Rheology of Surface Films. IV. Viscoelastic Properties of 6-Nylon Films at Air/Water Interface[1]

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Introduction

For the study of the fundamental rheological properties of surface films, it is desirable to investigate first a simple elastic film, being formed by a substance of known structure, which facilitates the interpretation of the experimental data in terms of molecular structure. Second, it is also necessary to extend the research to the viscoelastic films, in order to complete the investigation of surface rheology. In the course of this study, the author found[2] that the spread film of 6-nylon is a favorable material for our present purpose mentioned above, since it behaves as a purely elastic body at large areas, whereas it became viscoelastic when the compression advanced beyond a certain area. The aim of this report is to describe the rheological characteristics of 6-nylon film in detail in relation to their dependence to the degree of compression, magnitude of stress, temperature, and molecular weight of the sample, and to attempt some discussions thereupon.

Experimental

Materials.—Samples of poly-ε-capramide (6-nylon), whose molecular weights were controlled with benzoic acid, were kindly furnished from the Research Laboratory of Toyo Rayon Co. The average molecular weights were viscometrically determined[3], and the following results were obtained: 17300, 9100, 4600, 2800, and 1000. Unless otherwise stated, the sample of molecular weight 17300 was mainly used. Prior to the measurement, all the samples were washed with water, alcohol, and benzene, and dried in vacuum.

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[1] Presented at the Annual Meeting of the Chemical Society of Japan, April. 1954, Tokyo.

[2] T. Tachibana and K. Inokuchi, *J. Colloid Sci.*, 8, 341 (1953).

[3] M. Watanabe, *J. High Polymer* (Japan), 6, 216 (1949).

Spreading Condition.—The sample was spread from a mixed solution of benzene and phenol (3 : 1 in volume) on distilled water. The film was initially spread to 90 Å^2/residue from 0.05% solution. Before compression, about twenty minutes were allowed for the equilibrium to be attained. Unless otherwise stated, the film was compressed down to a desired area at a rate of 60 cm^2/min. and held at least for two hours before measurement. Film compression mainly studied was attained down to about a few Å^2/residue.

Apparatus.—Surface rheometer used was the electromagnetic driving type reported in the foregoing paper[4]. The size of the trough and the detailed measures of the apparatus were the same as shown there. The apparatus was set in an air-thermostatted cabinet and the humidity in it was maintained at an almost saturated state by hanging up some water-immersed cloths in the cabinet. The temperature control of water in the trough was carried out by passing the thermostatted water into the jacket at the bottom of the trough. The temperature near the surface of the water was measured by means of a thermistor. Accuracy of temperature control was about ±0.5°C. The stress being applied to the film at all compressions was always controlled so that a suitable amount of strain (within 2 degrees of angle) occurred under shearing stress. The duration of the measurement was limited within about thirty minutes.

For the numerical evaluation of the viscoelastic quantities, equations (4) and (5) in the previous paper[4] were used with the implicit assumption that the film under test is isotropic and homogenous. With less compressed films, this assumption may be approximately valid. With highly compressed films, however, in which the films are no longer isotropic, and this assumption will not necessarily be valid, no accurate evaluation but more approximation of the viscoelasticity was attained.

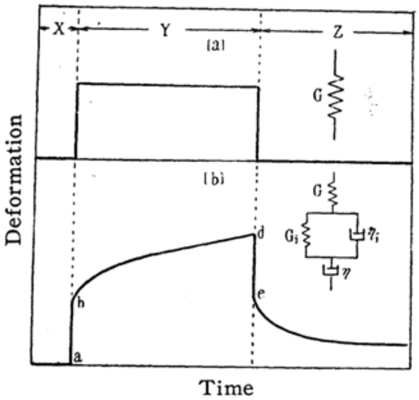

Fig. 1. Strain-time curves of 6-nylon. (a), at less compressed film, (b), at compressed film beyond about 40 Å^2/residue. X represents the dead time, Y, the time, the stress being applied, and Z, the time after the stress is removed.

Results and Discussion

General Remarks on the Rheological Properties.—As shown in Fig. 1, the strain-time curve of 6-nylon film was divided into two types according to the degree of compression of the film, i.e., a simple elastic type of less compressed film (about 75–40 Å^2/residue) and a viscoelastic type of considerably compressed film (less than about 40 Å^2/residue). For convenience' sake, the descriptions will be divided into two parts: time-independent mechanical property and a time-dependent one.

Part I. Time-independent Mechanical Property (Instantaneous Elasticity)

(1) Effect of Stress

It was found that the stress-strain relation generally depends upon the past history of shearing when the stress was first applied to the film. So, experiments, involving repeated process of application and removal of stress, were performed. Successive strains were thus obtained, stresses being gradually increased. Typical examples of these patterns, determined with the film at 42 Å^2/residue were shown in Fig. 2. It is seen that, at moderately small stress, each strain was perfectly identical, no hysteresis being observed as in Fig. 2 a-b. Under large stresses, however, considerable shortening of each strain was evident at the first one or two cycles, though it became less marked upon further repetition of straining tending to a limiting value as in Fig. 2 c-h, especially in h.

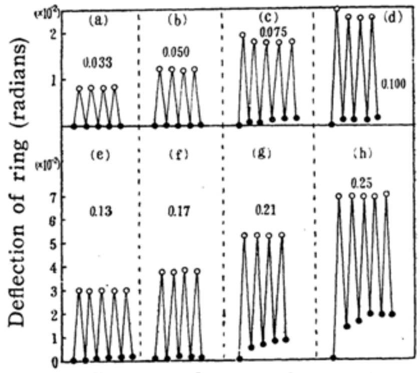

Fig. 2. Pattern of successive straining of the film at 42 Å^2/residue at 28°C, stress being varied in each run, the values of which are indicated above each figure in dyne per cm. Open circles represent the instantaneous strain under stress, and full circles, the strain under removal of the stress.

It is worthy of noticing that the film become more rigid as the rhythmic strain was

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[4] K. Inokuchi, This Bulletin, 27, 432 (1954).

applied to the film. Such a phenomenon may well be compared to "rheopexy" or "work hardening" at bulk. It is plausible to consider that the elasticity of film, simply set up by compression, involves certain unstability in bond formation. Thus, it is presumable that the rhythmic motion, applied to the film, orients and aligns the film molecules, thereby accelerating the attainment of more stable bond formation. Such a mechanism may also be inferred from the property of the ordinary fibre, in which the increase of the tensile strength develops under extension.

When the plots were made using the first value of each strain series, a linear stress-strain relationship was obtained which bent down at larger stress as in Fig. 3. On the other hand, if the curve were plotted using the fourth value of strain series, the nearly straight line was obtained almost up to the point of rupture. Even once the rupture took place under too large stress, only several minutes were sufficient for recovering the film structure. In Fig. 3, crosses indicate that the strain, determined five minutes after rupture, is in good coincidence with those before rupture.

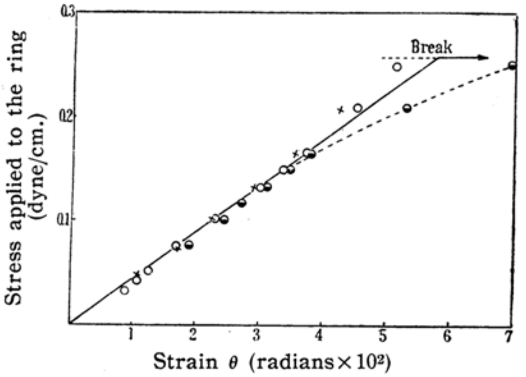

Fig. 3. Stress-strain relation obtained from Fig. 2. Half circle plots were obtained from the first strain of each group of the strain cycles, open circles, from the fourth strain. Crosses represent the plots obtained five minutes after rupture of the film.

Nearly linear relation between stress and strain was generally observed with films at large areas, where only an instantaneous elastic response appeared under stress. On the other hand, with films at small areas, where creep appeared under stress, the plots tended to bend towards the strain-axis above a certain value of stress, though they produced a good straight line at moderately small stresses. Hysteresis was negligible as far as the linear portion was concerned. It was thus presumed that the film at all compressions would be Hookean for at least moderately small stress.

The stress-strain curves at constant rate of strain were also determined, since they are significant for studying the film properties, especially the properties of weakening or fatigue preceding the rupture, which cannot adequately be analysed in terms of viscoelastic deformation alone. The form of the curves are of course dependent on the rate of strain, and the family of the curves depicted in Fig. 4, were obtained under a fixed rate of strain. In this figure, it is seen that at large areas, e.g., at 42 Å²/residue, a good straight line up to the film rupture was obtained, whereas as the area decreased, the plastic portion became evident before rupture set in. In addition, we see that with reducing area, elastic modulus (the slope of the linear portion) remarkably increased, but the strain at yield (length of the elastic portion) became shorter and shorter. Moreover, it is noticed that with highly compressed films (12 and 7 Å²/residue), the creep after yield was well-definable, without causing any gross rupture. Such behavior clearly represents that the film which was simply "brittle" at less compressed state, transformed to "tough" as the compression proceeded, the mechanical properties becoming closer to that of bulk.

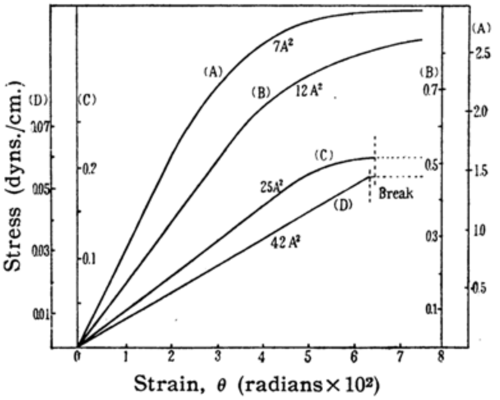

Fig. 4. Stress-strain curves of 6-nylon at constant rate of strain (1.05×10⁻2 radian per minute). Curve (A), 7 Å²/residue; (B), 12 Å²/residue; (C), 25 Å²/residue; and (D), 42 Å²/residue. Temperature 20°C.

It is really surprising that the film at less compressed state, not at highly compressed one, actually exhibits an ideal elastic behavior, which can hardly be seen at the ordinary bulk materials, upon which some discussions will be made in the next paper.

(2) Effect of Aging Time at Constant Temperature

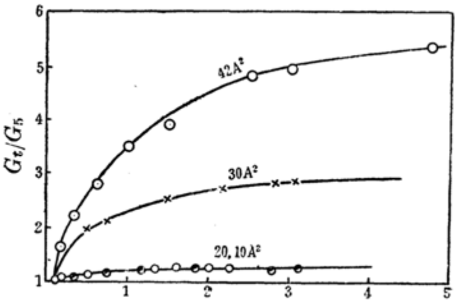

Fig. 5. Effect of aging time on the instantaneous modulus of rigidity at temperature 20°C. Abscissa indicates the aging time, t, defined as the time measured from the end of compression, ordinate, the ratio of rigidity at time $t(G_t)$ for that at 5 minutes of $t(G_5)$.

Time effect of elasticity was examined. In Fig. 5, instead of the actual value of the elastic modulus, ratio of instantaneous elastic modulus at time t for that of five minutes after the end of the compression, was plotted against the gelation time. It is seen that within the first ten minutes, there occurred a rapid increase in the modulus of elasticity, but this was followed by a very gradual approach to a steady state. Moreover, it was found that such an aging effect was remarkable with films at large areas, whereas it became less serious with highly compressed films. The large effect of aging at less compressed films may well be accounted for by the greater ease of orientation and alignment of the film molecules, which tends to form the stable bond than in the case of high compression. It is also noticed from these curves that the time of about two hours, which was allowed to elapse before all the measurements other than this were started, is practically sufficient to attain the steady state of elasticity.

(3) Effect of Temperature

When the temperature was raised to 38°C and chilled at the initial temperature, considerable increase in rigidity was noted, indicating that the temperature hysteresis does exsist. But when the sample was spread at moderately high temperature (38°C), and cooled and held at about 7°C for about ten hours, hysteresis was practically eliminated between the curves for increasing and decreasing temperature as seen in Fig. 6.

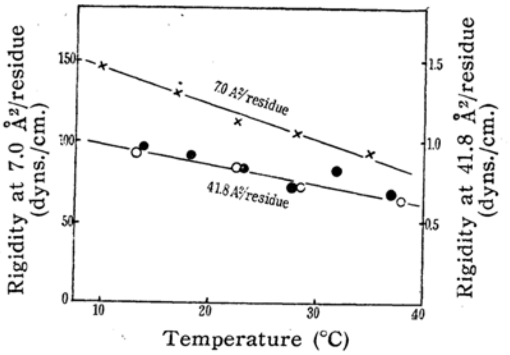

Fig. 6. Effect of temperature on the instantaneous modulus of rigidity. Rate of temperature change, 0.1°C per minute. Crosses show the plots at 7.0 Å²/residue, circles, those at 41.8 Å²/residue. The degree of temperature hysteresis was seen by the open and full circles, the former being those obtained with increasing temperature, the latter with decreasing temperature.

Temperature dependence of the instantaneous elastic modulus G, defined as S/θ, was depicted in Fig. 6. It was seen that the plots may yield a straight line, with negative inclination which was similar for films at all compressions. Thus, the following equation may hold between G and temperature, T.

$$G=a+bT \tag{1}$$

where a, and b, are constants, b being negative. Such a temperature dependence is the same as the bulk material of nylon whose tensile strength decreased with increase in temperature⁵⁾.

According to Wieland and Snyder⁶⁾, the stress, F, can be resolved as follows

$$F=F_u+F_s, \tag{2}$$

where F_u represents energy term, and F_s, entropy term. The entropy term, F_s, is given by the relation

$$F_s=T(\partial F/\partial T)_\theta. \tag{3}$$

Since our present discussion is confined to the Hookean elastic part,

$$F=G\cdot\theta$$

Thus,

$$F_s=T\cdot\theta\cdot(dG/dT). \tag{4}$$

Assuming that F_u is independent of temperature, it follows from the equation (1), (2), and (4) that F_s is negative because of the negative sign of dG/dT (or b), and this term decreased, as the strain increased, whereas the stress due to energy, F_u possesses increasing positive value with increasing strain.

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5) T. Alfrey, "Mechanical Behaviors of High Polymers", p. 518 (1948).

6) W. B. Wiegand and I. W. Snyder, *Trans. Inst. Rubber Ind.*, 10, 234 (1934).

If we compare this thermal data with that of rubber⁷⁾, this film corresponds to that of highly stretched rubber in which advanced degree of crystallization occurs. When this film is compared to that of resting muscle⁸⁾, in which F_u is increased, and F_s decreased with advancing strain, the property is analogous to the highly organized structure of resting muscle. From those observations, it is suggested that 6-nylon film is not rubber-like, but of rather orderly arranged crystalline structure. Such a view may also be inferred from the property of crystallite formation in bulk.

(4) Relation between Elastic Modulus and Film Concentration

Change in modulus of rigidity with reducing area was quantitatively examined. By performing the compression at constant rate, it was possible to overcome the hysteresis of elasticity and to characterize the transformation of the film phase. Fig. 7 shows the rigidity-area curve, which was determined at a compression rate of 9.6 cm²/min. It is seen in this figure that the modulus increased continuously as the compression proceeded down to about 33 Å²/residue, where a plateau started. Further compression did not appreciably increase the rigidity until the areas of 24 Å²/residue was reached after which the rigidity was found to increase again with reducing area, this time more steeply. To make clear this relation, the logarithm of both modulus of rigidity G, and the reciprocal of area, $1/A$—a surface concentration—was plotted as seen in the inset of the figure. It is seen that these plots at larger areas than the plateau fall on a straight line with slight deviation, while those at smaller areas than the plateau produced a fairly good straight line. Thus, it was found that the experimental results were charcterized by the slopes of the lines, namely by the value p of the following equation

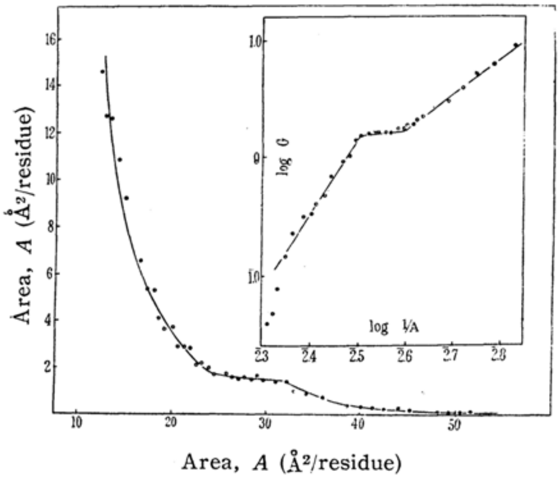

Fig. 7. Rigidity-area (G-A) curve obtained under a constant rate of compression (9.6 cm²/minute). Inset indicates the log G—log $1/A$ relation.

$$G=c(1/A)^p \tag{5}$$

where c and p are constants. At larger and smaller areas than the plateau, p's were approximately calculated as 6 and 3, respectively. It may be that a film structure, once established at large areas, transformed to another type according to the degree of compression. The plateau region is thought to be a transition state of film structure under compression. As will be mentioned in the next paper, the plateau in the rigidity-area curve was consistent with the plateau which appeared in the pressure-area curve.

If we assume an approximate value as the thickness of the film under test, the modulus of rigidity in bulk would be calculated from the value of surface modulus of rigidity, G. The film thickness was presumed from the spreading amount and the density of the solid. The modulus of rigidity in bulk, corresponding to the area of 40 Å²/residue was calculated as 1.2×10^7 dyns./cm², whereas those corresponding to the area of 20 A²/residue and 7.0 Å²/residue, were 4.6×10^7, and 5×10^8 dyns./cm², respectively. Uéno and Fuchino⁹⁾ obtained 55 kg./cm² as Young's modulus of elasticity of unstretched fibre of 6-nylon, from which the modulus of rigidity in bulk was calculated as 1.9×10^9 dyns./cm², assuming the poisson ratio 0.4. Although, with the film of high compression, precise evaluation of the film rigidity is impossible because of the failure of the isotropy of the film, the general trend is that the value calculated from the surface modulus at large areas was considerably smaller than that in bulk, whereas the values became closer to each other with reducing area. Such a disagree- ment of rigidity modulus between the bulk and the surface film would not be surprising, because the structure of spreading film is generally not the same as that in bulk. Such a difference in structure, however, is thought to be less pronounced as the compression advanced to form multimolecular layers, since the values at high compression became close to that of bulk.

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7) E. Guth, *Ann. N.Y. Acad. Sci.*, 47, 723 (1947).

8) E. Guth, *Ann. N.Y. Acad. Sci.*, 47, 743 (1947).

9) S. Ueno and K. Fuchino, *J. Textile Research* (*Sen'i-gakukai-shi*), 45, 324 (1951).

(5) Molecular Weight Dependence of Gelation Area

The area, at which the film first manifests elasticity under compression is significant for the study of the film structure, and is called here "gelation area" (A_g), the unit being Å^2/residue. Fig. 8 shows how the gelation area is affected by the molecular weight of the spead material. It was found that the gelation area versus degree of polymerisation *D.P.* plots yielded a straight line showing an increase in A_g with increase in *D.P.*, so long as *D.P.* is not very high. However, with *D.P.* above a certain value, it tended to a maximum value of about 75 Å^2/residue.

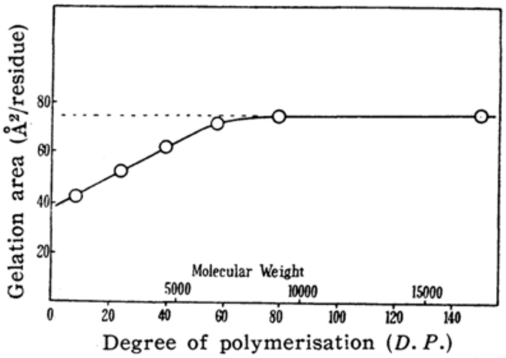

Fig. 8. Gelation-area versus molecular weight relation.

It is apparent that the gelation area inevitably necessitates the mutual contact of the neighboring molecules. So, the gelation area must closely be related to the degree of molecular extension. Since at the gelation point, the molecules are linked together, the degree of molecular extension would chiefly be determined by the flexibility of molecular chain.

With molecules, whose chain length is relatively short, the smaller value of A_g would be expected, the lower *D.P.* is, because the moleculer extension due to the flexibility of the molecular chain might be come less pronounced with decreasing chain length. In an extreme case of monomer films, A_g would be very close to the co-area of the residue itself. As seen in Fig. 8, extrapolation of the A_g-*D.P.* curve to zero *D.P.* yielded about 37 Å^2/residue, which is fairly consistent with the co-area of residue, lying flat on water surface (molecular model gives 40.2 Å^2/residue).

On the other hand, with the molecule, whose chain length is sufficiently long, it will be expected that the area per residue is independent of *D.P.*, since further increase in *D.P.* beyond a certain limit, would merely cause repetition of the flexible unit of chain. This was experimentally verified as shown in Fig. 8, in which A_g became independent of *D.P.*, when *D.P.* was over about 80.

It is generally accepted that chain polymers in solution take a spatial configuration of nearly random coiling, if there is no special interaction between chains. Applying this analogy to the surface, and assuming a two-dimensional random-coil model for the chain configuration of the film molecules, it can be deduced from simple statistical calculations that the mean area occupied by one molecule is proportional to *D.P.*, that is, the mean area per residue is independent of *D.P.* except for the chains of extremely short length. This seems to explain the above experimental result.

It must be noticed, however, that the maximum value of A_g is only twice as the co-area of residue, which is too small if we assume the two-dimensional random coil of a molecular chain. Moreover, it is surmised that, if the random coil of the molecular chain might be assumed, the value of *D.P.* at point of levelling off of the curve should be far small, being less than one-tenth of that in Fig. 8, at most. These results lead us to the postulation that the configuration of molecular chains at water surface is not likely in the case of random-coil, but may presumably be an extremely stretched one, possessing less flexibility. Such a molecular configuration may rather be favorable for the alignment and association between adjacent molecular chains which lead to the formation of rigid gel-structure.

(6) Molecular Weight Dependence of the Film Elasticity

Instantaneous modulus of rigidity was plotted against the molecular weight of the

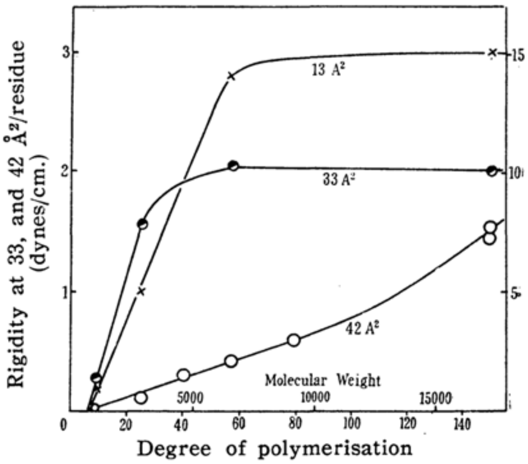

Fig. 9. Rigidity versus molecular weight relations at various areas.

sample at various areas. As depicted in Fig. 9, two types of the curve were obtained. At a highly compressed state (13 and 33 $\AA^2$/residue), rigidity increased proportionally with *D.P.* as far as *D.P.* is relatively low, but they approached asymptotically to a maximum value when *D.P.* was over about 80. Moreover, it was found that extrapolation to zero rigidity failed to pass through the origin, cutting the *D.P.* axis by about 5. Such a form of the curve is entirely similar to that obtained with material in three-dimensional state[10]. Kanamaru and Koyama[11] also obtained the similar curve with nylon fibre.

On the other hand, the spreading at a less compressed state, 42 $\AA^2$/residue, failed to exhibit the saturation curve as shown above. That is, the rigidity increased linearly with *D.P.* up to *D.P.* value of about 150. Extrapolation of the curve to zero rigidity coincided with the same point for the more compressed film.

Although the current view[12,13] of the strength-*D.P.* relation of the fibre or yarn is that the mechanical strength of material is affected by the two factors, the one is a frictional force between the chains (*D.P.*-dependent), and the other a primary valence force of the main chain (*D.P.*-independent)., it is not suggested that the strength of the spread film can readily be explained from this view point. The author should like to consider that the degree of cristallite formation is intimately related to this phenomenon. As is generally accepted, fine structure of the crystalline polymers are considered to consist of the dense, tightly packed crystalline regions interspersed with less-dense amorphous regions, and the latter, being weaker than the former in mechanical strength, may be determinant for the establishment of the overall mechanical property. It is further believed that one and the same molecule may pass through two or more amorphous regions. Thus, it will be expected that the mechanical strength becomes independent of *D.P.*, when *D.P.* is sufficiently high. A similar consideration may also be applied for the case of the compressed film of 6-nylon, for instance at 13 and 33 $\AA^2$/residue, since, as will be described in the next paper, the structure of the compressed film is thought to bear considerable resemblance to that in bulk.

With the films at large areas, however, the condition may be somewhat unfavorable for the crystallite formation, because the molecular configuration is confined within the two-dimensional plane, and the molecules are more loosely packed than in the above case. It follows that, due to the imperfect crystallite formation, amorphous region extends to a longer part of the molecule, and the mechanical strength may become dependent of *D.P.* up to a higher value of *D.P.* Thus, the simple increase in rigidity with *D.P.* at 42 $\AA^2$/residue may result. Such a view must be verified further with various kinds of material, and experiments with spreading films, which facilitate the control of the concentration of molecules with the same material, may be very useful for the investigation of this problem.

(7) Effect of pH of the Substrate Water

Gelation areas were measured under various pH of the substrate water (Fig. 10). Control of pH was carried out with hydrochloric acid and sodium hydroxide, and a glass electrode system was used to measure pH values. It was found that gelation area markedly decreased on the acidic substratum, though no remarkable influence was observed in the pH range between 2 and 10. On the 2 N sulfuric acid aqueous solution, the film failed to exhibit the elasticity above the areas of about 40 $\AA^2$/residue. Below this area, the film elasticity was found to decrease on the strong acidic solution. Such a result may well be consistent with the plausible view that the hydrogen bridge between the iminogroup of one residue and the carbonyl of another is respon sible for the film elasticity, since such a bond would be very weak on high acidic substratum.

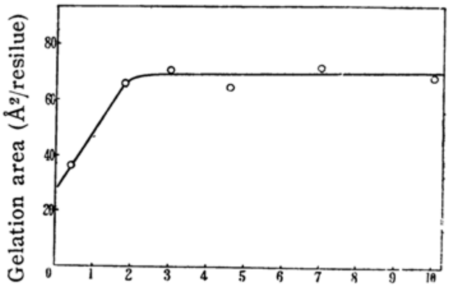

Fig. 10. Effect of pH of the substrate water upon the gelation-area, temperature 13–16°C.

Part II. Time-dependent Mechanical Properties

(1) Formal Analysis of the Strain-time Curve under Constant Shear Stress

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[10] A. M. Sookne and M. Harris, *Ind. End. Chem.*, **37**, 478 (1945).

[11] K. Kanamaru and F. Koyama, *J. Chem. Soc. Japan (Ind. Chem. Sec.)*, 1273, **46**, (1943).

[12] K. H. Meyer, and H. Mark, Der Aufbau der Hochpolym. org Naturstoffe (Leipzig, 1930), p. 153.

[13] R. R. Sulivan, *J. Appl. phys*, **13**, 157 (1947).

Since, as mentioned above, the mechanical properties of the film at compressed state was complicated, it seemed convenient to represent the behavior with a series of the mechanical models: an instantaneously recoverable spring having an elastic modulus G, atime-dependent slowly recoverable spring of elastic modulus G_i set in parallel with a dashpot of viscosity, η_i, and a non-recoverable viscosity, η (see the inset of Fig. 1). The delayed elastic response is generally represented by a series of definite numbers of retardation times. So we now examine how many retardation mechanisms are necessary to represent practically the form of the experimental curve for delayed elasticity. As a typical example of the analysis, the strain-time curve at the area of 7.0 Å^2/residue was used.

According to the usual analysis of rheology[14], the form of the curve for the delayed elastic response is expressed by the following equation

$$\gamma=\sum_{n=1}^{i}A_i(1-e^{-t/\tau_i}), \tag{6}$$

where γ represents the delayed elastic strain at time t, A_i, a constant, and τ_i a retardation time. Letting Q be equal to $(\Sigma A_i-\gamma)$, which corresponds to the distance between "b-c" curved line and "p-c" straight line measured along the strain axis of Fig. 11 (shadow region), the equation (6) follows,

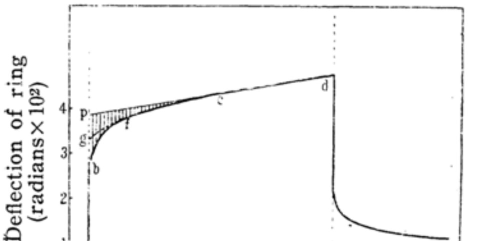

Fig. 11. Strain-time curve at 7.0 Å^2/residue, temperature 35°C. Stress applied to the ring, 5.0 dynes per cm.

$$Q=\sum_{n=1}^{i}A_i e^{-t/\tau_i} \tag{7}$$

Letting τ_1, τ_2,..., a series of the retardation times involved in the film, be arranged in the decreasing order of magnitude and assuming that τ_1 is preferentially large compared with the other retardation times, τ_2, etc., log Q, when plotted against time, should give a straight line for large value of t. Except for the region of the initial several minutes, the above relation was valid in Fig. 12 (circle plots), which shows a straight line intersecting log Q axis at A_1. Putting this straight line back into Fig. 11, the dotted line "f-g" was obtained, which represents the equation (7) involving single retardation time. From this figure, it can readily be seen that single retardation mechanism does not serve to represent the experimental data with sufficient accuracy.

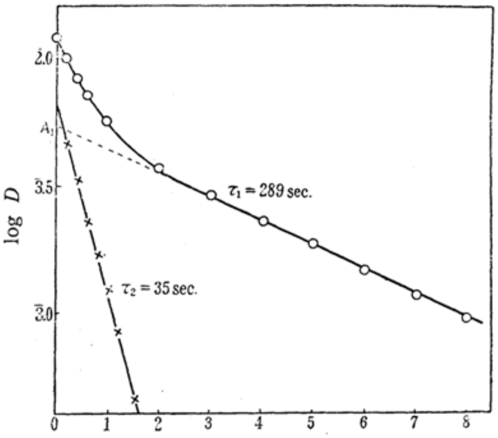

Fig. 12. Log Q versus time plots, corresponding to the curve in Fig. 11.

If the relation mentioned above proved to hold, equation (7) further predicts that log $(Q-A_1e^{-t/\tau_1})$ should also become linear with large value of t, provided $\tau_1>\tau_2$. This was also valid as shown in the lower part of Fig. 12 (cross plots), from which τ_2, and A_2 were obtained from the inclination of the linear part of the line and the intercept on the ordinate axis, respectively. Since, in the present experimental conditions, it was difficult to determine the accurate form of the curve of the initial period of several seconds, a further series of retardation times following τ_2, was not taken into our consideration.

In brief, it was found that duplicate retardation mechanisms, in which longer and shorter retardation times are involved, seem adequate to describe the delayed elastic response of this film. If the initial displacement of the ring due to an instantaneous elasticity and the creep of constant rate of motion are represented by θ_0, and λt, respectively, where λ stands for the rate constant of motion, the overall strain of the ring, θ, would be expressed by the following equation of the six parameter model,

$$\theta=\theta_0+A_1(1-e^{-t/\tau_1})+A_2(1-e^{-t/\tau_2})+\lambda t. \tag{8}$$

A similar degree of agreement between equa-

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[14] T. Alfrey, "Mechanical Behaviour of High Polymers," Intersci. Publ. New York, (1948), p. 58.

tion (8) and the observed curve was found to hold for all the data obtained with films at high compression, though films at less compression, e.g., 20 to 30 Å²/residue, where the contribution of the time-dependent strain was comparatively small, single retardation time was found to be practically adequate to express the delayed elastic strain. Such a form of the creep curve was just similar to that of the three-dimensional hydrogels of agar-agar, reported by Fujita and others[15].

Assuming that $G=KS/\theta_0$, $G_1=KS/A_1$, $G_2=KS/A_2$, $\eta_1=G_1\tau_1$, $\eta_2=G_2\tau_2$, and $\eta=KS/\lambda$, S represents the stress applied, and K, a constant involving shape factor, numerical values of the various areas, were obtained as shown in Table I.

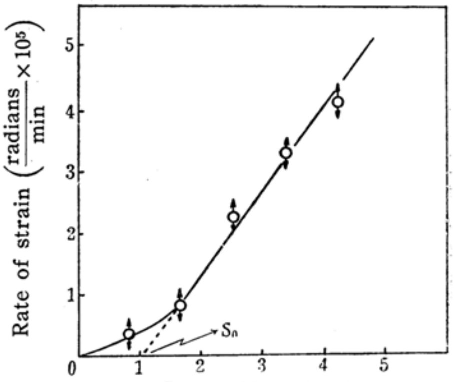

Fig. 13. Stress dependence of the rate of stationary flow at the film of 7.0 Å²/residue.

TABLE I

VARIOUS PARAMETES IN THE MECHANICAL MODEL IN C.G.S. UNIT TEMPERATURE 20°C

C.G.S. unit / Area Å²/residue	Instantaneous Elasticity	Delayed Elastic Parameters						Stationary Flow Viscosity
	G	G_2	τ_2	η_2	G_1	τ_1	η_1	η
42	0.38	—	—	—	—	—	—	—
25	1.6	—	—	—	19.5	113	2.2×10^3	7.8×10^3
12	11.2	109	17	1.9×10^3	107	72	7.7×10^3	1.3×10^4
7	112.3	1590	27	4.3×10^4	675	126	8.5×10^4	7.0×10^5

Although the observed values obtained with the same film were considerably reproducible, those obtained with a different run of experiments were found to scatter to a considerable extent. This seemed to be more pronounced at highly compressed film, while it was less serious at large areas. This may be due to the difficulties of obtaining conditions of forming exactly the same gel-structure.

(2) Stationary Flow Properties

(a) **Effect of Stress.**—Stress effect on λ of equation (8) was examined. As shown in Fig. 13, λ-S plots curved at small stress, with convex curvature against the strain axis, while, at higher stress, λ increased linearly with increasing stress, although the experimental plots scattered to some extent. If the intercept of the straight line on the stress axis was represented by S_0, such plots would be approximated by the equation,

$$\theta_f=K(S-S_0)t/\eta \qquad (9)$$

where θ_f is the displacement due to the flow, η, a parameter having the dimension of surface viscosity. Such a flow behavior, which is well-known as Bingham's plastic flow, was always observed in all the flow region of the films.

(b) **Effect of Temperature.**—The effect of temperature on η was also studied. It was found that the viscosity decreased with increasing temperature as should be expected. To make this clear, the logarithm of η was plotted against the reciprocal of the absolute temperature ($1/T$) as depicted in Fig. 14.

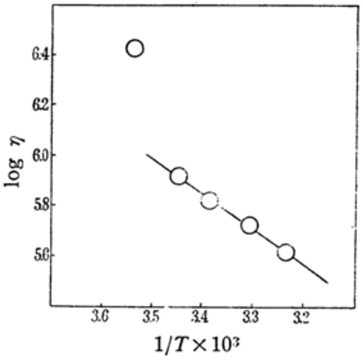

Fig. 14. Temperature dependence of the viscosity coefficient (η) at the film at 7.0 Å²/residue.

We see that the temperature dependence of the viscosity follows the well-known Andrade

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[15] H. Fujita, K. Ninomiya and T. Homma, This Bulletin, 26, 20 (1953).

equation and the corresponding apparent activation energy E was approximately estimated as 6.4 kcal./mole. This value is in good agreement with that obtained in bulk[16], and, from this, it is assumed that the flow mechanism of such films is similar to that in bulk. Although it is difficult to know what this means, such a magnitude of energy may suggest that the strength of flow unit involved in it is the interaction of a secondary nature as would be expected from the molecular structure of 6-nylon, which permits the hydrogen bondings between NH and CO of adjacent chains of molecules.

Such a temperature dependence was almost the same for all compressions of the film. It was found, however, that the films, which were compressed to the areas of 12—15 Å^2/residue, were the exception. Although the films of such a degree of compression took no special attitude as far as the stress effect was concerned, the viscosity of this film decreased far more markedly with rise of temperature than that of the other compressions. The author[17] reported a surface film of ovalbumin which suffered melting at room temperature under a certain condition. The fact observed here with 6-nylon may have some similarity with this phenomenon. Detailed mechanism requires further studies.

(3) Transcient Creep Properties

As is understood from the equation (8), these properties can be characterized by the parameters A_i, and τ_i. It was found that the values of both parameters was considerably less reproducible compared with the instantaneous elasticity and stationary flow, the experimental errors amountung to about 30% or more. In Fig. 15, instead of A_1, the modulus of retarded elasticity G_1, defined by KS/A_1, was plotted, together with τ_1, against stress. Fig. 16 gives the temperature dependence of G_1 and τ_1. We can see in these figures that the values of G_1 decreased with increasing stress. It is to be noted that the delayed elasticity is non-Hookean unlike the instantaneous elasticity. The value of G_1 decreased with increasing temperature, in a manner just similar to G. Because of the negative sign of the temperature dependence of G_1, the nature of the delayed elasticity was considered to be energy effect rather than entropy effect, as was the case with instantaneous elasticity.

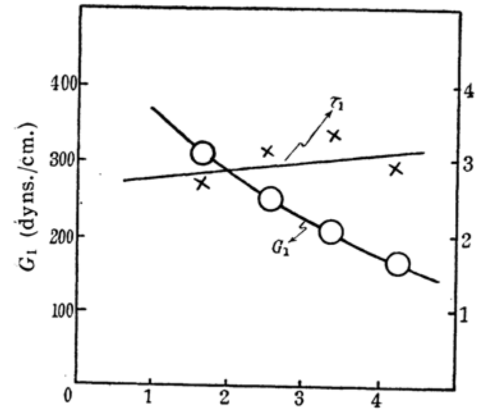

Fig. 15. Stress dependence of parameters in the delayed elastic mechanism. The area, 7.0 Å^2/residue. Circles represent the delayed elasticity (G_1), crosses, the retardation time (τ_1).

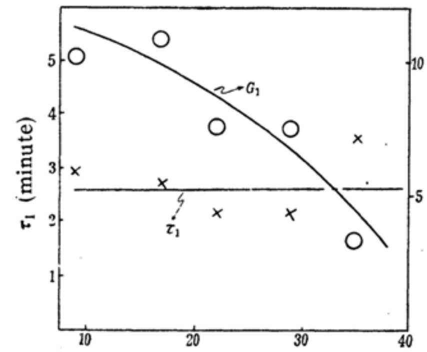

Fig. 16. Temperature dependence of each parameters in the delayed elastic mechanism. The area, 7.0 Å^2/residue. Circles represent the delayed elasticity G_1, crosses, retardation time, τ_1.

The dependence of τ_1 upon the stress as well as temperature was considerably scattered, being similar to the Fujita's[15] data obtained with agar-agar hydrogel. Although definite conclusion could not be drawn on either stress or temperature effect on the retardation times, it would be likely that the retardation time is little influenced by temperature or stress. Such charactersitics of A_1 and τ_1 were similar also in the case of A_2 and τ_2.

(4) Stress-relaxation Test at Constant Shear Strain

(a) **Formal Analysis of the Curves.**—This test was carried out by reading the microammeter of the circuit of the rheometer at suitable intervals of time, when the current passed through the coil was controlled by adjusting the potentiometer so that the deflection of the ring, which occurred instantaneously after applying the stress, was held

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[16] K. Fuchino, H. Okada, and N. Sagane, *J. High Polymer Chem.* (Japan), 7, 19 (1950).

[17] K. Inokuchi, This Bulletin, 26, 500 (1953).

constant throughout the experiment. A family of the curves in Fig. 17, obtained at different temperatures showed that considerably fast decay of the stress appeared at the early stage of time, followed by a slow decay at longer periods of time. Results of duplicate experiments are also indicated with a dotted line for the curve of 33°C. In general, relaxation of slow decay is relatively reproducible, whereas that of fast decay showed less reproducibility.

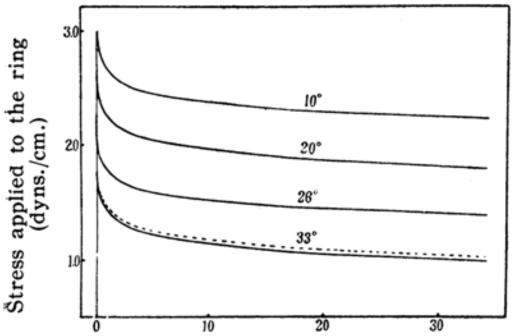

Fig. 17. Stress-relaxation curves at constant shear strain of the film at 7.0 Å_2/residue at varying temperatures. Deflection of the ring, 2.5×10^{-2} radians.

It was considered here that the experimental curves obtained could be expressed by a series of several Maxwellian relaxations as being written by the following equation

$$S=A\Sigma_i' e^{-t/\tau_i'}$$

where S represents the stress applied, τ_i' a constant termed as a relaxation time, and A'_i, a constant. Check of the equation was made just in the same manner as was the case of the creep test in the foregoing section. As a result, it was found that three elements of Maxwellian relaxation were at least necessary to fit the whole data of the experimental plots except for the initial stage several seconds. In the present film, τ_1', τ_2' and τ_3', have the order of magnitude of 10^4, 10^2 and 10^1 second, respectively. Such a trend was always found with each curve obtained. Assuming that $G'_i=S_i/A'_i$, where $S=\sum S_i$, each value of the parameters, G and τ, were calculated as seen in Table II. Accurate determination of the numerical values of the third relaxation mechanism was, however, rather difficult, so we had to be contented with approximations.

TABLE II

VARIOUS PARAMETERS OF THE MECHANICAL MODEL OBTAINED FROM THE STRESS-RELAXATION CURVES IN Fig. 17

Parameters in C. G. S. unit / Temperature (°C)	G_1'	G_2'	G_3'	τ_1'	τ_2'
10	44.9	5.6	3.9	2.1×10^4	1.4×10^2
20	37.6	5.2	5·2	1.5×10^4	1.6×10^2
26	29.4	4.6	7.8	1.4×10^4	1.3×10^2
33	22.2	4.8	4.8	0.9×10^4	1.4×10^2

(b) **Temperature Dependence of the Relaxation Times.**—Assuming Arrhenius equation, apparent activation energies, E'_1 and E'_2, corresponding to τ_1' and τ_2', respectively were obtained by plotting logarithms of τ_1' and τ_2' against $1/T$. It is to be noticed that temperature dependence of both relaxation times markedly differed, that is, longer relaxation time, τ_1', is considerably temperature-dependent, giving $E'_1 \fallingdotseq 5$ kcal./mole, whereas shorter relaxation time, τ_2', exhibited almost no temperature dependence, namely $E'_2 \fallingdotseq 0$.

Activation energy of longer relaxation time, 5 kcal./mole, is fairly consistent with that of flow obtained with the creep curve in the preceding section. This value of activation energy for relaxation is in good harmony with the view that the gel-structure of this film consists of cross-linking at points of contact of a secondary strength. The fact that the shorter relaxation time was independent of temperature, is inferred from the result of the creep test that the retardation time, τ_1, failed to exhibit any definite temperature dependence.

Although, at the present stage, molecular interpretation of the temperature-independent relaxation mechanism is not clear, it would be reasonable to suppose that this relaxation is chiefly associated with the frequency factor in Arrhenius equation, presumably with the activation entropy for relaxation. In any case, it was pointed out here that the compressed film under test involves at least two kinds of relaxation mechanism of different modes.

(5) Correspondence between the Two Mechanical Models

In the above description, two types of mechanical model were presented: the one (model A), obtained from the creep test, the other (model B), from the stress relaxation test. If each parameter operating in the models is linear in nature, both models should be equivalent to each other, and values of parameters of one model are obtainable, when those of the other are known. In order to study the extent of correspondence of the mechanical models, duplicate measurements of creep and stress-relaxation were carried out with one and the same film, since the data obtained from the experiments on different films scattered considerably even when the same experimental conditions were considered to be secured. The results obtained were arrayed by means of the mechanical models in Fig. 18, in which respective numerical values of each parameter were given in c.g.s. unit. It was stated above that six parameters were adequate to express the overall form of the curves up to the initial several seconds. For the sake of simplicity, however, the mechanical models of four parameters were used in this connexion, parameters belonging to the shortest retardation times (within one minute) being neglected. In this figure, blackets in model (A) give the values calculated from model (B).

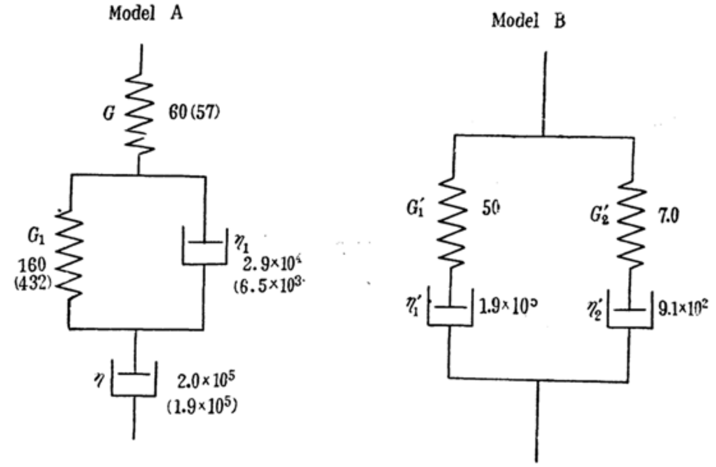

Fig. 18. Mechanical models of 6-nylon.

It is indicated that satisfactory agreement was obtained between the observed and calculated values, so far as instantaneous elasticity and stationary flow viscosity are concerned. As to the delayed elastic part, however, considerable disagreement of the values was seen. Such a degree of departure may well be expected, since it was shown above that parameters operating in the delayed elastic mechanisms as well as those in the shorter relaxation ones were considerably irreproducible, and that the delayed elasticity is non-Hookean (non-linear).

Such a state of affairs makes it difficult to draw a definite conclusion as to the consistency of the model of delayed elastic mechanism. It may, however, be said that our mechanical models presented above are sound for describing the static viscoelastic behaviors of the film, so far as the simple elastic part and stationary flow part are concerned.

Summary

(1) Using a surface-rheometer, the strain-time curves at constant shear stress, the stress-relaxation curves at constant strain, and the stress-strain curves at constant rate of strain were determined with the spread films of 6-nylon at air/water interface, and the rheological data were measured in relation to their dependence upon stress, temperature, and molecular weight of the sample under varying compressions, and were arrayed in the light of the mechanical models.

(2) It was found that the rheological characteristics of the film were classified into two types according to the degree of compression, i.e., a simple elastic type at large areas which involves a Hookean elasticity alone, and a viscoelastic type at considerably small areas, which is characterized by an instantaneous elasticity, the delayed elasticity, and stationary flow under constant stress.

(3) The stress-strain curves at constant rate of strain revealed that the film, which was simply brittle at large areas transformed to tough as the compression proceeded, the mechanical properties resembling to that in bulk.

(4) It was also observed that the film strength, which was readily set up after compression, was considerably improved by the rhythmic strains applied to it, indicating the two-dimensional rheopexy.

(5) Instantaneous elastic modulus versus area curve showed a conspicuous plateau at the areas from about 33 to 24 Å²/residue, which suggests that at least two different phases are experienced during the process of compression.

(6) Temperature dependence of the instantaneous elasticity suggests that the elasticity is mainly due to the energy effect rather than entropy effect.

(7) Molecular weight variations of the film elasticity and of the gelation area were examined together with their pH dependence of the substratum, and discussions were made in molecular terms.

(8) The stationary flow under constant stress behaved as a plastic flow, which is characterized by a yield stress above which flow practically begins to occur. Apparent activation energy of flow was estimated as about 6 kcal./mol.

(9) Overall forms of the strain-time curves and of the stress-relaxation ones were found to be well fitted by the mechanical models of six parameters.

(10) From the temperature dependence of the relaxation times, it was suggested that at least two different modes of relaxation mechanism do exist within the films of high compression.

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