

Studies on Nylon Monolayers. I. Pressure-Area Curves for Nylon Monolayers on Water

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The conditions under which nylon monolayer spread on water exhibits a reproducible and well-defined F - A curve favorable for detailed investigation of the surface chemical properties of nylon were studied. For this purpose monolayers of Nylons 6 and 8 were spread from such solvents as methyl alcohol, methyl alcohol saturated with calcium chloride, aqueous solution of 90% formic acid and the mixture of phenol and benzene in 1 : 3 volume ratio. The effects of the nature of these solvents, the volume of spreading solution, surface aging and substrate pH on the properties of spread film were studied. It was found that the monolayers can be classified into two different types of film, A and B, according to the behavior of F - A curve against compression. The type A film appeared usually at the first compression of the spread film. F - A curve of A film varied according to the nature of the spreading solvent and the film was unstable. It readily underwent change to type B by being allowed to stand after the film was compressed to a certain extent, by increasing the volume of the spreading solution or merely by compressing film A to a sufficiently high surface pressure. F - A curve of type B film obtained was almost independent of the nature of the spreading solvent and repetition of compression and expansion of the film.

The surface pressure-area curve (F - A curve) of nylon monolayer on distilled water has been studied by many investigators¹⁻⁶⁾ since the study by Crisp.⁷⁾ Recently studies on monolayers of nylon homologues having from three to twelve CH_2 groups in a monomer chain have been reported.⁸⁾ However, in most of these studies, various spreading solvents were used without confirming the reproducibility of F - A curves of the monolayers, *viz.*, most of the F - A curves were obtained only by a single compression of the film. Thus, it is very difficult to draw any conclusion as to whether or not the F - A curves are reversible, film substance changes its state, loss of the film substance occurs, and aging or hysteresis appears upon compression and expansion of the film. It is rather unexpected that such fundamental studies have not yet been well established although these troublesome phenomena frequently occur upon careful observation. Accordingly, the present author felt it necessary to examine first of all a well defined condition under which reproducible measurements of nylon monolayer

are possible.

The present study deals with the effect of the nature of the spreading solvent, amount of spreading solution, aging and substrate pH upon the nature of monolayers of Nylons 6 and 8.

Experimental

Materials. The samples used in the present study were Nylon 6 of Toyo Rayon Co. and Nylon 8 of Nippon Rayon Co. For the purification,⁹⁾ the flakes of Nylon 6 were dissolved in the aqueous solution of formic acid and those of Nylon 8 in methyl alcohol, and both samples were precipitated by adding water to these solutions. The precipitates were extracted with ethyl ether for about 20 hr, using Soxhlet apparatus and the extract was evaporated to dryness *in vacuo*. The spreading solvents used were methyl alcohol saturated with calcium chloride (CM), methyl alcohol (MA), aqueous solution of 90% formic acid (FA) and the mixture of phenol and benzene in volume ratio of 1 : 3 (BP). Surface active contaminants were removed from the solvent by ordinary methods to the extent that the solvents, when spread on water, evaporated and compressed, showed the surface pressure being less than 0.1 dyn/cm which was the sensitivity of the surface balance. The concentration of nylon in the solutions was 0.3 mg/ml. Water was obtained by refluxing first an aqueous solution of acidic, then alkaline potassium permanganate, followed by repeated distillations. The substrate solution used was distilled water or dilute hydrochloric acid.

Methods. The surface pressure was measured by Wilhelmy type surface balance of ± 0.1 dyn/cm accuracy. The trough and barrier made of polymethyl methacrylate were crylate a coated with purified paraffin. The size of the trough was $200 \times 60 \times 10$ mm. The hanging-plate

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was made from microscope cover glass of $11.0 \times 7.5 \times 0.13$ mm in size. The spreading solution of nylon was slowly applied by a micro-syringe onto the surface. Unless otherwise stated, an aliquot of $15 \mu\text{l}$ of sample solution was spread on water surface of 120 cm^2 in area, and the compression of the film was started 20 min after the spreading. This was found sufficient for the film to attain a steady state. This film was compressed at the rate of 8 mm/min by a mortar driven barrier. The rate is conventionally chosen but is the one usually adopted in such measurements.⁵⁾ The trough was enclosed in a glass cabinet and the evaporation of water from and the dissolution of carbon dioxide into the substrate water were avoided by passing a current of humid nitrogen free from carbon dioxide slowly and continuously. The measurements were carried out in an air thermostat held at $25 \pm 0.5^\circ\text{C}$.

Results and Discussion

The Effect of the Nature of Spreading Solvent. The F - A curves for Nylons 6 and 8 monolayers spread from CM, MA, FA and BP are shown in Figs. 1a, 1b, 2a, 2b and 2c. The first compression curves of F - A are denoted by A. After the first compression to a sufficiently high surface pressure, the films were expanded to the initial area, and the second compression was started

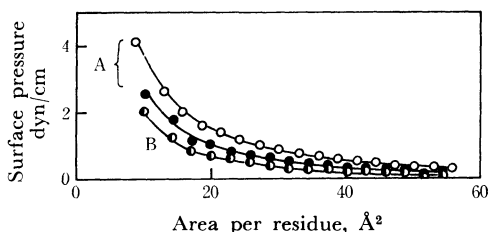


Fig. 1a. F - A curves of Nylon 6 monolayer spread from CM.

- : First compression, on distilled water (film A)
- : First compression, on hydrochloric acid (pH 1.6) (film A)
- ◐: Second compression of above two films (film B)

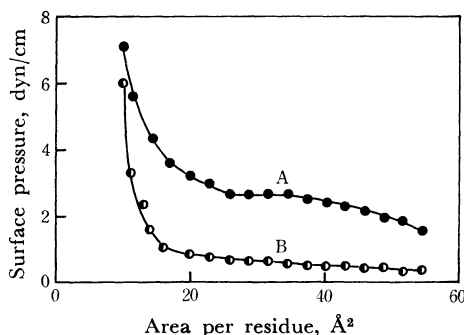


Fig. 1b. F - A curves of Nylon 6 monolayer spread from BP on distilled water.

- : First compression (film A)
- ◐: Second compression (film B)

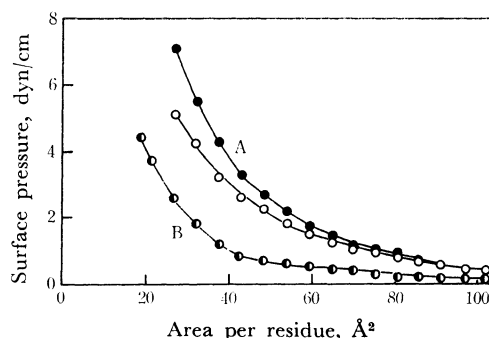


Fig. 2a. F - A curves of Nylon 8 monolayer spread from MA.

- : First compression, on pH 6.1–2.0 (film A)
- : First compression, on pH 1.1 (film A)
- ◐: Second compression of above two films (film B)

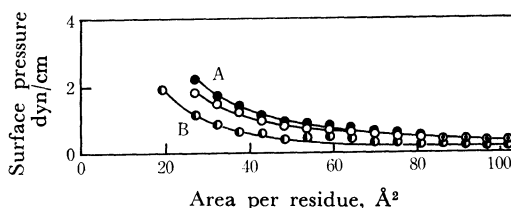


Fig. 2b. F - A curves of Nylon 8 monolayer spread from FA.

- : First compression, on distilled water (film A)
- : First compression, on hydrochloric acid (pH 1.1) (film A)
- ◐: Second compression of above two films (film B)

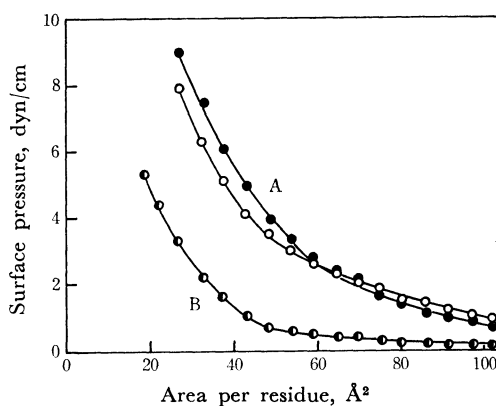


Fig. 2c. F - A curves of Nylon 8 monolayer on distilled water.

- : First compression, spreading solvent; BP (film A)
- : First compression, spreading solvent; CM (film A)
- ◐: Second compression of above two films (film B)

after allowing them to stand for about an hour. The F - A curves thus obtained are denoted by B.

In some cases expansion and compression were repeated but the results gave the same F - A curve as that of B. It was shown that two types of film A and B are obtained in all cases, namely the film appearing at the first compression and the film at the second and further compressions. The film of the type A obtained by the first compression varies in the shape of F - A curve according to the nature of the spreading solvent, while the type B film is more condensed and the differences in F - A curve due to the nature of solvent and the repetition of the compression are far smaller than the type A film. From these facts together with the fact that the F - A curve of the type B film is fairly reproducible, the present author considers it best to measure the B film for the study of nylon monolayer under a well defined condition. Independence of type B film of the rate of compression is likely to hold since the shape of F - A curve of this film is independent of the effective rate of compression (the rate referred to the fractional area) which actually changes when an apparent rate is held constant at 8 mm/min. Type B film is also independent of the aging as mentioned later. The present study has been made also under such conditions.

In this connection, it is noted that most studies on nylon monolayers reported up to the present were made for the film corresponding to that of type A of our experiments, and discussion based upon such measurements inevitably becomes ambiguous and unreliable. For the film of the type B, we further examined the loss, if any, of the film substance due to its dissolution into the substrate. For this purpose, the spreading solution was applied with and without the aid of a specially prepared glass applicator having a small hollow at its top as shown in Fig. 3. The applicator was immersed

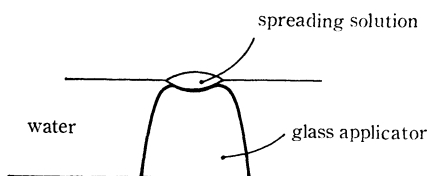


Fig. 3. Schematic representation of glass applicator.

just beneath the water surface and the spreading solution was slowly applied at the top of the applicator. Hardly any difference was observed between the F - A curves of monolayers spread with and without the aid of the applicator for both Nylons 6 and 8 dissolved in BP, CM, and MA except for the monolayer of Nylon 8 spread from FA, where the monolayers spread without using the applicator exhibit lower F - A curves both for A and B films as shown in Fig. 4. The difference in the case of FA solvent may be due to its insufficient nature as a spreading solvent. As shown in Table I, it is evident that FA is larger in density and surface

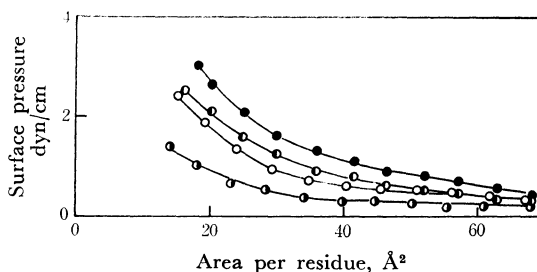


Fig. 4. F - A curves of Nylon 8 monolayer spread from FA on distilled water.

With glass applicator
 ●: First compression
 ○: Second compression
 Without glass applicator
 ○: First compression
 ●: Second compression

TABLE I. PHYSICAL PROPERTIES OF SOLVENT

Solvent	Density (d_4^{20})	Surface tension (γ^{20})
FA	1.220	37.6 dyn/cm
MA	0.7915	22.6
CM	0.9264	22.9
BP	0.9766	30.4

tension than other solvents. These differences in properties suggest the less spreadability and the larger tendency to draw the solute into the substrate solution in the case of FA. Thus, the use of FA without the applicator is not favorable for spreading Nylon 8, while the coincidence as a whole of F - A curves of B type for the other different solvents may be taken as an indication of the film free from the loss of the substance during spreading. As to the film dissolution into the substrate solution during or after spreading the film, we further note that F - A curve of film B is reproducible under repeated compressions during which the possibility of the rapid reversible dissolution and redeposition of the film substance were confirmed not to occur except for the case in Fig. 4. This rapid dissolution and redeposition, if they happen, might produce pressure increase on the clean side of the water surface of Langmuir trough, but they could not be detected actually even after a long aging of the film under a high surface pressure. These facts lead to the conclusion that the dissolution of nylon into the subsolution is considered negligible for the monolayers except for the Nylon 8 monolayer spread from FA without using the applicator. The glass applicator was herefore used hereafter only in the case of FA as a spreading solvent.

Aging of Film before Compression. The effect of aging of the spread film on the F - A curve was measured for both Nylons 6 and 8 monolayers. After the monolayer was spread from the solution it was left to stand for from 20 min to 20 hr before

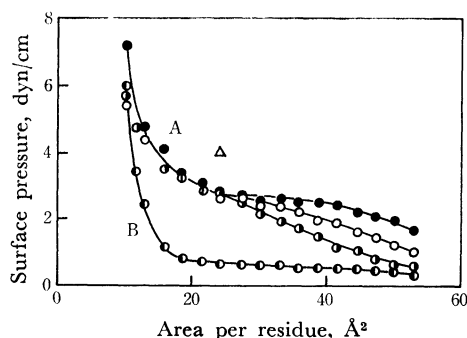


Fig. 5. Nylon 6 dissolved in BP on distilled water.

- : First compression after 20 min aging (film A)
- : First compression after 3½ hr aging (film A)
- ⊙: First compression after 18 hr aging (film A)
- ⦿: Second compression of above three films (film B)
- △: Surface pressure under a rapid compression

the compression was started. There was no appreciable difference in the F - A curves for the films spread from CM and MA, but the F - A curve for Nylon 6 spread from BP (Fig. 5) which was more expanded than the one spread from CM showed a tendency of aging. In Fig. 5 pressure decreased during a prolonged aging of about 18 hr and the F - A curve of type A gradually shifted towards type B. When the original film of type A was compressed 20 min after spreading up to the molecular area of about $24 \text{ Å}^2/\text{residue}$, at relatively high speed (about 10 times the ordinary rate, 8 mm/min) the surface pressure increased to the point indicated by the open triangle in Fig. 5 which is higher than the corresponding point on curve A obtained under the ordinary rate of compression (solid circle). Thus type A film of Nylon 6 spread from BP apparently exhibited a more expanded behavior than that from the other solvent when it was compressed immediately after the spreading. However this state seemed unstable and the film showed a tendency to condense even when it was left to stand at a lower surface pressure without compression. The plateau region described in an other report⁽⁵⁾ was also observed in F - A curve for Nylon 6 (Fig. 1b) obtained by compressing the film 20 min after the spreading. This may be explained as a result of mutually opposite actions of pressure increase by compression and decrease by the above mentioned tendency of film condensation presumably becoming distinct at higher pressure.

Effect of the Volume of Spreading Solution.

In order to examine the effects of the volume of spreading solution and the initial amount of film substance on the surface pressure, F - A curve of Nylon 6 film spread from 15 μl (standard volume)

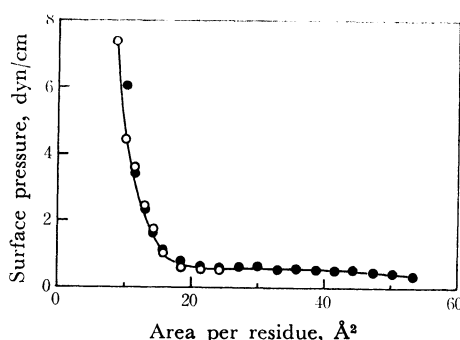


Fig. 6. F - A curves of Nylon 6 monolayer spread from BP on distilled water.

- : 15 μl spreading solution; second compression
- : 30 μl spreading solution; first compression

and 30 μl of the BP solutions on the aqueous surface of the same area (120 cm^2) were compared (Fig. 6). When the film was spread from twice the standard volume of spreading solution, the F - A curve of type B appeared at the first compression and no change occurred on further repetition of expansion and compression as shown by open circles in Fig. 6. This is markedly different from the F - A curve for the film spread from 15 μl solution shown in Fig. 1b and also in Fig. 6.

The Nylon 8 monolayers which were spread from 5, 10, 15 and 20 μl of MA solutions showed, under repeated compression, transition in type of F - A curves from A to B for all films except for the one spread from 5 μl solution which showed only one type of film A. The last case is expected to occur since the extent of compression of the film as expressed in area per residue is apparently insufficient to change A film to B.

As can be seen in Fig. 2a, film B is condensed to about one half of film A. Therefore, it may be presumed that a reaction like condensation of nylon monomer residues has occurred in this case in the monolayer of type B as a whole. This is probably due to the tendency of film contraction particularly increasing at high compression of film A. Types of the film, spread and compressed under varying amounts of spreading solution are shown in Table 2.

TABLE 2. THE TYPE OF FILM UNDER VARIOUS CONDITIONS

Spreading solution	Spreading volume	First compression	Further compression
Nylon 6 in BP	15 μl	A	B
	30 μl	B	B
Nylon 8 in MA	5	A	A
	10	A	B
	15	A	B
	20	A	B

Concentration of spreading solution, 0.3 mg/ml
Initial spreading area, 120 cm^2

A general tendency can be seen that the type A film appears at first compression and type B film at second and further compressions. Type A film obtained by spreading monolayer of Nylon 6 from BP solution is unstable and shows a tendency to undergo transition into type B by merely being kept at the initial spreading state of fairly large area, or by immediate compression of the film after being spread from twice the standard volume of the solution of the specified concentration. In the case of Nylon 8 film spread from MA, it is observed that the surface pressure of the type A film drops rapidly and the type B film finally appears when it is compressed and kept at certain small area. These facts also indicate the importance of the ratio, R , of the amount of film substance to the initial area of spreading for the study of nylon monolayer. It is likely that the appearance of the type A film only, A and B films, and B film only is dependent respectively on the value R being below, within, and beyond a certain range proper to the substance.

Effect of Substrate pH. The effect of acid in the substrate water on nylon film has mostly been studied with sulfuric acid having concentration greater than 1 N, where the F - A curve is more expanded than that on distilled water.^{1,3,7,8)} However, useful information can also be obtained from measurements of the film on acid substrate of concentration below 0.1 N, since nylon exhibits an amphoteric nature in this region.⁹⁾ Measurements were made for the F - A curve of the nylon monolayer on hydrochloric acid of concentration ranging from zero to 0.1 N. Measurement of the type A film on the acid substrate gave the result that both the F - A curves of Nylon 6 monolayer spread from CM solution and Nylon 8 monolayer from MA solution showed the film of more expanded type on acid than on distilled water (Figs. 1a and 2b) while Nylon

8 film from MA solution gave a curve almost independent of pH ranging from 2.0 to neutral (Fig. 2a). The film was more expanded than for the former two films, but contrary to the former films the area decreased below pH 1.1 (Figs. 1a and 2a).

It is known that the nylon molecules are usually in the extended state in acid solution where the molecules bear positive charges due to the addition of H^+ ion to the amide group.⁹⁾ A similar state of affairs may prevail in the case of monolayers shown in Figs. 1a and 2b, but this effect cannot explain the condensation of monolayer of Nylon 8 at pH 1.1 shown in Fig. 2a. The type B film of Nylon 8 obtained from MA also gave films independent of pH. Thus we have found fairly stable nylon monolayers of type B and in some cases type A which are obtained by spreading MA solution of Nylon 8 on acid and neutral water substrate.

In conclusion it should be emphasized that for the study of the monolayer of nylon on water, it is important to establish the conditions of monolayer preparation and of F - A curve measurement. Thus, it is necessary to specify clearly the nature of solvent, the concentration and the amount of spreading solution, pH of the substrate, the method of application of the spreading solution, the manners of compression and expansion of the monolayer with regard to the reproducibility of F - A curves and the aging of the monolayer. A check of the preservation of the substance in the monolayer during the spreading and compression is also important, although it is not carried out because of the difficulty of practice.

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