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Studies of Nylon Monolayers. II. Compression Characteristics of the Nylon 8 Monolayer on Water

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It was reported in the preceding paper that two types of film, A and B, can be distinguished in *F-A* curves for monolyers of Nylons 6 and 8 on the basis of the difference in behavior in relation to compression and expansion. In the present experiment, the compression and expansion were repeated for the monolayers of Nylon 8 spread from methyl alcohol in order to study the *F-A* characteristics of these films in detail. It was found that, during the process of first compression, the pressure drops rapidly and the transition of film A to film B occurs beyond a certain degree of compression of the monolayer. The transition was interpreted as the condensation of the monomer residue of the nylon molecule. The equations of the state for the expanded film were found to apply better than Singer's equation for both types of film, A and B. Further, the effect of the concentrated sulfuric acid solution (3 and 6 N) as a substrate on the *F-A* curve was examined. There were little difference in the behavior of the monolayers on 3 N sulfuric acid irrespective of the spreading solvent used, but the difference was marked on dilute hydrochloric acid.

In the preceding paper,[1] two types of film, A and B, were distinguished in *F-A* curves for the monolayers of Nylons 6 and 8 on the basis of the difference in behavior of the film in relation to compression and expansion.

In the present paper we will study these films in detail. Nylon 8 spread from methyl alcohol (MA) was used for the study of the *F-A* curve, because MA gives the most stable film on a neutral substrate, thus facilitating the measurement. Singer's approximate formula for polymer film and the equation of expanded film were applied to these data, and their applicability was checked. The effect of the concentrated sulfuric acid solution as a substrate on the *F-A* curve of Nylon 8 was also studied.

Experimental

The sample of Nylon 8 used was purified by dissolving it in MA and then by precipitating on addition of water. The precipitates were treated with ethyl ether in order to remove any impurities and were then dried *in vacuo*. MA was used mainly as a spreading solvent, but in some special cases formic acid (FA) and benzene-phenol mixture (BP) were also used. The concentration of nylon in the spreading solution was 0.3 mg/m*l*. The distilled water was prepared by refluxing an aqueous solution of acidic potassium permanganate and by distilling it three times, first with the addition of excess alkali. Aqueous solutions of 3 and 6 N sulfuric acid were used as substrates. The surface pressure was measured by a Wilhelmy balance using a glass hanging-plate. Special care was taken to withdraw the sufficiently-dipped plate just prior to the measurement in order to keep the receding angle at zero. The surface pressure-area curves (*F-A* curves) were plotted under various experimental conditions, as has been described in the preceding paper.[1]

Results and Discussion

Repetition of Compression and Expansion. A typical *F-A* curve for Nylon 8 is shown in Fig. 1. In this figure, the monolayer spread from the MA solution on the aqueous surface of a large area at pH 6 was first compressed, then expanded, and finally again compressed. The compression of the film was started from the point 0 to the point 1, as is shown in Fig. 1; then, after 15 min's rest at the point

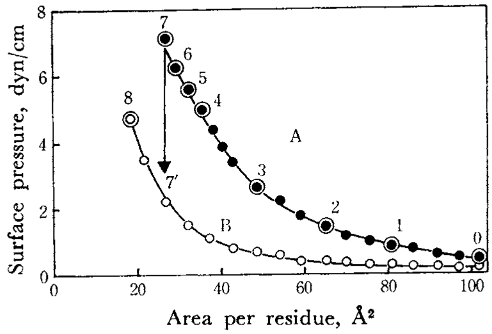

Fig. 1. *F-A* curve of Nylon 8 dissolved in MA on distilled water.
●: Film A
○: Film B

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[1] T. Seimiya, This Bulletin **43**, 301 (1970).

1 and the confirmation of no change in the surface pressure, the film was expanded again to the point 0 and finally compressed further to the point 2. Thus, the compression and expansion to the point 0 were repeated till the point 7 was reached along the curve A. An abrupt and irreversible change occurred at the point 7 where the surface pressure fell to the point 7′ simply on standing, as is indicated in Fig. 1. Such a change occurred rather suddenly and rapidly when the surface film was compressed to a 24—27 Å²/residue. Further compression proceeded along the curve B and the point 8 was reached. The full curve of the film B was realized when the film A, after the compression to the point 7, was expanded to the initial area of the 0 point and the second series of compression was started. The point 8 was again reached at the end of such compression. A further series of expansions and compressions of the film resulted in the same curve B.

The above behavior has been proved to occur for the monolayer spread from the solution which had been aged for from 0 to 50 days after preparation. It has been reported that the surface pressure depression occurs when the spreading solution is kept for a long time after preparation; this has been ascribed to the hydrolysis of nylon by sulfuric acid in the spreading solvent.[2] However, no such effect was found in the present experiment.

In order to examine the dissolution of nylon film into the substrate water, we have made two experiments. In the first experiment, each solvent, MA and FA, was dropped on the monolayer surface at the points of compression of 2, 3, 7′, and 8, but no change could be observed in the surface pressure after the dissolution of these solvents. In the second experiment, the surface pressure of the clean side of the substrate surface coexisting with the monolayer on the opposite side was measured. It was found that the pressure remained zero for about 1 to 2 hr after the spreading of the monolayer, even under a high compression of the film at the point 7′. These two facts, together with the reproducibility of the F-A curve mentioned above, confirm that the film substance is not lost from the monolayer either by a drag of the solvent as it spreads and dissolves in water or by a direct dissolution from the monolayer after it has been spread on the water.

Equation of State. First, an approximate form of Singer's equation[3] for the monolayers of polymers:

$$FA = kT(1+A_0/A)/x \qquad (1)$$

was tested for its applicability. Here, A_0 denotes the co-area of a residue in a molecule, and x, the degree of polymerization. The plot of FA against $1/A$ is shown in Fig. 2. As is shown in this figure, a linear relation is obtained for the film B; this suggests a fairly good applicability of the above equation, but for the film A the plots largely deviates from linearity. Next, the applicability of the equation of the state for an expanded film:[4]

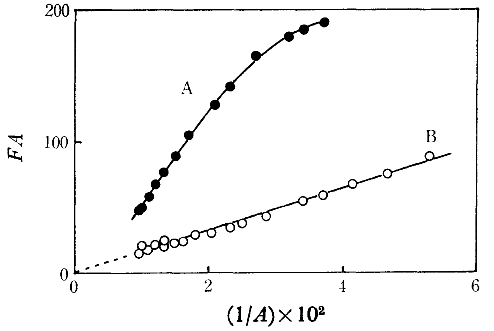

Fig. 2. Examination of Singer's approximate equation.

●: Film A
○: Film B

$$(F-F_0)(A-A_0) = kT \qquad (2)$$

was examined. Here, F_0 denotes a constant, independent of F and A. By means of a trial-and-error method, values of F_0 and A_0 were found which gave the best linearity when $F-F_0$ was plotted against $1/(A-A_0)$. As is shown in Fig. 3, the plots are on straight lines passing through the point of origin both for the A and B films. Here, $F_0 = -1.35$ (dyn/cm), and $A_0 = 9$ (Å²/residue) for the film A, and $F_0 = -0.35$, and $A_0 = 10$ for the film B. The values of $F_0 = -1.30$, and $A_0 = 10$ can also be used to show a good linear plot for the film A. Thus, it is evidnet that, as a whole, Eq. (2) expresses the behavior of both the A and B films better than Eq. (1). Further, the constant of the right-hand side of Eq. (2) was calculated from the inclination of the two straight lines, A and B, in Fig. 3. The values

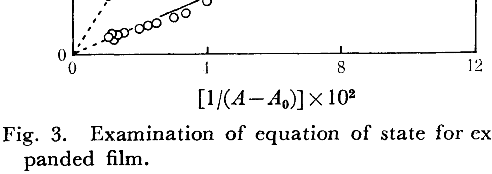

Fig. 3. Examination of equation of state for expanded film.

●: Film A
○: Film B

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[2] H. Hotta, This Bulletin, **27**, 80 (1954).

[3] S. J. Singer, *J. Chem. Phys.*, **16**, 872 (1948).

[4] I. Langmuir, *ibid.*, **1**, 756 (1933).

are about $1/3\,\boldsymbol{k}T$ and $1/10\,\boldsymbol{k}T$ for the A and B films respectively, instead of the $\boldsymbol{k}T$ shown in Eq. (2). This indicates that the equation:

$$(F-F_0)(A-A_0) = i\boldsymbol{k}T$$

is applicable for both films, with $i=1/3$ for the film A and $i=1/10$ for the film B. Thus, two equations:

$$(F-F_0)(3A-3A_0) = \boldsymbol{k}T$$

and $$(F-F_0')(10A-10A_0) = \boldsymbol{k}T$$

are obtained for the A and B films. This means that the actual co-areas of the nylon residue are about three times and ten times as large as the co-area of the apparent residue. Thus, the groups of residues of these sizes seem to behave as a kinetic unit in the films A and B, and the condensation of the film may be understood as the formation of such clusters of residues in a polymer molecule.

Behavior of Nylon Monolayers on the Concentrated Acid Substrate. In the previous work,[1] the effect of acid on the nylon monolayer was studied by measuring the *F-A* curve on a dilute acid solution (concentration below 1/10 N), but in the present experiment concentrated sulfuric acid which is commonly used for studies of the nylon monolayer, was used as the substrate solution.[5-8] The *F-A* curve obtained for the monolayers on 3 and 6 N sulfuric acid solution are shown in Fig. 4. For the substrate of the 3 N sulfuric acid solution, the film A shows nearly the same *F-A* curve as on distilled water, but it tends to flatten when the compression proceeds beyond the area of about 35 Å²/residue. The film B exhibits the same curve as that of the monolayer spread on distilled water and no flattening is observed. When the 6 N sulfuric acid solution is used as the substrate, the expansion of the film is more marked than that of the film on distilled water for both the films A and B, as is shown in Fig. 4. As has been described before,[1] the film of Nylon 8 gives type-A curves of varying degrees of condensation on the dilute acid substrate; however, it expands again when the substrate becomes strongly acidic. These expansions of film on a strong acid substrate can be explained in terms of interaction between the monolayer and the hydrogen ion, interaction which results in repulsion among the molecules in the charged monolayer. As has been mentioned above, the *F-A* curve obtained on the strong acid substrate shows a tendency to flatten in the high-pressure region. However, it is not proper to explain this as a property of the equilibrium state, as is generally done:[2,5-9] it is better explained as a non-equilibrium state of the transition of the film from A to B, as has been noted.

In the preceding paper,[1] it has been reported that the *F-A* curves on distilled water differ according to the solvents used, as is shown in Fig. 5. However, for the films spread on the 3 N sulfuric

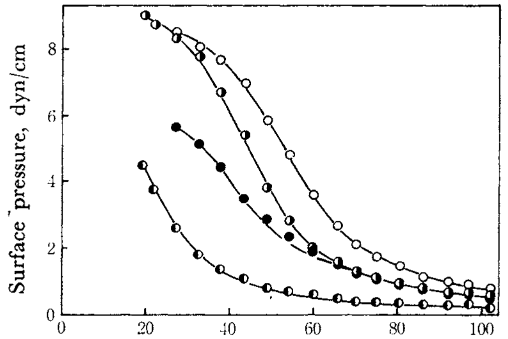

Fig. 4. *F-A* curves of Nylon 8 monolayer spread from MA on sulfuric acid.
●: 3 N, film A ○: 6 N, film A
◐: 3 N, film B ◑: 6 N, film B

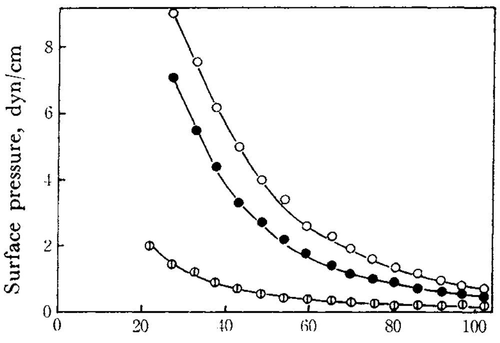

Fig. 5. *F-A* curves of Nylon 8 monolayer on distilled water.
●: Spread from MA
○: Spread from BP } film A
⦶: Spread from FA

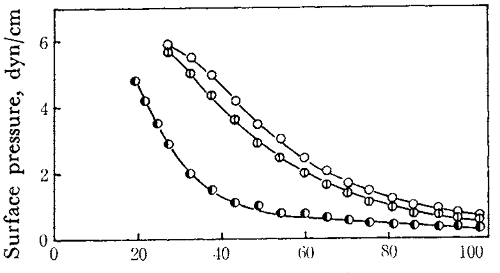

Fig. 6. *F-A* curves of Nylon 8 monolayer on 3 N sulfuric acid.
○: Spread from BP } film A
⦶: Spread from FA
◐: Spread from BP and FA, film B

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[5] D. J. Crisp, *J. Colloid Sci.*, **1**, 161 (1946).

[6] C. W. N. Cumper and A. E. Alexander, *Trans. Faraday Soc.*, **45**, 235 (1950).

[7] G. E. Hibbered and A. E. Alexander, *Pro. 3rd Int. Congr. Surface Activity*, **2**, 145 (1960).

[8] T. Yamashita, This Bulletin, **38**, 430 (1965).

[9] K. Inokuchi, *ibid.*, **29**, 490 (1956).

acid substrate, only a little difference could be noted for the films spread from MA, FA, and BP solvents, as Figs. 4 and 6 show. The *F-A* curves of the nylon monolayer on an acid substrate of the 3 N sulfuric acid solution are often reported to show a tendency to expand more than that on the substrate of a neutral pH because of the absorption of the hydrogen ion.[5-8] However, for Nylon 8 no such phenomena are found, at least not for the solvents of MA and BP.

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