CHEMISTRY LETTERS, pp. 395-398, 1986.

PREPARATION OF MONOLAYER FILMS OF AROMATIC POLYAMIC ACID ALKYLAMINE SALTS AT AIR-WATER INTERFACE

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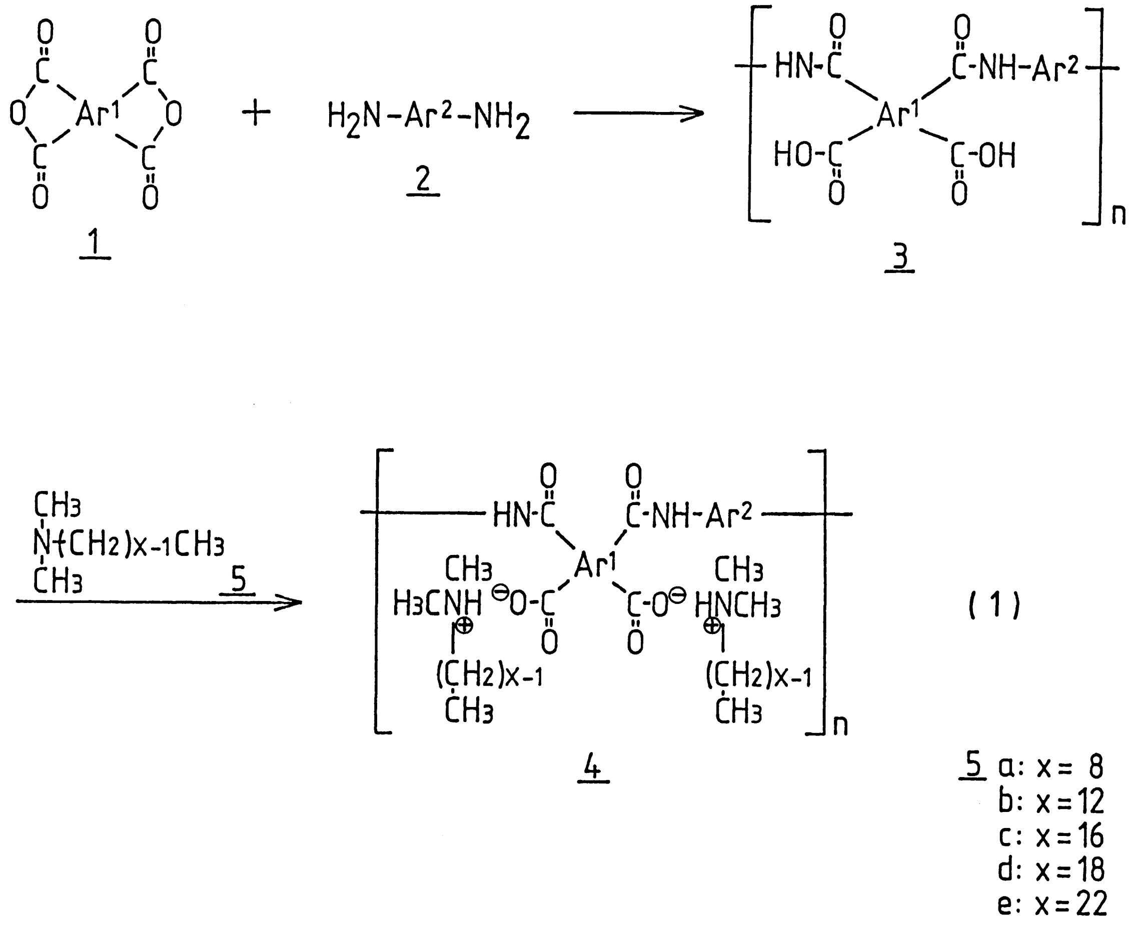
Thin films of polyamic acid alkylamine salts which possess long alkyl side chain were successfully prepared at air-water interface. It was concluded that the polymer salts had a monolayer structure in which aromatic rings of the polyamic acids lied flat on the water surface.

Much attention has been focused on Langmuir-Blodgett technique because it is a relatively simple way to control molecular ordering.1) Polymeric monolayers which possess higher thermal and mechanical stability compared with monomeric ones have been prepared by polymerization of amphiphilic monolayers having polymerizable functions such as diacetylenes,2) olefines,3) and aminoacid esters.4) Direct preparation of monolayers of preformed polymers have also been reported, including polypeptides,5) synthetic polypeptides,6) and alternative copolymers of polymaleic anhydride.7) Herein, a successful preparation of the monolayer films constructed by wholly aromatic polyamic acid alkylamine salts which possess long alkyl substituents is described.

Aromatic polyamic acids 3 are generally synthesized by the reaction of tetracarboxylic anhydrides 1 and diamines 2 as shown in Eq. 1.8) Polyamic acids 3 used in the present work and their inherent viscosities are summarized in Table 1. The solution of 3 as polymerized was diluted with a mixture of N,N-dimethylacetamide (DMAc) and benzene (1:1) to a concentration of 1 mmol/L, while a solution of alkylamine 5 in the same mixed solvent with the same concentration was prepared. These two solutions were combined to produce polyamic acid salts 4 just before spreading on deionized water. The measurement of surface pressure-area relationships (Π-A curves) was carried out with ca. 1.8 cm/min of the compression speed at 20 °C.9)

Figure 1 shows Π-A curves of polyamic acid salt 4a where the molar ratio of polyamic acid 3a and dimethyl-n-hexadecylamine 5c was varied. Each curve rises steeply and the collapsed pressures fall with increasing the ratio of 3a to 5c.

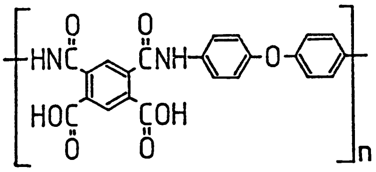
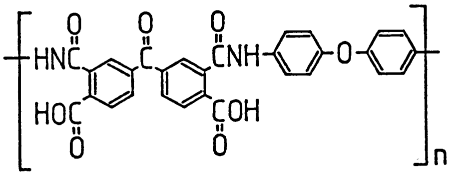
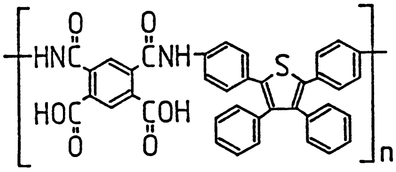
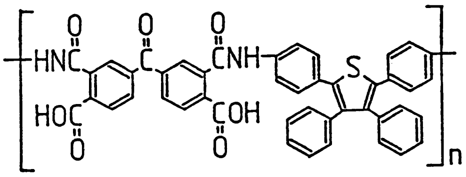
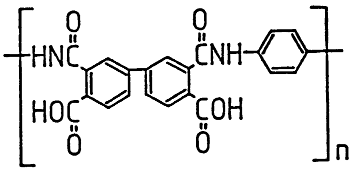
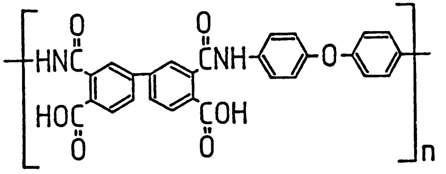


Polyamic acid 3a itself could not be spread into film (curve A). The collapse point reached at 40 dyne/cm (curve D) when the ratio of 3a to 5c is 1:2, i.e. an equimolar amount of carboxylic function and amine is present. Extrapolation of the steep rise of curve D to zero pressure gives a suface area of 138 Å^2, which is in good agreement with the corresponding calculated value for a repeat unit of the polymer by use of the HGS molecular model in which aromatic rings of polyamic acid 3a lie flat on the water surface. This value of the surface area strongly supports that the spread film on the water surface had the monolayer structure. When an excess of 5c was employed (curve E), the extrapolated surface area did not increase markedly compared with the case of curve D.

In the next stage, the length of long alkyl side chain of alkylamine 5 was varied as shown in Fig.2, under the constant ratio that 3a to 5 was 1:2. The extrapolated area increased with the length of alkyl chain, and the surface area occupied is almost constant when the carbon number of the alkyl chain is longer than sixteen, that is 5c. (See curves C, D, and E in Fig. 2)

To investigate scope of the present method, a variety of polyamic acids 3b-3f were applied for the preparation of monolayers. Two equivalents of alkylamine 5c were used to produce various polyamic acid alkylamine salts 4b-4f under the same conditions as those described above. In all cases, steeply rising Π-A curves were obtained, and the values of each extrapolated surface area are summarized in Table 2. The difference between the area of 4a and that of 4b is almost equivalent with

Table 1. Structure and Inherent Viscosities of Aromatic Polyamic Acids 3

	Polyamic acid	η_{inh}(dL/g)[a]
3a		1.25
3b		0.73
3c		1.55
3d		1.20
3e		0.44
3f		0.69

a) Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

the difference between 4c and 4d, corresponding to the surface area of benzoyl function which is calculated to be about 20 Å^2 by the use of a molecular model. Similally, the observed area of phenoxy group from the difference between 4e and 4f as well as that of phenyl group from the difference between 4a and 4f are in good agreement with the corresponding calculated values.

The present method offers a convenient preparation of the monolayers of aromatic polyamic acid alkylamine salts which are precursors of polyimide films well known as highly thermally stable polymers. Deposition of the polyamic acid alkylamine salts monolayers onto appropriate plates, subsequent imidation, and characterization of the final polyimide mono- and multilayer films will be discussed elsewhere.

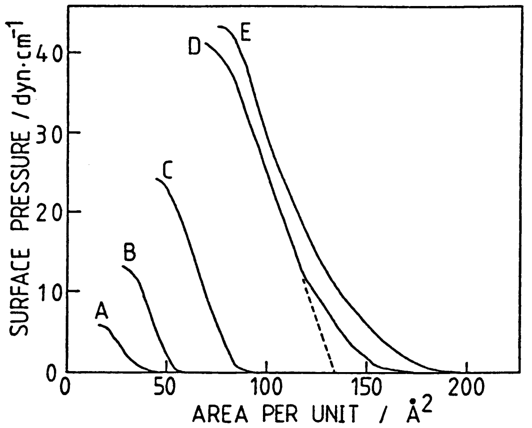


Fig. 1. Π-A curves of polyamic acid salts 4a varying the ratio of 3a to 5c. A; polyamic acid 3a, B; 3a:5c=2:1, C; 3a:5c=1:1, D, 3a:5c=1:2, E; 3a:5c=1:4. X-axis is area per repeat unit of 4a.

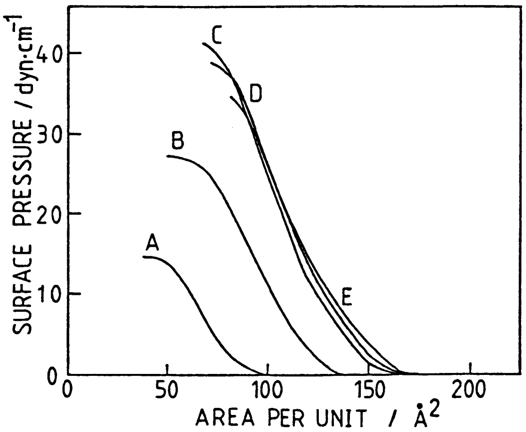


Fig. 2. Π-A curves of polyamic acid salts 4a varying alkylamine 5. A; 5a, B; 5b, C; 5c, D; 5d, E, 5e. X-axis is area per repeat unit of 4a.

Table 2. Extrapolated Surface Areas of Polyamic Acid Salts 4

Polyamic Acid Salt 4	Surface Area Å^2/Unit$^{a)}$
4a	138
4b	165
4c	139
4d	160
4e	130
4f	150

a) Repeat unit of polyamic acid salts 4.

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9) 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.

(Received January 10, 1986)