Surface Chemistry of the Polyamide Series. III. Monolayers of Nylons from ω-Aminocarboxylic Acids at the Air/Water Interface

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Polyamides of the nylon type are prepared from diamines and dicarboxylic acids or from ω-aminocarboxylic acids, and they are commonly designated by the numbers of carbon atoms per monomer unit. For example, polyhexamethylene sebacamide, $(\text{-HN(CH}_2)_6\text{NHCO(CH}_2)_8\text{CO-})_n$, and polyundecanamide, $(\text{-NH(CH}_2)_{10}\text{CO-})_n$, are Nylon 610 and Nylon 11 respectively. It has been found that the melting points of nylons with odd numbers of CH_2 groups per monomer unit are lower than those with even numbers.1-4) This fact has been ascribed to the deficient hydrogen bond formation of the former nylons.1,2) Kinoshita5,6) has shown that the odd number of CH_2 groups in polyamides does not lead to a deficient hydrogen bond formation, but that it in general gives rise to a configuration somewhat similar to the pleated sheets structure proposed by Pauling and Corey7) for the structure of polypeptide. This configuration was called the γ-form. On the other hand, polyamides with even numbers of CH_2 groups usually contain two different crystalline forms, α and β, which have the same chain repeat distance and differ only in the side-by-side arrangement of molecules.

In this connection, it is interesting to study the effect of the numbers of CH_2 groups on

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1) G. Champetier and R. Aélion, *Bull. soc. chim. France*, **1948**, 683.

2) R. Hill and E. E. Walker, *J. Polymer Sci.*, **3**, 609 (1948).

3) D. D. Coffman, G. J. Berchet, W. R. Peterson and E. W. Spanagel, ibid., **2**, 306 (1947).

4) D. D. Coffman, N. L. Cox, E. L. Martin, W. E. Mochel and F. J. Van Natta, ibid., **3**, 85 (1948).

5) Y. Kinoshita, *Makromol. Chem.*, **33**, 1 (1959).

6) Y. Kinoshita, ibid., **33**, 21 (1959).

7) L. Pauling and R. B. Corey, *Proc. Nat. Acad. Sci. U. S. A.*, **39**, 253 (1953).

the nature of the monolayers of a series of nylons. Although the monolayers of several nylons have been studied,[8-15] no studies have been carried out along this line. Accordingly, in the present work, a series of nylons with 2 to 11 CH_2 groups per monomer unit (Nylons 3 to 12) prepared from ω-aminocarboxylic acids have been studied at the air/water interface in order to investigate the correlation of the film porperties with the numbers of CH_2 groups per monomer unit. The film of Nylon 9 at the oil/water interface and that of polyurea, polynonamethylene urea ($-(CH_2)_9-HNCONH-)_n$, at the air/water interface have also been studied in order to prove the role of the van der Waals attractive force between hydrocarbon groups in polyamide monolayers.

Experimental

Materials. — Nylon 3 (poly-β-alanine) prepared from acrylamide was supplied by Professor S. Murahashi of Osaka University. The insoluble fraction in boiling water was used in the present experiment. Its intrinsic viscosity was 0.432 (in 90% formic acid at 25°C). Nylon 4 (n=87) were prepared from pyrrolidone by Dr. Y. Joh of the Mitsubishi Rayon Co., and Nylon 5 (n<25), from piperidone by Mr. T. Konomi of the Toyo Spinning Co. Nylons 7, 8 and 10 were supplied by Dr. Y. Kinoshita and Nylon 12 by Dr. M. Ito of the Toyo Rayon Co. The intrinsic viscosities of these nylons were more than 0.9 (in cresol at 25°C). Nylons 7, 8 and 10 were the same samples as those used in Kinoshita's investigation.[5] Nylon 11 (m=16000) was a gift from Dr. V. Ambekar of L'école Supérieure de Physique et de Chimie de Paris. Nylon 6 (Amilan), Nylon 9 and polynonamethylene urea were commercial products.

Nylons 3, 4 and 5 were used without further purification. Nylon 6 was purified by precipitation from a solution in formic acid by adding water. The chips or fibers of Nylons 7 to 12 and polyurea were immersed in benzene for 24 hr. and then in ethyl alcohol for the same length of time. All the samples were dried at 80°C in vacuo for 3—4 hr.

Nylons 3 to 9 were spread from solutions in 90% formic acid, Nylons 10, 11 and 12, from solutions in a 1 : 1-mixture (v/v) of dichloroacetic acid and trifluoroacetic acid, and polyurea, from trifluoroacetic acid. Nylon 9 was also spread from a solution in trifluoroacetic acid. The concentrations of these solutions were 0.2—0.3 mg./ml.

A subsolution containing 40% ammonium sulfate or concentrated sulfuric acid was treated with active charcoal before use in order to remove any surface-active contaminants.

Methods. — The surface pressure was measured by the Wilhelmy methods; the surface potential, by the ionizing air-electrode method; the surface viscosity, by the rotatory oscillation method, and the interfacial pressure, by the ring method. The surface moment was calculated from the surface potential using the Helmholtz equation. The details of the experimental methods have already been described in Part I of this series.[16]

Results

Nylons 3, 4 and 5 were spread on a 40% ammonium sulfate subsolution because stable films were not obtained on distilled water. For the sake of comparison, Nylon 6 was also spread on the same subsolution. The surface pressure-area (Π-A) curves of these nylons are shown in Fig. 1. The film of Nylon 3 was of the condensed type, while those of Nylons 4, 5 and 6 were of the expanded type.

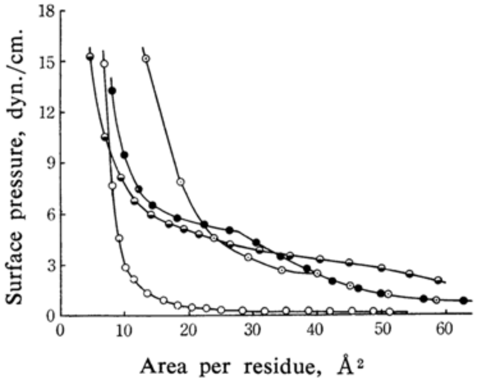

Fig. 1. Surface pressure-area curves of Nylon 3 (○), Nylon 4 (●), Nylon 5 (◒) and Nylon 6 (⊙) on 40% ammonium sulfate at 23°C.

The Π-A, surface moment-area (μ-A) and surface viscosity-area (η_s-A) curves of Nylons 6 to 12 on distilled water are shown in Figs. 2 to 8 respectively. The interfacial presssure-area (Π_i-A) curve of Nylon 9 at the petroleum ether/water interface is also shown in Fig. 5. The Π-A and μ-A curves of Nylons 6 to 9 on the concentrated sulfuric acid subsolutions (3 N and 6 N) are shown in the corresponding figures.

The film of Nylon 6 on distilled water was of the expanded type. The area per residue was somewhat smaller than that on 40% ammonium sulfate. The film of Nylon 7 on distilled water was rather more condensed than that of Nylon 6, although the film was of the expanded type.

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

[9] C. W. N. Cumper and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 235 (1950).

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

[11] T. Isemura and K. Hamaguchi, ibid., **27**, 125 (1954).

[12] H. Hotta, *J. Colloid Sci.*, **9**, 504 (1954).

[13] K. Inokuchi, This Bulletin, **28**, 453 (1955).

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

[15] G. E. Hibberd and A. E. Alexander, *Proc. 3rd Int. Cong. Surface Activity*, **2**, 144 (1960).

[16] Part I of this series: T. Yamashita and T. Isemura, This Bulletin, **38**, 420 (1965).

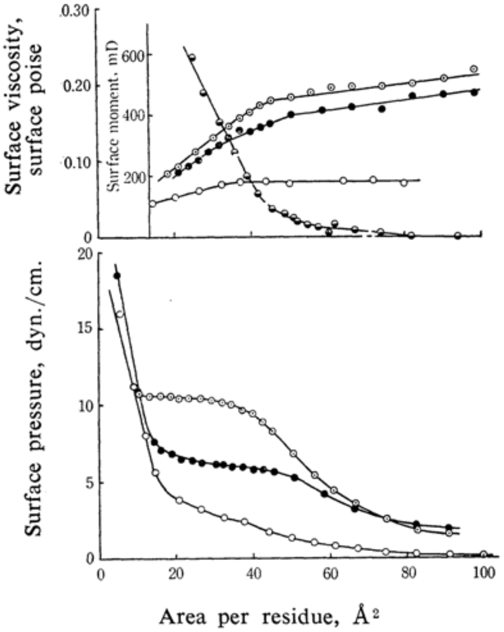

Fig. 2. Surface pressure-area and surface moment-area curves of Nylon 6 on distilled water (○) and on sulfuric acid (3 N, ●; 6 N, ⊙), and its surface viscosity-area curve on distilled water (◒) at 22°C.

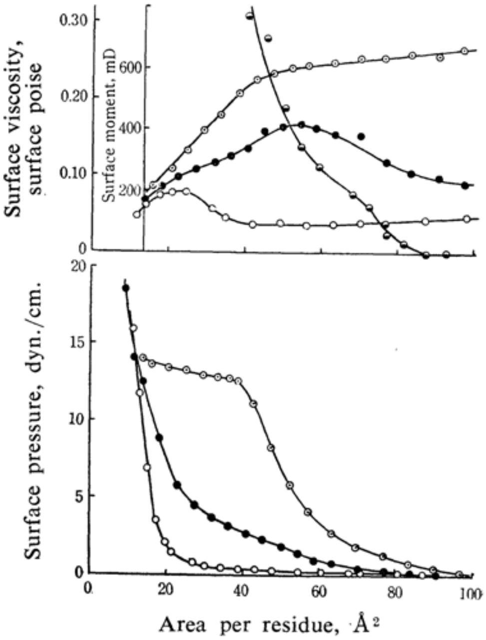

Fig. 4. Surface pressure-area and surface moment-area curves of Nylon 8 on distilled water (○) and on sulfuric acid (3 N, ●; 6 N, ⊙), and its surface viscosity-area curves on distilled water (◒) at 21°C.

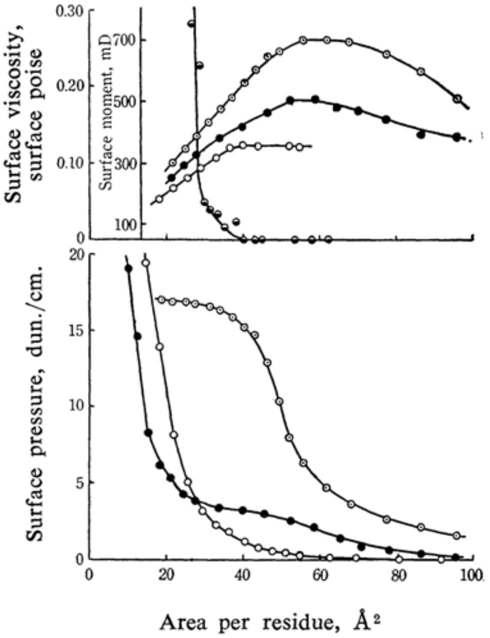

Fig. 3. Surface pressure-area and surface moment-area curves of Nylon 7 on distilled water (○) and on sulfuric acid (3 N, ●; 6 N, ⊙) at 21°C, and its surface viscosity-area curve on distilled water (◒) at 17°C.

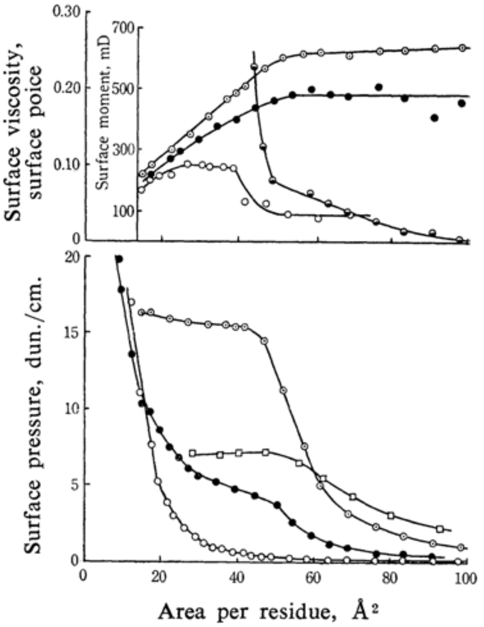

Fig. 5. Surface pressure-area and surface moment-area curves of Nylon 9 on distilled water (○) and on sulfuric acid (3 N, ●; 6 N, ⊙) at 24°C, and its surface viscosity-area curve on distilled water (◒) at 24°C and interfacial pressure-area curves at the petroleum ether/distilled water interface (□) 18°C.

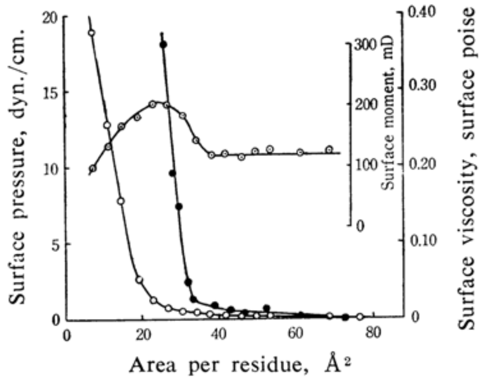

Fig. 6. Surface pressure-area (○), surface moment-area (⊙) and surface viscosity-area (●) curves of Nylon 10 on distilled water at 21°C.

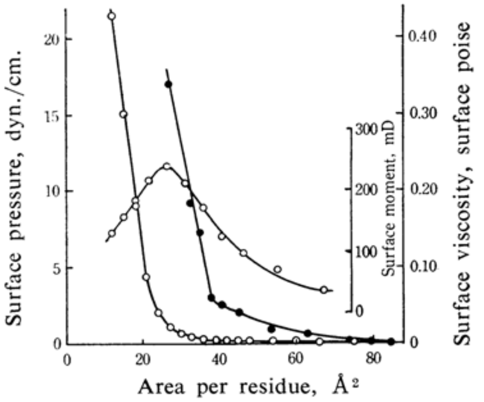

Fig. 7. Surface pressure-area (○), surface moment-area (⊙) and surface viscosity-area (●) curves of Nylon 11 on distilled water at 21°C.

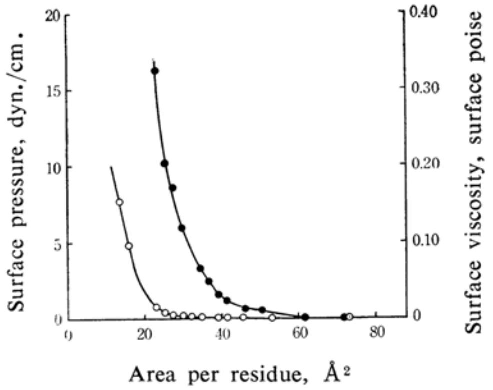

Fig. 8. Surface pressure-area (○), surface viscosity-area (●) curves of Nylon 12 on distilled water at 17.5°C.

The films of Nylons 8 to 12 were of the condensed type on distilled water, and their areas per residue were quite small. Trifluoroacetic acid is one of the strongest hydrogen bond-breaking agents. The film of Nylon 9 spread from a solution in this solvent gave a Π-A curve on distilled water (not shown in Fig. 5) completely identical with that spread from a solution in formic acid on the same subsolution (shown in Fig. 5). Further, the Π-A curve of this nylon spread from a solution in formic acid on 40% ammonium sulfate (not shown in the figure) was nearly identical with that on distilled water, and the change in the initial spreading areas of Nylons 8 to 12 did not affect practically the Π-A relations on distilled water. Judging from these facts, the poor spreadiag of Nylons 8 to 12 seems to be the result of neither the presence of an insoluble fraction in the spreading solution nor the dissolution of polymers in the aqueous phase.

Constant values of surface moments were not obtained with the films of Nylons 8 to 12 on distilled water. The surface moments increased with the compression of the films and they reached the maxima. The surface moment of Nylon 12 was not reproducible. The maximum value, however, was lower than that of Nylon 11.

On the 3 N and 6 N sulfuric acid subsolutions, a remarkable expansion of films and an increase in the surface moment were found with Nylons 6 to 9. The stronger the acidity, the greater the effect.

The Π-A, μ-A and η_s-A curves of polynonamethylene urea on distilled water are shown in Fig. 9. This polymer also gave a condensed film.

The film characteristics of Nylons 6 to 12 and polyurea are summarized in Table I, where A_δ is the area per residue at the minimum compressibility of the film; $A_{\Pi\to 0}$,

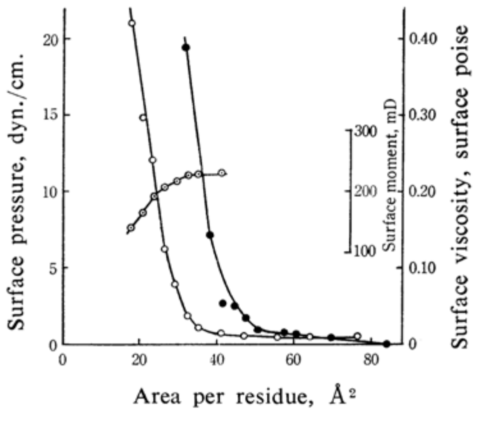

Fig. 9. Surface pressure-area (○), surface moment-area (⊙) and surface viscosity-area (●) curves of polynonamethylene urea on distilled water at 20°C.

TABLE I. FILM CHARACTERISTICS AND CALCULATED CLOSE-PACKED AREAS OF NYLONS 6 TO 12 AND POLYNONAMETHYLENE UREA

Polymer	Subphase	A_δ Å^2/ residue	$A_{\pi\to 0}$ Å^2/ residue	A_μ Å^2/ residue	μ Dm	A_η Å^2/ residue	Calculated close-packed area Å^2/residue
Nylon 6	DW	14.4	20.0	37	180 (c)	82	$\frac{17.24}{2}\times\frac{9.56}{2}=41.2$
	3 N H_2SO_4				400 (at 51 Å^2/res.)		
	6 N H_2SO_4				445 (at 46 Å^2/res.)		
Nylon 7	DW	22.0	27.0	40	355 (c)	40	9.85×4.9×sin 77° =47.0
	3 N H_2SO_4			52	502 (m)		
	6 N H_2SO_4			56	700 (m)		
Nylon 8	DW	17.6	19.0	25	198 (m)	87	1.23×9×4.77=52.8
	3 N H_2SO_4			54	420 (m)		
	6 N H_2SO_4				600 (at 52 Å^2/res.)		
Nylon 9	DW	19.2	22.8	26	252 (m)	104	1.23×10×4.77=58.7
	3 N H_2SO_4			54	480 (c)		
	6 N H_2SO_4				615 (at 56 Å^2/res.)		
Nylon 10	DW	18.0	20.0	25	205 (m)	72	1.23×11×4.77=64.5
Nylon 11	DW	21.5	23.0	26	240 (m)	85	14.9×4.9×sin 77° =71.1
Nylon 12	DW	18.0	20.0			61	1.23×13×4.77=76.3
Polynonamethylene urea	DW	27.2	30.0	32	255 (c)	84	1.23×12×4.77=70.4

DW: Distilled water.

the area per residue where the straight portion of Π-A curve is extraporated to $\Pi=0$; A_μ, the area per residue where the surface moment begins to decrease; $\mu(m)$ and $\mu(c)$, the maximum and the constant values of the surface moment respectively, and A_η, the area per residue where the surface viscosity is first detected.

For the sake of comparison with the observed limiting areas per residue, namely, the values of A_δ or $A_{\Pi\to 0}$, the close-packed areas for α- or β-forms of Nylons 6 to 12 were calculated from the unit cell dimensions of their crystals as estimated from X-ray diffraction data. The results are shown in Table I, where the distance between chain atoms of Nylons 6 to 12, and polyurea, with the exception of Nylons 6,[17] 7[18] and 11[18] (for which the X-ray diffraction data are available), is assumed to be 1.23 Å for fully extended chains, judging from the distance between chain atoms of Nylon 6$\left(\frac{17.24^{17)}}{2\times 7}=1.231\text{ Å}\right)$, Nylon 7$\left(\frac{9.35^{18)}}{8}=1.231\text{ Å}\right)$, Nylon 11$\left(\frac{14.9^{18)}}{12}=1.24\text{ Å}\right)$, and Nylon 66$\left(\frac{17.2^{19)}}{14}=1.23\text{ Å}\right)$. The distance between neighboring chains is assumed to be 4.9× sin 77° = 4.77 Å on the the basis of those of Nylons 7,[18] 11[18] and 66.[19] These values are also used for the calculation of close-packed areas of Nylon 3, Nylon 4 and polynonamethylene urea.

Discussion

Nylon 3.—Nylon 3 gives a film of the condensed type on 40% ammonium sulfate. Its A_δ and $A_{\Pi\to 0}$ values are 8.2 Å^2 per residue and 9.0 Å^2 per residue respectively. These values are much smaller than the calculated close-packed area for a fully extended chain (23.5 Å^2 per residue). It has been found[20,21] that polyglycine cannot be spread under any conditions because glycyl residues are particularly strongly hydrogen-bonded because of the absence of side chains. As Nylon 3 also lacks side chains, and as the chain repeat distance is rather short, the hydrogen bonds would be very

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[17] D. R. Holmes, C. W. Bunn and D. J. Smith, *J. Polymer Sci.*, **17**, 159 (1955).

[18] W. P. Slichter, ibid., **36**, 259 (1959).

[19] C. W. Bunn and E. V. Garner, *Proc. Roy. Soc.*, **A189**, 39 (1947).

[20] J. T. Davies, *Trans. Faraday Soc.*, **49**, 949 (1953).

[21] T. Yamashita and T. Isemura, This Bulletin, **35**, 929 (1962).

strong, as in the case of polyglycine. This might be the cause of the poor spreading and the condensation of the Nylon 3 film.

Nylons 4, 5 and 6. — In contrast with the condensed film of Nylon 3, the films of Nylons 4, 5 and 6 are of the expanded type on a 40% ammonium sulfate subsolution. Nylon 6 also gives an expanded film on distilled water. Kink points are found in the Π-A curves of Nylons 4 and 6.

The kink point of the Π-A curve of Nylon 6 appears at 37.5 Å^2 per residue on distilled water and at 40 Å^2 per residue on 40% ammonium sulfate. The π-A curve of this nylon on distilled water has already been reported by some workers.[10,12,14] The present result is in general agreement with theirs. The kink point was also found by them at nearly the same area as in the present study. The surface moment of Nylon 6 on distilled water begins to decrease at 37 Å^2 per residue, which is in good agreement with the area at kink point and the A_μ values reported by Hotta[12] and Inokuchi.[14] The surface viscosity of this nylon begins to rise at 82 Å per residue. This value is much smaller than that found by Isemura and Hamaguchi.[11] The larger area found by them seems to be caused by the interaction between polymer and solvent because they used a mixture of cresol and benzene as a spreading solvent. They, however, found a characteristic area at 80 Å^2 per residue, which agrees well with the A_η value in the present study.

It has been found[16] that poly-α-aminoisobutyric acid gives a monolayer of the expanded type. A striking difference, however, exists in the surface viscosities between the films of this polymer and Nylon 6. The surface viscosity of the former first appears at an area (12 Å^2 per residue) considerably smaller than its limiting area (A_δ = 20.0 Å^2 per residue), where the surface pressure is remarkably high, while that of the latter is detected at a larger area (82 Å^2 per residue) than the calculated close-packed area for fully-extended chains (41.2 Å^2 per residue), where the surface pressure is sufficiently low. In the film of the former, interaction between polymer chains is scarce because it is difficult for the hydrogen bonds between keto and imino groups to be formed because of the steric hindrance of α-disubstituted methyl groups. On the other hand, the much larger A_η value of Nylon 6 suggests that the interaction between polymer chains is quite strong. Near the A_μ, the polymer molecules at the surface begin to come in contact with each other to construct a loose network structure because of the hydrogen bonding between amide groups.

The areas at the kink points of the Π-A curves of Nylon 4 (ca. 28 Å^2 per residue on 40% ammonium sulfate) and Nylon 6 (37.5 Å^2 per residue on distilled water, 40 Å^2 per residue on 40% ammonium sulfate) agree fairly well with the calculated close-packed areas (29.3 Å^2 per residue for Nylon 4, 41.2 Å^2 per residue for Nylon 6). All the chain atoms of these polymers would lie on the water surface above the areas at the kink points. No kink point is found in the Π-A curve of Nylon 5. This polymer, however, might be spread in a state similar to those of Nylon 4 and Nylon 6, because the film is remarkably expanded. The polymer chains of Nylons 4, 5 and 6 are quite flexible at the surface because of the effect of the increased CH_2 groups. This might be the cause of the expansion of the films of these nylons.

There is some difference among the films of Nylons 4, 5 and 6 on the 40% ammonium sulfate subsolution, although they are all of the expanded type. Below the surface pressure of ca. 4 dyn./cm., the film of Nylon 5 is most expanded, as Fig. 1 shows. The surface pressure of Nylon 6 is much lower than that of Nylon 5 over the same area. The pressure reduction in the film of Nylon 6 is probably caused by the increased van der Waals attractive force between hydrocarbon groups. The van der Waals force plays an important role in the films of Nylons 7 to 12, as will be discussed in later sections.

Nylon 7.—The film of Nylon 7 on distilled water is of the expanded type. The film, however, is somewhat more condensed than that of Nylon 6 on the same subsolution. This is the result of the increased van der Waals attractive force between hydrocarbon groups. The film of Nylon 7 might be in an intermediate state between the expanded films obtained with Nylons 4, 5 and 6, and the condensed films obtained with Nylons 8 to 12.

The surface moment of this nylon is remarkably high, the highest among those of the nylons investigated. The A_μ value is 40 Å^2 per residue, which agrees with the A_η value. The surface moments of polyamides of the nylon type are mainly contributed by the C=O dipoles, as in the case of poly-α-amino acid with only hydrocarbon side chains.[22] The more vertical the C=O dipoles become in relation to the interface, the closer the surface moment will approach the maximum value of 360 mD.[23] The observed surface moment of Nylon 7 ($\mu(c)$ = 355 mD) is in good agreement with this value. Therefore, the C=O groups

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[22] J. T. Davies, *Biochim. Biophys. Acta*, **11**, 165 (1953).

[23] A. E. Alexander and J. H. Schulman, *Proc. Roy. Soc.* **A161**, 115 (1937).

of Nylon 7 might orientate rather vertically to the interface. In such an orientation of C=O groups, the hydrogen bonds can hardly be formed between amide linkages in the area above A_μ. It has already been found for the monolayers of poly-α-aminoisobutyric acid[16] on distilled water, and poly-DL-alanine[16] and poly-DL-leucine[20] on the acid subsolutions that the surface moment increases if the number of hydrogen bonds is reduced.

The surface viscosities of polymers primarily depend on the number of hydrogen bonds between different groups, as has been found with prolyl polypeptides,[24] poly-α-aminoisobutyric acid[16] and sarcosyl polypeptides.[16,25] The agreement of A_μ with A_η supports the view that hardly any hydrogen bonds can be formed between amide groups in the area larger than A_μ because the orientation of C=O groups is unfavorable for the hydrogen bond formation.

Differences in Film Properties between Odd- and Even-Numbered Nylons. — It has been found[1-5] that the melting points of nylons with odd and even numbers of CH_2 groups are quite different from each other. Some film characteristics of Nylons 6 to 12 on distilled water are shown in Fig. 10 against the number of carbon atoms per monomer unit. There exist striking differences between odd- and even-numbered nylons as in melting points. It should be noted here that the amino acid nylons with even numbers of CH_2 groups are described by odd numbers, and vice versa.

It is striking that the the Π-A curves of Nylons 8, 10 and 12 are nearly identical. Accordingly, the limiting areas, namely, the A_δ's or $A_{\Pi\to0}$'s of these nylons, are all nearly the same per residue, is as is shown in Table I. Nylon 9 and Nylon 11 also have nearly the same limiting areas per residue, although the areas are somewhat larger than those of even-numbered nylons. The maximum values of the surface moments of odd-numbered nylons are somewhat high compared with those of even-numbered nylons. The surface moment of Nylon 12 is not shown in Table I and Fig. 10 because of its poor reporducibility. Its maximum value, however, is lower than that of Nylon 11. The surface viscosities of odd-numbered nylons, with the exception of Nylon 7, begin to rise at larger areas than those of even-numbered nylons. These differences in film properties between odd- and even-numbered nylons will be discussed in the succeeding sections.

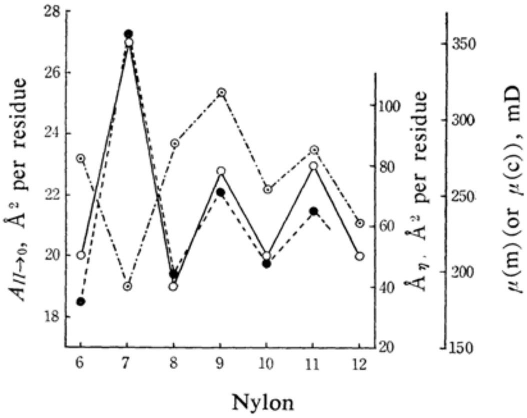

Fig. 10. Plots of $A_{\Pi\to0}$(○), A_η(⊙) and $\mu(m)$ (or $\mu(c)$) (●) values against the number of nylon.

The Condensation of the Films of Nylons 8 to 12.—In contrast with the condensed films of Nylon 9 at the air/water interface, the film of this polymer at the oil/water interface is highly expanded, as Fig. 5 shows. It has been found that the films of poly-α-amino acids[9,21] and some vinyl polymers[12] are expanded much more at the oil/water interface than at the air/water interface because of the release of van der Waals force between hydrocarbon groups. Accordingly, it seems that the van der Waals attractive force between hydrocarbon groups plays an important role in the remarkable condensation of these nylon films.

The hydrogen bonds between keto and imino groups of amide linkages is also responsible for the condensation of these films, because the film properties of nylons are remarkably affected on a concentrated sulfuric acid subsolution, thus causing the breaking of hydrogen bonds, and the surface viscosities of Nylons 8 to 12 are manifested at quite large areas, as will be discussed in the succeeding sections.

Thus, it seems that both the van der Waals force between hydrocarbon chains and the hydrogen bonds between keto and imino groups of amide linkages are responsible for the remarkable condensation of the films of Nylons 8 to 12 on distilled water.

Holt and Went[26] reported that, with the compression of the films, the hydrophilic amide groups of polyamide films remain at the surface, but that the polymethylene groups are, presumably, pushed out of the surface. The consistency of the observed small limiting areas per residue among even- or odd-numberd nylons suggests that the hydrocarbon chains leave the surface with the compression of the

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24) S. Ikeda and T. Isemura, This Bulletin, **32**, 659 (1959).

25) Part II of this series: T. Yamashita and T. Isemura, This Bulletin, **38** (1965).

26) P. F. Holt and C. W. Went, *Proc. 3rd Int. Cong. Surface Activity*, **2**, 49 (1960).

films and are folded because of the van der Waals attractive force between them. The hydrogen bonding between amide groups might also play a significant role in the stability of such folded structures. Similar folded structures have been found by Isemura and Hotta[27] for adsorbed films of long-chain dibasic acids. If the hydrocarbon groups leave the surface and are folded, the contributions of monomer units of even- or odd-numbered nylons to the limiting areas should be identical with each other. The somewhat larger areas of odd-numbered nylons than those of even-numbered ones might be due to the difference in the packings of folded chains. The difference in maximum surface moments between the two series of nylons is caused by the same factor.

The maximum values of the surface moments of Nylons 8 to 11 are between 200 and 250 mD. These values are somewhat higher than the constant values of the surface moments of poly-α-amino acids, which are in the range from 150 mD to 180 mD on neutral subsolutions;[16,20-22,25] It has been found that[16], for poly-α-aminoisobutyric acid on distilled water and poly-DL-alanine on a acid subsolution (3 N sulfuric acids), the constant values of surface moments are increased to ca. 210 mD because the hydrogen bonds between keto and imino groups are scarce in these films. Probably, the higher $\mu(m)$ values of Nylons 8 to 11 on distilled water than the $\mu(c)$ values of poly-α-amino acids on the neutral subsolutions is not caused by a small number of hydrogen bonds, but by a somewhat different orientation of C=O and H-N groups from that in poly-α-amino acids, accompanied by a remarkable change in the orientation of these groups during the folding process, because the presence of hydrogen bonds is proved, as has been and will be described in this paper.

The Surface Viscosities of Nylons 8 to 12.—The surface viscosities of Nylons 8 to 12 begin to rise at much larger areas than their limiting areas, as Table I shows. Near the area at A_η, the polymer chains of these nylons begin to come in contact with each other to form a network structure because of the interaction between keto and imino groups of different amide groups.

The A_η values of odd-numbered nylons are much larger than those of even-numbered nylons. This fact suggests that hydrogen bond formation between amide groups takes place more easily in the former nylons than in the latter nylons. It also seems that above the areas at A_η almost all the chain atoms of these nylons lie on the water surface, because the A_η values are larger than the calculated close-packed areas with the exception of Nylon 12, and with a higher compression of films the hydrocarbon groups would leave the surface and be folded.

It has been reported by several authors,[1,2,4,18] concerning the crystals of nylons, that in the fully-extended chains of nylons with even numbers of CH_2 groups, all the amide groups on one chain lie directly next to the amide groups on neighboring chains, so that the maximum degree of coupling is attained, while in the fully-extended chains of nylons with odd numbers of CH_2 groups, the parallel array leads to a close coupling of only half of the polar groups, although the antiparallel array allows the coupling of all the amide groups. The difference in A_η values in the present study between odd- and even-numbered nylons might be related to the difference in the probabilities of hydrogen bond formation between the two series of nylons. Although the deficient hydrogen-bond formation in crystals of nylons with odd numbers of CH_2 groups was denied by Kinoshita,[5,6] it might have some effect on the areas where surface viscosities appear because these areas are closely related to the initial stage of hydrogen-bond formation.

Polynonamethylene Urea.—The monolayer of this polymer has been investigated in order to prove the role of the van der Waals attractive force between hydrocarbon groups for the stabilization of a folded structure of polyamides of the nylon type. Polyurea, like Nylons 8 to 12, was found to give a condensed film on distilled water, although the limiting area is somewhat larger than those for nylons. The constant value of the surface moment was obtained over a very narrow range; it was 225 mD, which is of the same order of magnitude as the $\mu(m)$ values of Nylons 8 to 12. From these facts, this polyurea is considered to assume a folded structure near the limiting area, like even-numbered nylons, because this polymer contains 9 CH_2 groups per residue. Somewhat larger values of A_δ (27.2 Å^2 per residue), $A_{\Pi\to 0}$ (30 Å^2 per residue) and A_μ (32 Å per residue) are probably due to the contribution from another N-H group in the residue. At 84 Å^2 per residue, the surface viscosity was first detected. Near this area, the polymer molecules begin to come in contact and to interact with each other. With further compression, the hydrocarbon groups will be folded. The folded structure might be maintained both by the van der Waals attractive force and by hydrogen bonds.

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[27] T. Isemura and H. Hotta, This Bulletin, 23, 193 (1950).

The Effect of Sulfuric Acid on the Monolayers of Nylons.—As has been shown in Figs. 2—5 and in Table I, on concentrated sulfuric acid, a remarkable expansion of films and increase in surface moments are found with Nylons 6 to 9. The stronger the acidity, the greater the effect. It has been reported in Part I of this series[16] that, on concentrated sulfuric acid, poly-DL-alanine film is expanded much more than on distilled water, and that its surface moment increases from 150 mD ($\mu(c)$) to 215 mD ($\mu(c)$) and 256 mD (at 26 Å^2 per residue) on the 3 N and 6 N solutions respectively. These changes are due to the breaking of hydrogen bonds between ketoimino groups. The poly-α-aminoisobutyric acid monolayer,[16] in which hardly any hydrogen bonds are formed because of the steric hindrance of α-disubstituted methyl groups, also gives a high surface moment ($\mu(c)$, 214 mD) compared with poly-DL-alanine on distilled water. The surface moments of nylons on acid subsolutions are much higher than that of poly-DL-alanine on the acid, that of poly-α-aminoisobutyric acid on distilled water,[16] and the maximum contribution from the C=O group (360 mD).[23] Accordingly, a different cause must be sought for the remarkably high moments besides the breaking of hydrogen bonds. Such a high surface moment has also been found by Hibberd and Alexander[15] for Nylon 610 (1038 mD per two amide groups at the maximum on 3 N sulfuric acid).

The adsorption of hydrochloric acid by nylon fibers has been studied as a function of the acid concentration.[28] In the concentrated hydrochloric acid solutions, nylon absorbs more acid than would be expected from the number of amino groups present. This excess absorption has been attributed to the interaction of the acid with amide linkages. The amide groups of nylon behave as a base in an acid medium. The interaction of hydrochloric acid with –CONH– groups of nylon has been proved by Larose[29,30] from measurements of the infrared and near-infrared spectra of nylon treated with hydrochloric acid.

The addition of acid to the –CONH– group of nylon can be represented by:

$$\text{-CONH-} + \text{H}^+ \rightarrow \text{-CONH}^+\text{-}.$$

Thus, nylon film would be charged positively. As a result of the protonation to amide linkage, the surface moments are increased remarkably.

The folded structures of higher nylons on distilled water are unfolded on the subsolutions of sulfuric acid because the hydrogen bonds which would stabilize the folded structure are broken. The repulsion between charged groups causes a remarkable expansion of the film. The polymer chains are in a rather flexible state.

Summary

The surface films of a series of nylons prepared from ω-aminocarboxylic acids and with 2 to 11 CH_2 groups per monomer unit (Nylons 3 to 12) have been studied at the air/water interface in order to investigate the correlation of the film properties with the numbers of CH_2 groups. The film of Nylon 9 at the oil/water interface and that of polynonamethylene urea at the air/water interface have also been studied.

The film of Nylon 3 on the 40% ammonium sulfate subsolution was of the condensed type and the area occupied per residue was quite small, probably because of the especially strong hydrogen bonds between amide groups. On the other hand, the films of Nylons 4, 5 and 6 on 40% ammonium sulfate and that of Nylon 6 on distilled water were of the expanded type. These polymers might be spread in rather flexible states because of the effect of the increased number of CH_2 groups.

Nylons 8 to 12 and polyurea gave condensed films on distilled water, their limiting areas per residue being much smaller than the areas calculated for the fully extended chains. The condensation of the films might be primarily caused by the increased van der Waals attractive force between hydrocarbon groups, as has been proved by the remarkable expansion of Nylon 9 film at the petroleum ether/distilled water interface. The small limiting areas of these polymer films have been interpreted by assuming that the hydrocarbon chains are folded near these areas. Nylon 7 was found to give an intermediate film between expanded films, such as Nylons 4 to 6, and condensed films, such as Nylons 8 to 12.

Interesting differences in the film properties of odd- and even-numbered nylons have been found with Nylons 8 to 12. Odd-numbered nylons occupied somewhat larger areas per residue than even-numbered nylons, and the maximum surface moments of the formers were higher than those of the latters. This is the result of the difference in shapes of the folded chains between the two series of nylons.

The surface viscosities of Nylons 8 to 12, with the exception of the last, were first detected at larger areas than the close-packed areas calculated for the fully-extended

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[28] F. T. Wall and A. Beresniewicz, *J. Phys. Chem.*, **60**, 692 (1956).

[29] P. Larose, *Can. J. Chem.*, **35**, 1239 (1957).

[30] P. Larose, ibid., **39**, 2394 (1961).

chains. The areas found for even-numbered nylons were much smaller than those for odd-numbered ones. This may be attributed to the difference in modes of hydrogen bond formation between amide groups.

A remarkable effect of the concentrated sulfuric acid subsolution on the film properties of Nylons 6 to 9 has been found, and interpreted as being due to the protonation to the amide linkages.

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