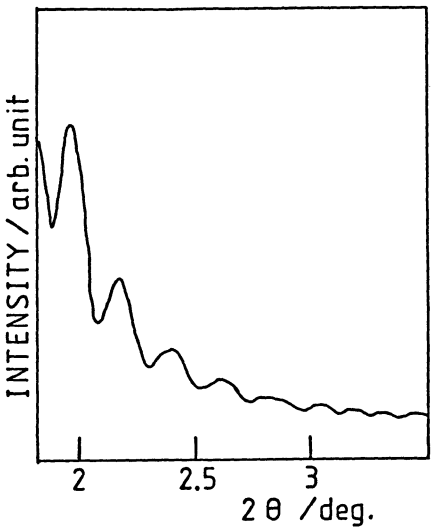


Fig. 4. X-Ray interference pattern of polyimide multilayer film 5, deposited 100 layers.

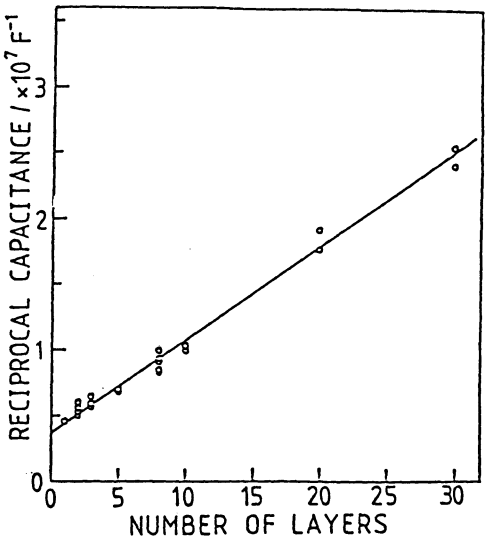


Fig. 5. Plots of reciprocal capacitsnce against number of layers of polyimide film 5.

value of about 3.3 which is in good agreement with that of the corresponding polyimide resin.[11] To our knowledge, the present monolayer 5 is the thinnest film ever produced. The surface of polyimide film 5 was observed by SEM to be as flat as that of polyamic acid salt film 4.

We believe that this new simple and efficient method for the preparation of polyimide mono- and multilayer films would bring about new technologies especially in microelectronics. Further details of the preparation and properties of the multilayer films will be presented in a near future.

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9) The inherent viscosity of polyamic acid 3 synthesized by the reaction of pyromellitic dianhydride 1 and 4,4'-diaminodiphenyl ether 2 in DMAc was 1.25 dL g^{-1} (measured at a concentration of 0.5 g dL^{-1} in DMAc at 30 C). This suggests that polymer 3 has sufficiently high degree of polymerization for fabrication to tough polyimide film. See Ref. 4.
10) The surface pressure-area curves were measured with an apparatus of Kyowa Kaimenkagaku Co. Ltd., Hydrophil balancing meter. The surface pressure was determined by Wilhelmy plate method.
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