# *Surface Chemistry of High Polymers. III. Some Relationships between the Monolayer of Non-electrolytic Linear Polymers*

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In the previous papers[1,2] we have studied the monolayer of copolymers of vinyl acetate and stearate at the air/water and oil/water interfaces to obtain information for the general behaviour of the non-electrolytic linear polymer. As a result of studying afterwards some other similar linear polymers, we found some interesting relationships between them. Therefore, we shall describe these results as the addendum to the previous studies.

## Experimental

We measured the surface pressure by the hanging plate method, and the surface potential by the vibrating electrode method at the air/water interface at room temperature (10~15°C.), and the interfacial pressure by the ring method at the petroleum ether (b.p. 100~140°C.)/water interface at about 20°C. The apparatus and procedure were almost the same as in the previous papers[1,2], but the specific caution for each individual polymer and some modifications for the rise in accuracy were taken.

Polymethyl methacrylate was spread on distilled water from benzene solution, polyacrylonitrile from dimethylformamide solution, and amilan (ε-aminocaproic acid polymer) from the solution in a mixture of concentrated sulphuric acid (10%), isopropyl alcohol (50%), and water (40%), respectively. Polymethacrylic acid was spread on ca. 0.01 N HCl from aqueous 20% pyridine solution.

**Materials**—Polymethyl methacrylate was reprecipitated with methyl alcohol from the benzene solution of a commercial product. Polyacrylonitrile was kindly supplied by Prof. M. Imoto in Osaka City University. Amilan was the same as in the preceding paper.[2] Polymethacrylic acid was prepared by the usual method by Mr. S. Otsuka in our institute. Although the degrees of polymerization of these samples were not properly measured, it is sure that they are far greater than the corresponding value in Table II to be discussed below.

## Results and Discussion

### Polymethyl Methacrylate and Undissociated Polymethacrylic Acid at the Air/water Interface:

The observed surface pressure-area curves and surface potential-area curves of polymethyl methacrylate and undissociated polymethacrylic acid are shown in Figs. 1 and 2, respectively, in which the result of polymethyl

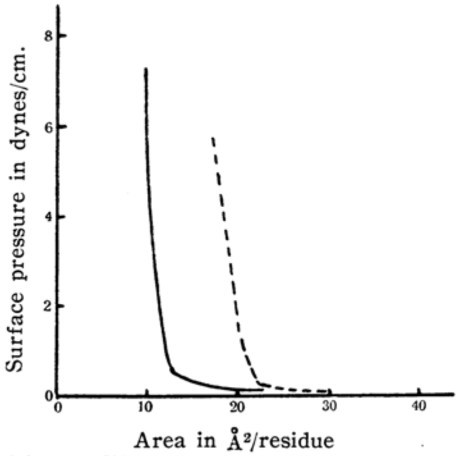

Fig. 1. The surface pressure-area curves of polymethyl methacrylate (- - - -) and polymethacrylic acid on *p*H 1.6 (——) at the air/water interface

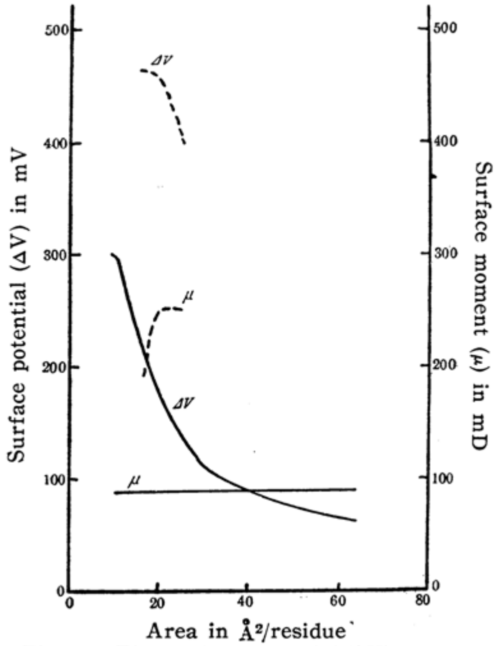

Fig. 2. The surface potential (ΔV) or surface moment (μ)-area curves of polymethyl methacrylate (- - - -) and polymethacrylic acid on *p*H 1.6 (——) at the air/water interface

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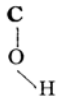
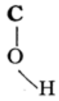
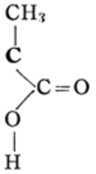
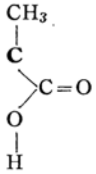
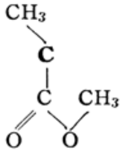
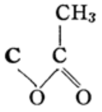
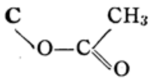
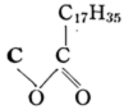
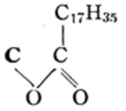
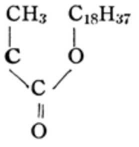
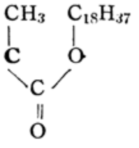
[1] T. Isemura, H. Hotta and T. Miwa, This Bulletin, **26**, 380 (1953).

[2] H. Hotta, ibid, **26**, 386 (1953).

methacrylate is shown by a dotted line and is almost identical with that reported by other investigators.[3,4] Especially, the reliable surface potential could not be obtained up to 25 Å$^2$/residue, similar to Crisp.[4] On the contrary, the curve for polymethacrylic acid could be obtained reliably at the wider range. The latter film might be sufficiently undissociated under the present condition as mentioned in the following paper.[5]

When we summarize the present results as well as the previous one,[1] the surface moment of some linear polymer films, calculated by the usual method as mentioned in the previous paper, was various in spite of their similar formulas as shown in Table I, in which the surface moment at the both areas of 25 Å$^2$ and 50 Å$^2$ per residue is listed in mD unit in parenthesis in the corresponding column and the carbon atom in the main chain is shown by **C**. The surface moment of polyvinyl alcohol in this table, which is quoted from the result of Crisp,[4] is corrected for residual acetate groups. On the other hand, the bond moment of C=O and C−O in vacuo is 2.5 and 0.86 D. unit, respectively.[6] Therefore, on considering these magnitudes and the orientation of these polar bonds at the air/water interface, their most plausible models consistent with the observed value of their surface moment as shown in Table I are proposed to make clear the differences between them. The area, from which the reliable surface moment could be obtained, is given in Table I. The physical meaning of these areas will be given in the next section.

TABLE I THE SURFACE MOMENT OF POLYMERS AT THE AIR/WATER INTERFACE

| Polymer | Surface moment (in mD unit) and the corresponding model per residue | | | | Area, from which the reliable surface moment can be obtained (in $\AA_2$ unit) | Literature |
|---|---|---|---|---|---|---|
| | at 25 Å$^2$ | | at 50 Å$^2$ | | | |
| Polyvinyl alcohol |  | (40) |  | (40) | 50 | (4) |
| Undissociated polymethacrylic acid |  | (90) |  | (90) | 65 | The present |
| Polymethyl methacrylate |  | (250) | — | — | 25 | The present |
| Polyvinyl acetate |  | (260) |  | (340) | 70 | (1) |
| Polyvinyl stearate |  | (260) |  | (260) | 55 | (1) |
| Polyoctadecyl methacrylate |  | (460) |  | (460) | 45 | (4) |

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[3] H. G. Saraswat and A. Kalyanasundaren, *J. Polymer Sci.*, **7**, 325 (1951).

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

[5] T. Isemura, H. Hotta and S. Otsuka, to be published in This Bulletin.

[6] C. P. Smyth, *J. Am. Chem. Soc.*, **60**, 183 (1938).

It is understood, first of all, by the low bond moment of C–O in comparison with that of C=O, that polyvinyl alcohol has the lowest surface moment in these polymers. Next, the various surface moments among polymethyl methacrylate, polyvinyl acetate and stearate and polyoctadecyl methacrylate in spite of their similar formula, can be understood by the present models in this table, that is, these models are designed so as to have a higher surface moment with the increase of the inclination of C=O bond, and a similar surface moment for a similar inclination. The remarkably low surface moment of undissociated polymethacrylic acid may be attributed to the horizontal orientation of C=O bond. The difference of the limiting area between polymethyl methacrylate and polymethacrylic acid shown in Fig. 1 is also understood in the light of these models. The difference of the surface moments of polyvinyl acetate at 25 Å² and at 50 Å² per residue is understood by using these models in consideration of their high flexibility as discussed thoroughly in the preceding papers.[1,2] The difference of the surface moment of polyvinyl stearate from that of polyoctadecyl methacrylate was already discussed in the previous paper.[1]

### Polymethyl Methacrylate and Polyacrylonitrile at the Petroleum Ether/water Interface:

The observed interfacial pressure-area curves of polymethyl methacrylate and polyacrylonitrile at the petroleum ether/water interface are shown in Fig. 3. We had to wait 25 minutes for the perfect spreading of them prior to every successive measurement.

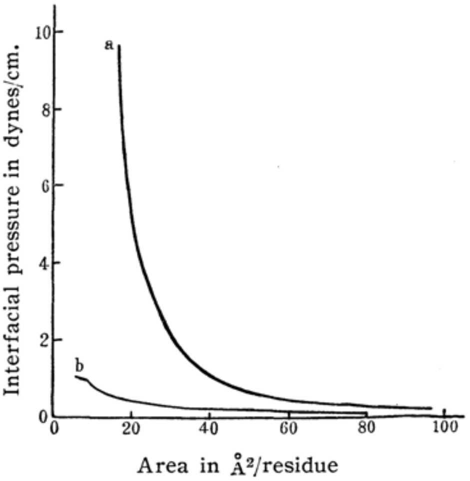

Fig. 3. The interfacial pressure-area curves at the petroleum ether/water interface: curve a, polymethyl methacrylate and curve b, polyacrylonitrile

Polyacrylonitrile could not be spread at the air/water interface. We calculated their statistical kinetic unit at the oil/water interface by inserting the results into the equation of

$$\pi A = \frac{kT}{n}\left(1+\frac{b}{A}\right) \qquad (1)$$

and extrapolating to infinite area as shown in Fig. 4, where $\pi$ is the interfacial pressure, $A$ the area per residue, $n$ the degree of of polymerization of this unit, and $b$ an interaction constant. The explanation of this equation is described in detail in the preceding paper.[2] The results shown in Table II, give the various values for the number of atoms in the main chain of this statistical kinetic unit, $n_{\text{atom}}$. In this table, the datum for polyvinyl acetate reported in the previous paper is also shown for comparison. The value for amilan was measured over again as mentioned in the next section.

TABLE II

THE STATISTICAL KINETIC UNIT OF LINEAR POLYMER AT THE OIL/WATER INTERFACE

| Polymer | $(n)_{A=\infty}$ in equation (1) | $n_{\text{atom}}$ (The number of atoms in the main chain of this unit) |
|---|---|---|
| Polyvinyl acetate | 19 | 37 |
| Polymethyl methacrylate | 23.5 | 47 |
| Polyacrylonitrile | 36.5 | 73 |
| Amilan (ε-aminocaproic acid polymer) | 6.9 | 48 |

In these polymers as shown in Table II, polyvinyl acetate gives the film of perfectly expanded type and the same surface pressure-area curve at the air/water and oil/water interfaces as mentioned in the preceding paper. Amilan and polymethyl methacrylate give the film of condensed type at the air/water interface, and the expanded film at the oil/water interface as shown in figures. Polyacrylonitrile can not be spread at the air/water interface, but gives the film of considerably condensed type even at the oil/water interface as shown in Fig. 3, and this film gives the negative slope in Fig. 4. Both the latter polymers take 25 minutes for perfect spreading at the oil/water interface, but the former both polymers can spread within 10 minutes. On the other hand, the areas, from which the reliable surface moment begins to be obtained, are shown in Table I.

When we compare the relationship between the type of film, the time needed for perfect spreading, the largest area per residue for giving the reliable surface moment and the value of $n_{\text{atom}}$, we notice that they are not independent of each other. That is, each quantity serves as a measure showing how the molecules are flexible (or rigid), or, how much they are interacted mutually, accompanying the effect of linkage as discussed in detail in the preceding paper.(2) With increasing flexibility, the surface pressure and the largest area for reliable surface moment increase, and the time for perfect spreading and the value of $n_{\text{atom}}$ decrease. The more quantitative interpretation of $n_{\text{atom}}$ will be given in the following paper.

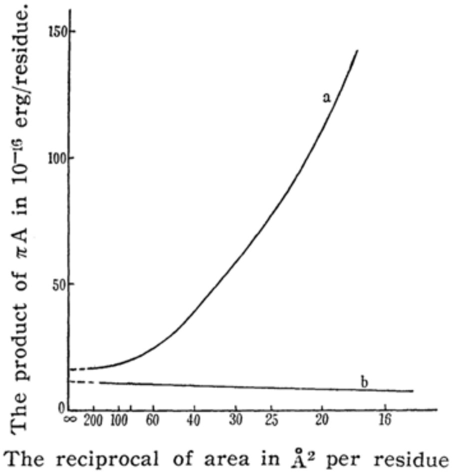

Fig. 4. The $\pi A - \frac{1}{A}$ curves of polymer at the petroleum ether/water interface: curve a, polymethyl methacrylate and curve b, polyacrylonitrile

The slightly negative slope of polyacrylonitrile in Fig. 4 seems to be due not to imperfect spreading, but to the increasing degree of condensation of film, on comparing the kink point in Fig. 3 with that of polymethacrylic acid in Fig. 1, which has no side chain in the surface as polyacrylonitrile. It is also consistent with the fact that polyacrylonitrile is insoluble except in dimethylformamide.

### Surface Chemical Effect of Hydrolysis of Amilan-in Dilute Surphuric Acid:

When we studied the monolayer of amilan in the preceding paper,(2) it was spread from the solution in 10% surphuric acid. Since it is well-known that the molecular weight of amilan decreases in surphuric acid by hydrolysis,(7) we examined this effect on its film by the above-mentioned methods. These results are shown in Figs. 5, 6 and 7 as the function of surface area per monomer.

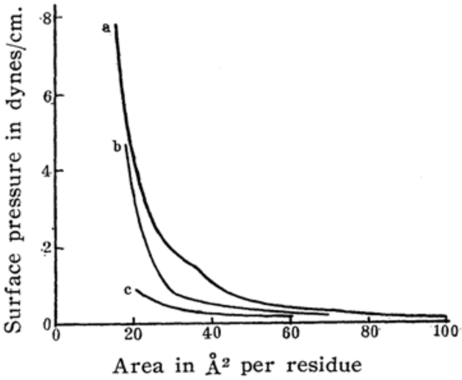

Fig. 5. The surface pressure-area curves of amilan at the air/water interface: curve a, within a first month, curve b, after 4 months and curve c after 8 months

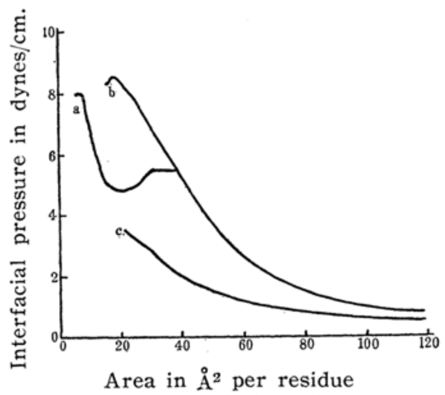

Fig. 6. The interfacial pressure-area curves of amilan at the petroleum ether/water interface: curve a, within a first month, curve b, after 4 months and curve c, after 8 months

The surface pressure-area curves at the air/water interface suffered no change within a month after preparing the solution and the curves were quite identical with the curve shown in Fig. 5. It has a kink point at 35 Å², below the area of which the pressure changed considerably with time. However, the curves obtained by using the solutions stood over four or eight months after preparation (curves b and c in Fig. 5), were lower in surface pressure than curve a, and there was no kink point in the former curves. On the other hand, the curves at the petroleum ether/water interface were also essentially unchanged within the first month. However, the kink point disappeared gradually with the age of the solution as shown in Fig. 6. Nevertheless the values of $n_{\text{atom}}$ in

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7) K. Hoshino and M. Watanabe, *J. Chem. Soc. Japan*, **70**, 170 (1949); *J. Am. Chem. Soc.*, **73**, 4816 (1951).

Table II were not affected even after 8 months.

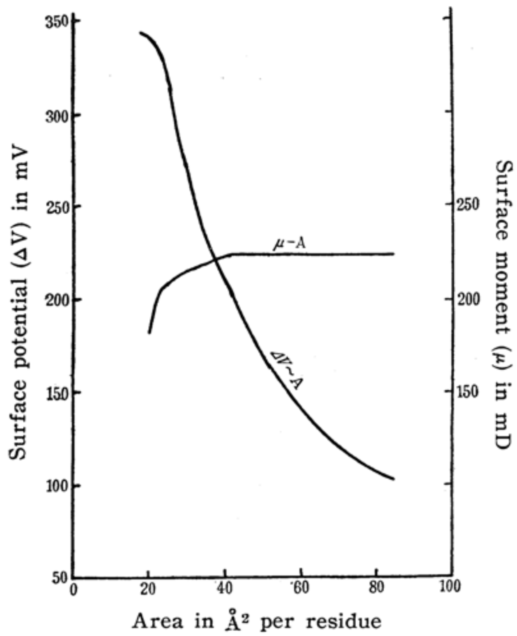

Fig. 7. The surface potential or surface moment of amilan at the air/water interface

The corresponding surface potential-area curves were almost unchanged even after 4 months as noticed from Fig. 7, and the reliable surface potential could be obtained from about 80 Å$^2$. However, the saturated tendency of surface potential at the area smaller than 23Å$^2$, became gradually indistinct with the age of the solution. On the other hand, the surface viscosity measured by the oscillating disk method is rapidly raised from about 80 Å$^2$.[8]

From these facts, it is concluded that there are two characteristic points, namely, 35 Å$^2$ and 80 Å$^2$ in amilan film at the air/water interface. The former corresponds perhaps to the intrachain transition as mentioned in the preceding paper. On the other hand, as the film is compressed, the polymer molecules at the surface begin to contact each other, and to construct a loose but homogeneous network structure. Such an area, where the homogeneous interchain structure is completed, corresponds to the latter characteristic point, from which the surface potential can be obtained reproducibly and the surface viscosity is rapidly raised.

Although it has been mentioned above that the effect of hydrolysis was not so remarkable during the first month, the observed values in the repeated experiments were fluctuated from the standard curve with the lapse of time, and the transition points became gradually indistinct with age. The surface pressure was fairly lower even in curve a in Fig. 5 than that reported by Isemura and Hamaguchi.[9] It might be due to either the strong hydrolysis in the initial period or to the difference of solvent and concentration at spreading.

## Summary

1. The various surface moments of like polymers can be understood in the light of the models in Table I, which are designed by considering the orientation of $C=O$ bond at the interface.
2. The flexibility of polymer film can be measured not only by surface pressure but also by the time for perfect spreading, the largest area from which the reliable surface moment can be obtained, or the number of atoms in the main chain of the statistical kinetic unit.
3. The effect of hydrolysis of a milan solution by sulphuric acid on its film was examined.

In conclusion, the author expresses his hearty thanks to Prof. T. Isemura for his kind guidance throughout the present work, and to Prof. M. Imoto of Osaka City University and Mr. S. Otsuka in our institute who kindly supplied the present samples. The cost of this research has been partly defrayed from the grant for Scientific Research Encouragement from the Ministry of Education given to Prof. T. Isemura, to whom the author's thanks are due.

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[8] T. Isemura and K. Hamaguchi, to be published in This Bulletin.

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