Rheology of Surface Films. V. Mechanical Behaviours and Structures of 6-Nylon at Air.Water Interface

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Introduction

In the preceding paper¹⁾, detailed description was made on the rheological characteristics of 6-nylon at air/water interface. It is desirable to investigate the film structure, which is responsible for the development of the rheological properties of the film. For this purpose, electron microscopic examination was carried out at various areas, together with the simultaneous determination of surface pressure and potential. Microfibrillar structures were thus revealed, and the change of the mechanical properties of the film, accompanied by the compression process, was discussed in terms of such structures.

Experimental

Materials and the experimental conditions were just the same as described in the preceding paper¹⁾. Unless otherwise stated, the sample was spread on distilled water from the mixed solution of benzene/phenol (3: 1 in volume) at the initial spreading area of about 90 A^2/residue. About twenty minutes were allowed to stand before the determination of the isotherms under the compression of constant speed 9.6 cm^2/min. For the determination of surface pressure-area curve (π-A curve), the surface balance of a float type was used, which was constructed by the present author²⁾. Surface potential was measured by means of a vibrating electrode apparatus. For the electron microscopic examination, the films were transferred onto the collodion support with use of the following technique. The collodion supports were held and touched parallel to the surface film on the substrate water and then immersed into the water. After the film was swept off, these supports were picked up through the clean surface of water, and dried. In order to avoid heterogeneity of the film near the enclosing barriers, all the film specimens were taken from the middle part of the enclosing area of the surface films. Hitachi HS-II type electron microscope was used.

Results

(I) Surface Pressure

(1) Force-Area Curve. — The general trend of the form of the π-A curve was shown in Fig. 1. Surface pressure at large areas gradually increased as the film was compressed until a distinct kink point (a) appeared at the area of about 37 A^2/residue. Below the area of the kink point, however, the pressure ceased to increase upon compression forming a high compressibility region— a plateau—, whereas the pressure again rose, on further reducing area below about 20 A^2/residue, more steeply up to the pressure of 40 dyn./cm. The end of the plateau is denoted as point (b) hereafter. The pressure relaxation after compression was sudden and pronounced below the kink point, and hence, the more the plateau became distinct, the slower the compression rate was.

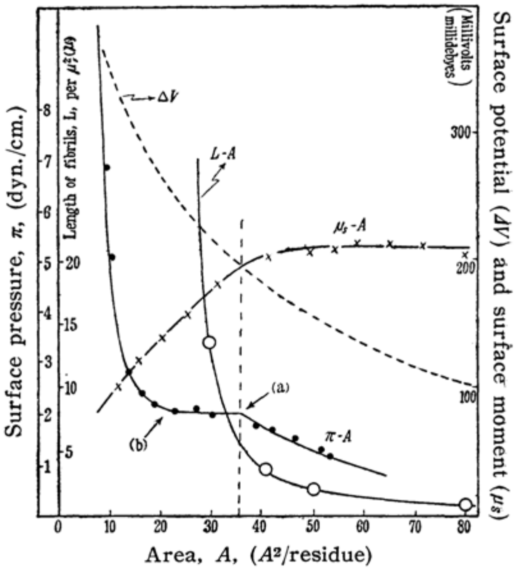

Fig. 1. Relationships of surface pressure versus area (π-A, full circles), surface electric moment versus area (μ_s-A, crosses), and amounts of fibrils versus area L-A, open circles). Broken line represents the surface potential versus area curve.

In view of our experience, it was likely that the Wilhelmy dipping slide method registered a more distinct kink point (a) than the case in which the float balance was used. This may be due to the considerable change

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1) K. Inokuchi, This Bulletin, 28, 453 (1955).

2) K. Inokuchi, This Bulletin, 26, 471 (1953).

of the wetting condition of the slide. In any case, it is evident that there occurred a sudden change in the film structure at the point (a).

(2) **Effect of the Composition of the Substrate Water.**—It has been emphasized that coherent films generally badly spread at air/water interface. So, it seemed necessary to examine the extent of the spreading under various conditions. The results were summarized in Table I, in which the areas of point (a), (b), and the limiting area (c), obtained by extrapolating the straight portion of the high pressure region[*2] (15 to 40 dyn./cm.) to zero pressure, were tabulated together with the pressure at the kink point. It was found that these characteristic areas were not appreciably influenced by the composition of the substrate solution, yielding identical values of (a)=37 A^2/residue, (b)=20 A^2/residue, and (c)=8.5 A^2/residue, respectively. On the other hand, the pressure was appreciably raised when spreading was made on the acidic solution (3 N sulfuric acid solution). That is, the film became expanded, as reported by Crisp[3] with nylon $[\text{-}(CH_2)_4\text{-}CO\text{-}NH\text{-}]_n$.

TABLE I

EFFECT OF THE SUBSTRATE WATER UPON THE π-A CURVE

Substrate water	a	b	c	Pressure at point (a)	Temperature
	A^2/residue			dyn./cm.	C°
Distilled water	37	20	7.5	2.2	21.5
3 N H_2SO_4	37	21	7.5	5.4	21.3
3% Urea	38	24	7.6	2.1	21.2
20% Urea	—	—	7.6	—	20.0

(3) **Effect of the Composition of the Dropping Solution.**—Spreading was also tested in relation to the composition of the dropping solution. Mixtures of benzene-phenol as a solvent, whose proportions vary from 2.5/7.5 to 9.2/0.8 (in volume), gave practically identical values of the characteristic area (a, b, and c), whereas the solution, whose benzene/phenol proportions exceeded 9.5/0.5, yielded far smaller areas than that above (Table II). The solvent of too large proportions of phenol made the experiment impossible, since the solvent was solidified at room temperature. Since 6-nylon does not dissolve, either in pure benzene or in pure phenol, this fact may indicate that the poor solvent caused bad spreading. when the sample was spread from the mixed solution of sulfuric acid and isopropyl alcohol (1/10 in volume), somewhat smaller characteristic areas were obtained than that from benzene-phenol solution. Since partial hydrolysis of the sample cannot be denied in strong sulfuric acid solution, reduced values of the characteristic points may partly be attributed to this. From the facts that the spreading areas were not appreciably influenced by the hydrogen bond breaking agents, and that the change of the composition of the dropping solution does not practically affect the extent of spreading except for the extreme case, it may be considered that spreading attains to saturation even on the distilled water.

TABLE II

EFFECT OF THE SOLVENT OF THE DROPPING SOLUTION UPON THE π-A CURVE

Solvent proportion in volume	a	b	c	Pressure at point (a)	Temperature
Benzene/Phenol	Area in A^2/residue			dyn./cm.	°C
2.5/7.5	—	—	8.5	—	19.4
7.5/2.5	37	20	8.5	2.4	19.5
9.2/0.8	36	20	8.4	2.4	19.4
9.5/0.5	20	11	5.7	2.4	20.3
9.8/0.2	—	—	—	—	21.6
H_2SO_4/Isopropanol 1/10	28	19	7.0	1.6	19.4

(4) **Molecular Weight Variations.**—As shown in Table III, it was found that the form of the π-A curve was not affected by the molecular weight of the sample so far as the molecular weight changed from 2800 to 17300. This phenomenon is similar to the case with the surface films of cellulose acetates reported by Borgin[4]. With the fraction of extremely low molecular weight 1000, however, a slightly small value of the point (a) was produced, and the plateau in the π-A curve was less distinct. When caprolactum, a monomer of 6-nylon, was spread on a sat-

TABLE III

EFFECT OF MOLECULAR WEIGHT OF 6-NYLON UPON THE π-A CURVE

Molecula weight	a	b	c	Present at point (a)	Temperature
	Area in A^2/residue			dyn./cm.	°C
17,300	37	20	8.5	2.2	21.5
4,600	37	—	7.8	2.5	30.0
2,800	38	—	7.5	2.5	20.0
1,000	31	18	4.8	2.4	20.5
Caplolactam	—	—	4.8	—	20.5

[*2] The high pressure region used for obtaining the point (c) did not appear in Fig. 1.

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

[4] K. Borgin, *Trans. Far. Soc.*, **49**, 956 (1953).

urated ammonium sulfate solution, a comparatively stable surface film was produced, having no plateau and showing less value of point (c) in the π-A curve, and exhibiting no elasticity covering the whole range of compression.

(5) **Compression-Expansion Hysteresis.**—Hysteresis of the π-A curve was also tested at various areas by exercising the compression and re-expansion at constant speed. Fig. 2 shows an example of the results thus obtained, in which the arrows represented a series of the hysteresis loop. In general, the pressure, when the film was re-expanded, became lower than that of the foregoing compression, such a trend was found to be slight at larger areas than the point (a), whereas it became appreciable at the areas below the plateau region. Marked hysteresis occurred below the areas of about 20 A^2/residue, where the steep increase in pressure took place. In this region, the pressure dropped down to almost zero only when the film was slightly re-expanded. Such a phenomenon may reasonably be related to the coherent nature of the film.

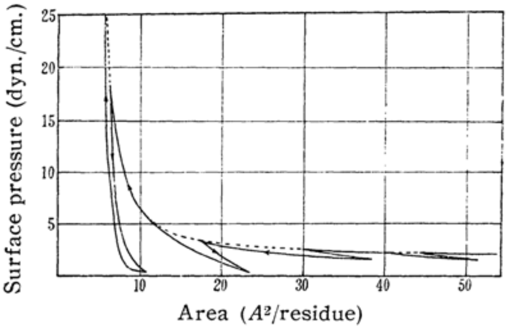

Fig. 2. Compression-expansion hysteresis curve. Temperature, 16°C. rate of expansion, 9.6 cm^2/min.

(6) **Anisotropy of Surface Pressure.**—It was observed that one drop of castor oil, the form of which was perfectly circular when dropped down onto the surface film of 6-nylon, became deformed to an ellipsoid as the film was compressed, the longer axis being at right angles to the direction of compression. This is schematically illustrated in Fig. 3. It was also observed that the deformation of the oil drop which thus occurred became relaxed as the time elapsed after compression. It was also found that two blades of the Wilhelmy dipping slide for measuring the surface pressure, which were so hung that one was parallel to the direction of compression, the other at right angles to it, respectively, registered different pressures below the area of about 40 A^2/residue, somewhat larger values being obtained with the latter slide. These facts readily show that the surface pressure became anisotropic under compression.

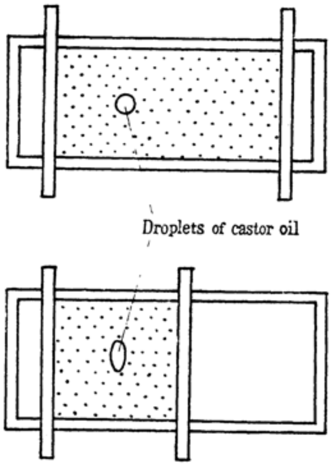

Fig. 3. Schematic illustrations of the anisotropy of surface pressure set up after compression of the films.

(7) **Effect of Temperature on Surface Pressure.**—Temperature dependence of the surface pressure at a fixed area was examined at various areas. Temperature change was performed at a rate of 10 minutes/temperature degree, and the results were listed in Fig. 4. The pressure decreased with the rise of temperature at all areas. Such a temperature effect is similar to that on the films of synthetic polypeptides[5]. Buna-N[6], and of the long chain Ureas[7].

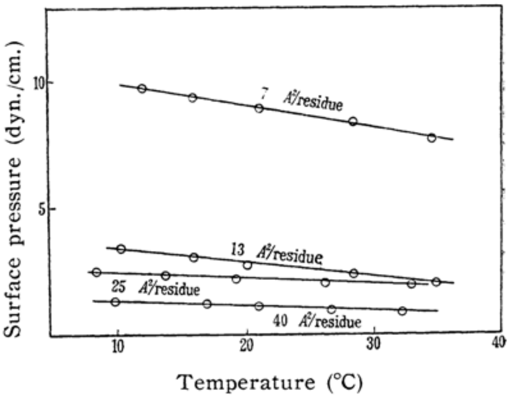

Fig. 4. Temperature dependence of surface pressures at various areas.

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[5] T. Isemura and K. Hamaguchi, This Bulletin, **25**, 40 (1952).

[6] K. Suzuki, *Kōshitsugaku-ronso* (Discussions of Colloid Science), **1**, 63 (1947).

[7] J. Glazer and A.E. Alexander, *Trans. Far. Soc.*, **47**, 401 (1951).

(II) Surface Potential-Area Curve

The surface potential versus area curve was shown together with the π-A curve in Fig. 1. The surface moment (μ_s), which persisted almost constant value about 230 millidebyes at large areas, began to decrease below the area of about 40 A^2/residue which was fairly consistent with the point (a) in the π-A curve.

(III) Electron Microscopic Examinations

It is of importance to inquire what structural change of the film corresponds to the

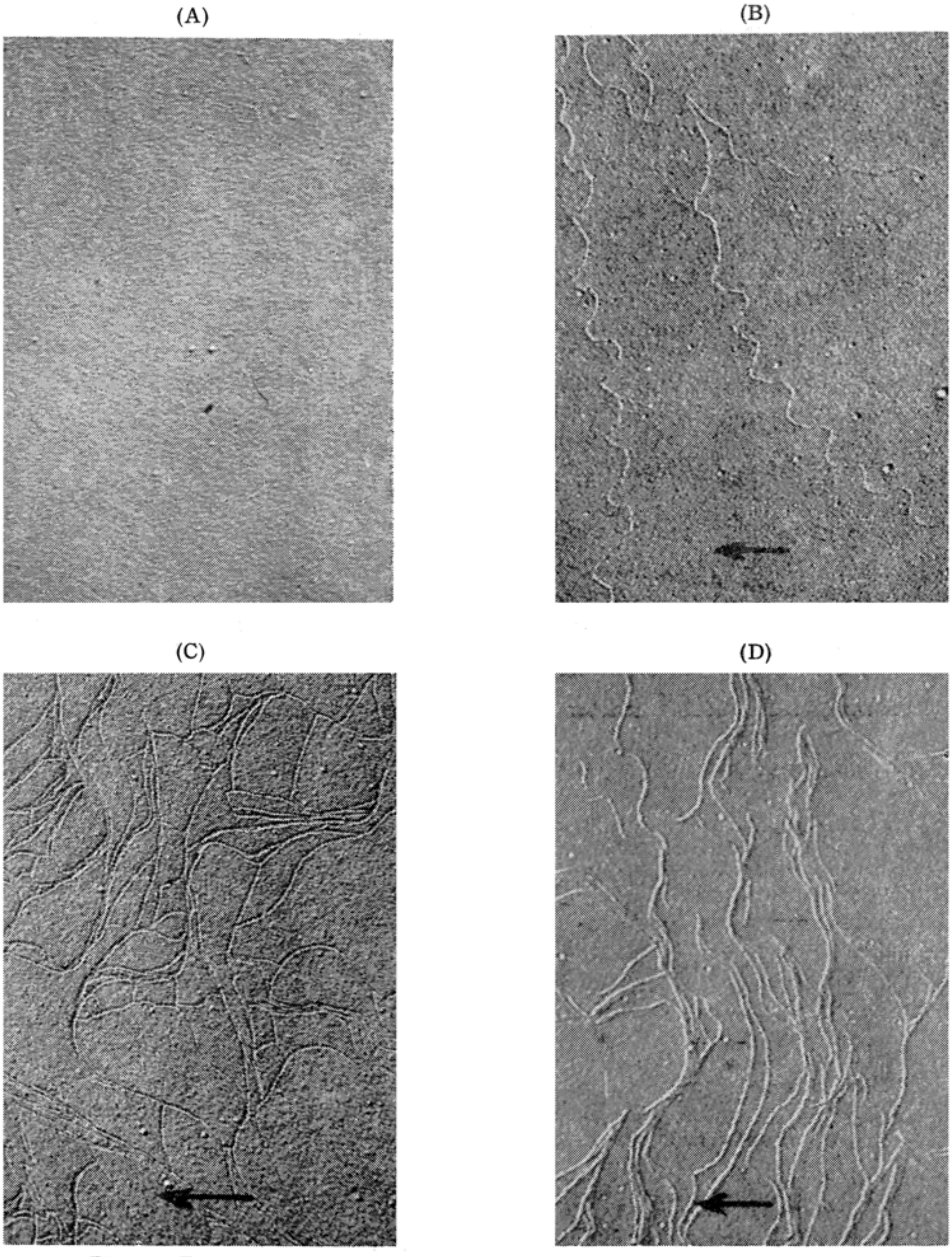
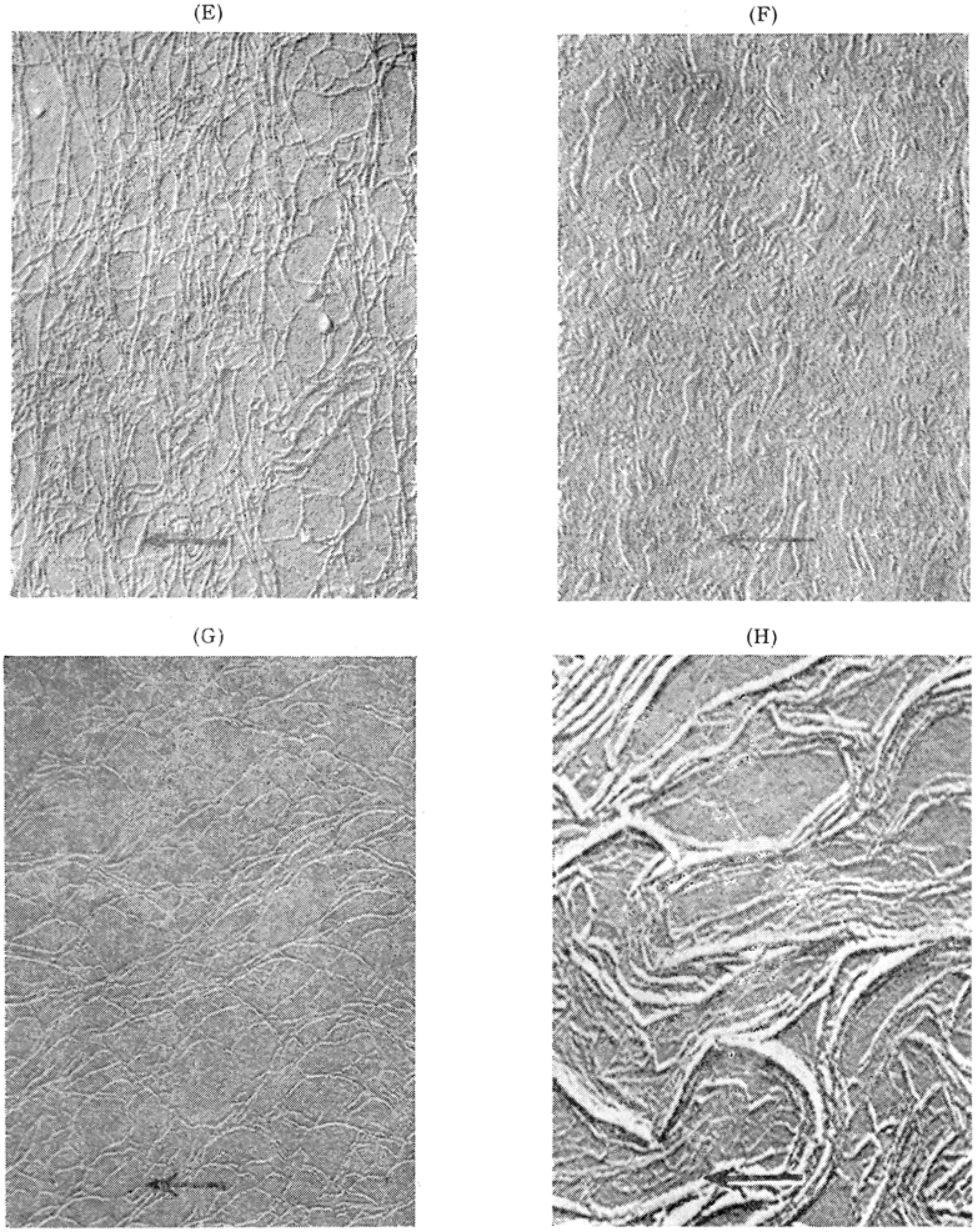


Fig. 5. Electron micrographs of monolayers of 6-nylon;
A, Blank, no film, magnification 13500;
B, Uncompressed films at 80 A^2/residue, magnification, 13500
C, Compressed films at 50 A^2/residue, magnification 13500
D, Compressed films at 40 A^2/residue, magnification 13500



(E) (F) (G) (H)

E, Compressed films at 30 A^2/residue, magnification, 13500
F, Compressed films at 18 A^2/residue, magnification, 13500
G, Uncompressed films at 18 A^2/residue, magnification, 13500
H, Uncompressed films of low molecular fraction at 18 A^2/residue, magnification, 135000
Arrows indicate the direction of compression.

characteristic areas (a) and (b). For this purpose, electron microscopic examination of the film[8], developed in our laboratory, have proved considerable merits.

A blank water sample is shown in Fig. 5A. Fig. 5B shows the film, taken at 80 A^2/residue at which the film was initially spread. There exist unspread materials which appeared as several fibrils running windingly. This film was compressed to various areas, at which the film specimens for electron microscopy were taken. Figs. 5C, 5D and 5E

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[8] T. Tachibana, K. Inokuchi and T. Inokuchi, *Nature* 176, 1117 (1955).

are the films compressed to 50 A^2/residue, 40 A^2/residue, and 30 A^2/residue, respectively. It is shown that as the reducing area, more fibrils appeared than those which were expected to increase by the compression of the films, and came to link together forming a network structure. It is to be noted that at 30 A^2/residue, fibrils oriented normal to the direction of compression. Such an orientation, which could hardly be seen above 40 A^2/residue, was more and more pronounced as the compression advanced. Fig. 5F is an appearance of the film, which was compressed to 18 A^2/residue. Bare portions inside the network of fibrils disappeared, the whole area of the film being covered by the skinlike texture. Fig. 5G shows the uncompressed film which was initially spread at 18 A^2/residue. In contrast with the compressed film, it was noted that uncompressed films have fewer fibrils, and showed no sign of orientation of microfibrils. The effect of the degree of polymerisation on the structure of surface films has also been revealed by electron microscope. In Fig. 5H is shown the structure of uncompressed films (M. W. 1000) spread at 18 A^2/residue. Comparison of Fig. 5G, and Fig. 5H shows that the low molecular weight fraction produced thicker microfibrils than the high molecular one.

The relationship between amounts of microfibrils and area were roughly evaluated from the micrographs at various areas. In Fig. 1, the avarage total sum of the length of the microfibrils per sq. micron was plotted against the area together with the π-A curve and the potential curves. It is seen in this figure that increase in microfibrils, which was relatively slight at large areas, became pronounced below about 40 A^2/residue. It is suggestive that this area is fairly consistent with the point (a) in the π-A curve as well as with the point of the levelling off in the surface moment-area curve.

Discussion

Microfibrillar Structure of Surface Films. —It is first noticed that electron micrographs exhibit microfibrils, the size of which is almost constant at all compression, being estimated close to 40 Å from the width of the shadow. Although it is not clear at the present stage why the molecular association is stable with this size, it is very interesting to refer the Ribbi's experiment[9] that demonstrated the submicroscopic fibrils of forming the structural unit in the fibre of 6-nylon. Since, as the film was compressed, more fibrils appeared than the increase which is to occur as the result of the compression alone, it is clear that the bare portions of the micrographs, at which the microfibrils are absent, also possess film molecules. Although it is difficult to inquire in detail the film structure of this bare portion, it is readily known from the simple calculation[*3] that the fraction of the molecules participating to form the microfibrils against the total amount of the spreading molecules is comparatively small at large areas, being about 10% at the point (a), and the remainder forms the bare portions of the films. Moreover, the co-area of the molecular residue at the bare portions of the area of point (a) is roughly estimated by counting the increase of about 10% to the value of the mean co-area of the point (a) (37 A^2/residue), and it is noticed that this value obtained is approximately consistent with the co-area of a residue of flat configuration calculated from the molecular model (40 A^2/residue). Hence, it may be assumed that the bare portions of the surface film at the point (a) possess close-packed molecules with their chains flat on water surface.

It was found from the rheological measurement that the film manifested a distinct elasticity below the areas of about 80 A^2/residue (gelation-area), which is about twice the area of the close-packed area. From the molecular weight dependence of the gelation-area, it was shown in the preceding paper that the film molecules took configuration which was considerably stretched and of less flexibility. Such a molecular configuration may be favorable for the alignment of adjacent molecular chains to form two-dimensional micellar structure. Such film molecules may come into contact with each other under compression to form a two-dimensional network at the gelation-area, at which a distinct elasticity begins to manifest itself. Thus, there must be a two-dimensional network covering the bare portion of the electron micrograph at 80 A^2/residue. Further compression would make

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9) Cf. E. Ribbi, *Nature*, **168**, 1082 (1951).

[*3] Percentage of molecules of forming the microfibrils against the total molecules (P) at the area of point (a) (mean co-area, 37 A^2/residure) is given as

$$\left\{\left(\frac{L}{m}\right)\times n\Big/\frac{1}{37\times10^{-8}}\right\}\times100,$$

where L is the mean total sum of the length of the microfibrils per μ^2, expressed in μ, the value of which at the point (a) is obtained as about 5 μ from Fig. 1, and m, the length of the residue which is 8.5 A with 6-nylon, and n, the number of molecules within the cross section of the microfibril. Assuming that a microfibril is made of the molecular chains, closely packed against each other and running parallel to the length of it, it follows that the cross section of the fibrils consists of about 64 molecules, since the cross sectional area of a molecular chain is calculated as about 20 A^2 from the molecular model. Hence, P is obtained as about 10%.

the network denser until a monomolecular layer of the close-packed molecules is formed at the point (a), though a few of the molecules happen to associate with each other to form microfibrils. Below the area of point (a), all the molecules at the monolayer portions are no longer allowed to stand flat on water surface, and the film may fall into collapse. This is indicated by the surface moment-area curve, which shows sudden decrease in electric moment below about 40 A^2/residue. It is likely that this collapsing process actually involves fibril formation of molecules in the monolayer, since it is visualized from Fig. 1 that a steep increase in the amount of microfibrils appears below the areas 35 to 40 A^2/residue, fairly coincident with the point (a). Thus, the onset of the plateau in the π-A curve is accounted for by the sudden increase in association of molecules to the three-dimensional direction (formation of microfibrils), in which the lateral pressure might relax on further compression. As visualized in Fig. 5E and F, with the advancing compression, the microfibrils become denser and denser until they cover the whole area at about 20 A^2/residue, below which the pressure again rises steeply, and the micrographs fail to exhibit any fibrillar structure, showing. a skinlike texture. At 18 A^2/residue (Fig. 5F), there exsist a number of islands of about 50 A thick upon the back texture. From these findings, it may be considered that the plateau region in the π-A curve corresponds to the stage of formation of monofibrillar layer, and that the compression below the plateau region results in bifibrillar layer which transforms to polyfibrillar layer on further compression. In brief, it was evidently proved that the surface film of 6-nylon possesses microfibrillar structures, which presumably develop from monomolecular network, and transform to polyfibrillar layer under compression process.

Rheological Characteristics of Surface Films.—As shown in the electron micrographs, surface concentration of microfibrils at larger areas than the point (a) is so small that they fail to link together. So it is considered that the microfibrils are not primarily concerned with the film elasticity, but the portions of the monolayer network (bare portions of the micrographs) are chiefly responsible for the development of the elasticity. On the contrary, it was found that the microfibrils link together at areas below about 40 A^2/residue, forming a network of microfibrils. This time, it is easily understood that the microfibrils play an important role in the development of the film elasticity. This trend may be pronounced as the film is compressed, since the network of the microfibrils become more and more dense. In short, two types of surface films are presented; a monomolecular network at larger areas, and a network of the microfibrils at smaller areas.

In the preceding paper¹⁾, it was reported in detail that the film at areas larger than about 40 A^2/residue behaves as a purely elastic body which is hardly seen in the ordinary materials at bulk, whereas it became viscoelastic as is often the case with the ordinary materials at bulk when the film was compressed to small areas. It is readily noticed that the ideal elastic film corresponds to the monomolecular network, and the viscoelastic film, to the network structure of microfibrils. Fibrillar structure is essentially the same as that of the bulk materials, and it is rather natural that the film of fibrillar structure shows viscoelasticity.

It is also suggested that, with the films of ideal elasticity, the cross-linkings of the molecular chains are necessarily homogeneous. As is indicated from Fig. 2, showing that the expansion hysteresis of the π-A curve is only slight at areas larger than the point (a) (the portion of the monomolecular network), it is easy to accept the thought that orientation and alignment of molecules at the monomolecular network may be relatively easy compared with the films at smaller areas, and the relatively homogeneous network may result. Ideal elasticity of the monomolecular film of 6-nylon may thus be explained.

Correspondence between Surface Pressure and Surface Elasticity.—There are many evidences which support the view that the apparent surface pressure exerted here is intimately related to the surface elasticity. It has been observed that the characteristic form of the force-area curve, involving the plateau, bears considerable resemblance to that of the rigidity-area curve. The sign of the temperature dependence on the surface pressure was found to be negative, being just the same with the case of surface rigidity as reported in the preceding paper¹⁾. Moreover, surface compressibility $\left(-\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}\pi}\right)$ was obtained from the π-A curve, and according to Bateman¹⁰⁾, the surface modulus of rigidity was calculated under the assumption that the film is isotropic and the poisson ratio 0.4. The calculated values were compared with the observed ones obtained with our direct measurement of the surface rigidity. The result is given in Fig. 6, in which

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10) J. B. Bateman and J. A. Chambers, *J. Phys. Chem.*, 45, 209 (1941).

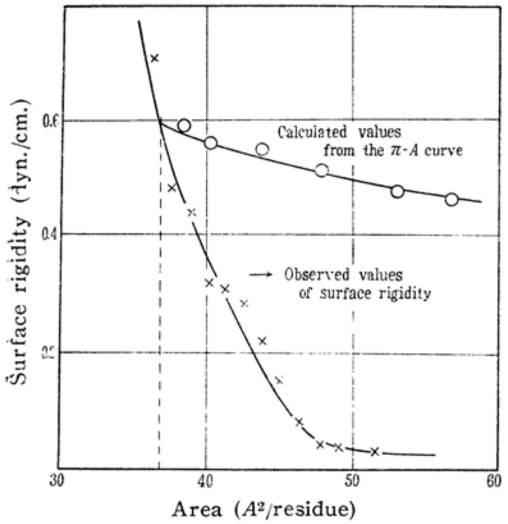

Fig. 6. Correspondence between surface pressure and surface rigidity.

considerable departure between the observed values and the calculated ones at larger areas became less serious as the reducing areas, and finally coincide with each other at the vicinity of 37 A^2/residue. Discrepancy of these values at larger areas may be plausible, since, at larger areas than the point (a), the observed pressures involve osmotic natures of the film molecules which do not participate in the formation of network. Coincidence of these values at the close-packed monolayer may possibly indicate that the surface pressure from the close-packed monolayer is wholly due to the internal stress of the solid film. These facts strongly suggest that the pressure exerted from the compressed films is not likely to have osmotic pressure of entropy nature as commonly considered, but is intimately related to the elasticity of solids.

Orientation of Microfibrils during Compression.—It is worth noticing that below about 40 A^2/residue, the microfibrils came to orient at right angles to the direction of compression. Extremely high compression of surface film gave rise to tiny visible striations running across the width of the through and finally produced fibrous threads which can be picked up from the water surface. It was observed that the structure of such films exhibited an array of microfibrils developed in straight lines orienting in a parallel manner to the striation or to the fibre. On the other hand, as shown in Fig. 5G, the uncompressed film initially spread at small area, e. g., 18 A^2/residue, gave winding microfibrils which had no sign of orientation.

It was demonstrated above that the compression process makes the surface pressure anisotropic, the pressure against the right angles to the direction of compression being larger than that parallel to it. This is not surprising, because it is considered that the film under investigation is not fluid, but probably solid. It is easily surmised that the orientation effect of the film molecules is brought about from this anisotropic nature of the surface pressure, which may probably orient the molecules with their long axis to the right angles to the direction of compression, in order to relax the pressure difference set up readily after compression.

The author believes that these interesting results provide a new line of evidence for the information of surface films of crystalline polymers.

Summary

(1) Surface films of 6-nylon at air/water interface were investigated by means of electron microscopic observation together with the study of the surface pressure and potential.

(2) An unique structure involving the microfibrils of about 40 A thick were revealed which are formed from the monomolecular network at large areas, and are transformed to polyfibrillar layer during the compression process.

(3) Network structures of the film were divided into two types: a monomolecular network at large areas, and a network of the microfibrillar structure at small areas. Rheological characteristics of 6-nylon film were explained in terms of such structures.

(4) Many evidences were provided which support the view that the surface pressure measured with this film is not likely to have the osmotic pressure as commonly considered, but is intimately related to the surface elasticity of the film.

(5) It was observed that the compression process orients the microfibrils at right angles to the direction of compression. This phenomenon was explained by the anisotropy of surface pressure set up by the compression of the film.

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