Surface Chemistry of High Polymers. I. Non-electrolytic Flexible Linear Polymers at Air/Water Interface

Toshizo ISEMURA, Hiroshi HOTTA and Teruo MIWA.

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Introduction

It is a well-known fact that some natural polymers such as protein[1,2,3] and some synthetic polymers such as polymethacrylates[4,5] and polypeptides[6] spread as a monolayer at both air/water and oil/water interfaces. It is expected that the molecular structure, the kinds as well as the amounts of polar groups and also the size of non-polar or polar side chains will affect the behaviour of surface films of the polymers. Studies on the surface films of polymers of known structure will give some information for the elucidation of the behaviour of important natural polymers as proteins. The shape of the polymer molecules at the interface is probably different under the influence of the surface force from that in the bulk phase. The shape of the polymer molecule at the interface in relation to its molecular structure and the kinetic unit of the molecule at the interface are problems to be investigated. It is also very interesting to investigate the mechanical properties of the surface film of the polymer in relation to the molecular structure and to compare with the properties in the bulk system.

At the outset, the linear non-electrolytic polymers, namely, polyvinyl acetate, polyvinyl stearate and some copolymers of different compositions between vinyl acetate and vinyl stearate were studied at the air/water interface by measuring surface pressure-area and surface potential-area relations. In the present paper, the results obtained and some considerations on the results will be presented.

Experimental

Materials—Polyvinyl acetate was prepared from vinyl acetate by emulsion polymerization using ammonium persulphate as the catalyst. In most of the experiments, polyvinyl acetate was used in that condition if no special indication was given. However, reacetylated polyvinyl acetate was sometimes used for the elimination of the effects of branched polymers. Polyvinyl acetate was hydrolysed to polyvinyl alcohol, which was again tranformed into polyvinyl acetate by acetylation using acetic anhydride. Polyvinyl stearate and the copolymers of vinyl acetate and vinyl stearate were prepared by Prof. S. Murahashi and Mr. S. Otsuka in our institute. The composition of these copolymers are shown in Table I. These polymers were spread on distilled water from benzene solution.

Methods and Apparatus—Surface pressure was measured by three methods. In low pressure region less than ca. 3 dynes/cm, it was measured by film balance of Adam type of double torque system using torsion wires of phosphor-brone of 0.12 mm. and 0.07 mm. in diameters. The molecular weight determination was carried out by this method. In high pressure region, surface pressure was measured by either hanging plate or ring method.

In the experiments with the film balance of Adam type or hanging plate type, the polymer was spread on the substrate in a rectangular tray $16 \times 60 \times 1.2$ cm. by an automatic microvolume pipette so as to occupy more than 100 A^2. per monomer. The surface concentration was changed by compression with a paraffined glass barrier in the usual manner. On the other hand, the surface concentration was changed with successive addition by injection through a micrometer syringe

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[1] I. Langmuir and V. J. Schaefer, *Chem. Rev.*, **24**, 181 (1939).

[2] H.B. Bull, "Advances in Protein Chemistry," **3**, 95(1947).

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

[4] D.J. Crisp, *J. Colloid Sci.*, **1**, 49 (1946).

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

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

Table 1

Composition of Copolymers Used in the Present Experiment

Sample	Initial mole percentage of vinyl stearate at synthesis	Mole percentage of vinyl stearate in copolymer	Mean molecular weight per vinyl unit
A (Acetate)	0	0	86
E	10	—	—
B	20	20.0	130
C	50	58.6	217
D	80	82.6	272
S (Stearate)	100	100	310

when the surface pressure was measured by the ring method using a glass cylinder. The details of the technique of successive injection method will be given in the next paper in relation to the investigation of the oil/water interface.

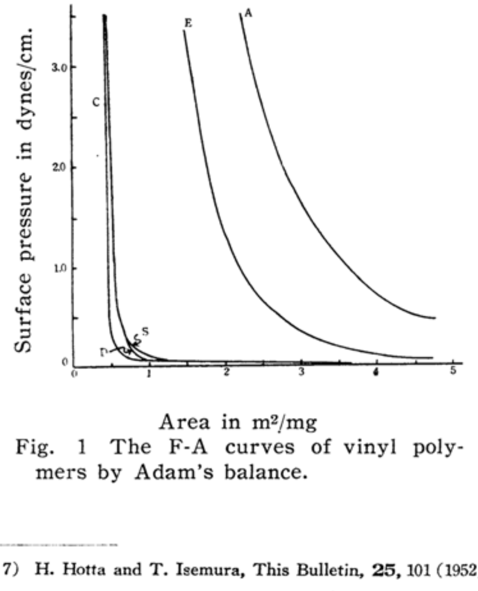
Surface potential was measured by vibrating electrode method. The apparatus used was essentially the same as used in our previous investigation, however, with some necessary modification to adapt it for the present purpose.[7]

Results

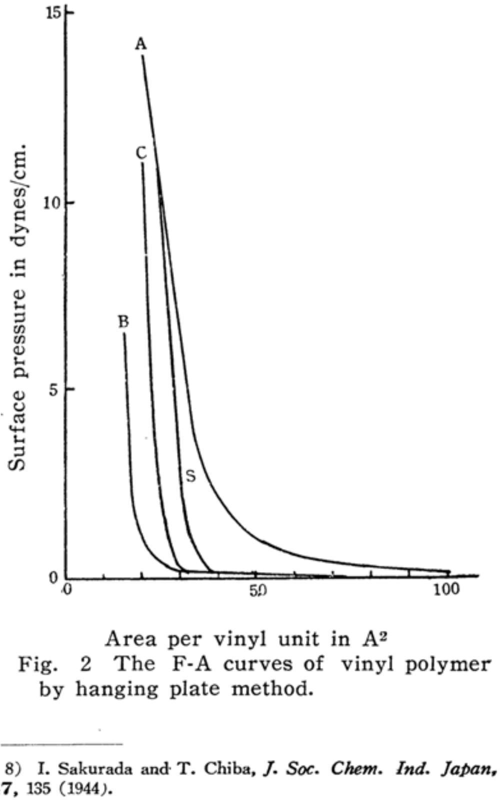
The experimental results obtained are shown in Figs. 1~7, in which the notations of curves are common in Table I, respectively. Polyvinyl acetate gave a film of expanded type as shown in Figs. 1 and 2. The degree of polymerization gave no appreciable effect on the F—A curve. Polyvinyl acetate prepared by reacetylation showed no essential difference on F—A curve from that of the original polyvinyl acetate. The FA—F curve of the polyvinyl acetate was not strictly linear but slightly convex upward, and was almost independent of the degree of polymerization. If the linear relation between FA and F is assumed, the molecular weight of the spread polymers may be determined from Fig. 3 as in the case of proteins. The molecular weights thus determined were 7,000~10,000 as shown in Table II, and were extraordinarily less than that determined from its intrinsic viscosity $[\eta]$, using the relation[8]

$$\overline{P}=(\text{Antilog}\frac{[\eta]}{0.28}-1)\times 2000\ , \ \ldots\ldots(1)$$

and not to be compared with it.



Area in m²/mg
Fig. 1 The F-A curves of vinyl polymers by Adam's balance.



Area per vinyl unit in A²
Fig. 2 The F-A curves of vinyl polymer by hanging plate method.

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[7] H. Hotta and T. Isemura, This Bulletin, **25**, 101 (1952).

[8] I. Sakurada and T. Chiba, *J. Soc. Chem. Ind. Japan*, **47**, 135 (1944).

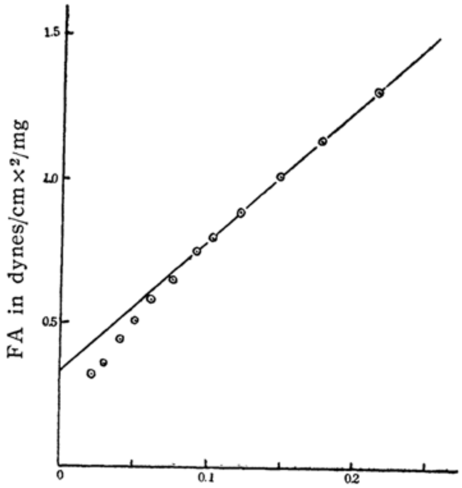

Fig. 3 The FA-F curve of polyvinyl acetate (sample "c")

On the other hand, FA—F curve for polyvinyl stearate was linear as shown in Fig. 4. Its molecular weight from this curve was 41,000.

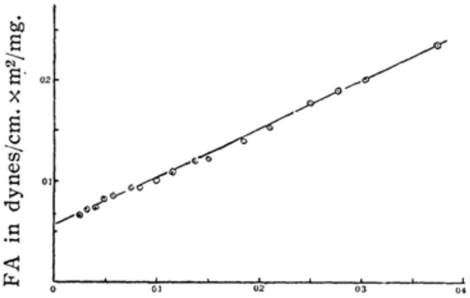

Fig. 4 The FA-F curve of polyvinyl stearate

Table 2

Molecular Weight of Vinyl Polymers Used in the Present Experiment

Polymer	Sample	Molecular weight from		
		pressure Surface	Viscosity	Osmotic pressure
Polyvinyl acetate	a	10,000	58,820	—
	b	7,020	69,350	—
	c	7,920	110,500	—
	d	9,240	—	110,000±5,000
Polyvinyl stearate	e	41,000	—	70,000

Sample "a" was prepared by reacetylation of sample "b".

In the experiments shown in Fig. 1, the reading of surface pressure was taken 30 seconds after every compression. In the experiments shown in Fig. 2, the rate of compression was 1 A².$/$monomer/2 minutes. The surface pressure of the polyvinyl acetate was not changed with time after every compression up to 7 dynes/cm. However, with the copolymers and polyvinyl stearate, the pressure was changed considerably with time after every compression, when the surface pressure exceeds 0.2 dynes/cm. The limiting area per monomer determined by extrapolation of linear portion of F—A curve to zero pressure was about 55 A². for polyvinyl acetate. Polyvinyl stearate gave a coherent film and its limiting area per monomer was 30 A². The condensation of film by the introduction of vinyl stearate in the copolymer was considerable. The limiting area per monomer was less than that of polyvinyl stearate, if the copolymer contains more than 20% of vinyl stearate. In Fig. 5 are shown the F—A curves obtained by successive injection method.

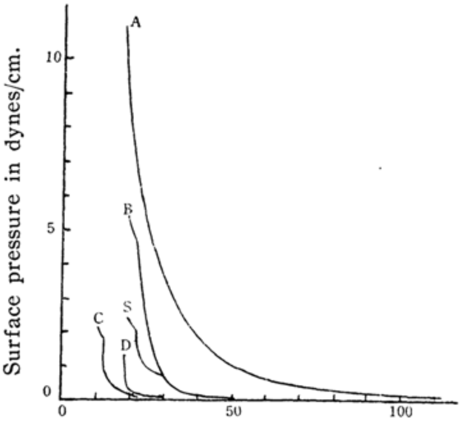

Fig. 5 The F-A curves of vinyl polymers by successive injection method

The surface potential and surface moment are shown in Figs. 6 and 7. The surface moment per monomer, μ, was calculated from Helmholtz's formula,

$$\mu=\frac{\Delta V}{4\pi n} \quad \text{.................}(2)$$

using the average ground molecular weight in Table I, where ΔV is the surface potential, and n the number of monomer unit per unit area. Fig. 6 is the results obtained by compression method, and Fig. 7 that by successive injection method. When the experiments were carried out by the compression method, the surface potential was fluctuated markedly until the surface area per monomer decreased to far less than 100 A². The reliable values were obtained only in the region shown in Fig. 6. In spite of the fairly good reproducibility of F—A curves, the reproducibility of the surface potential curves was not satisfactory and was dependent on the composition of the polymers. Its reproducibility of polyvinyl acetate was the highest, and next highest was that of polyvinyl stearate. The order of reproducibility was as follows,

$$A>S>D>C>B.$$

The results shown in Figs. 5 and 7 were those obtained by the successive injection method as already mentioned. The area is the apparent area calculated from the injected amount, simply by dividing the total area by the injected mass. In this case, the fluctuation of surface potential, as observed in the compression method, was hardly observed at all.

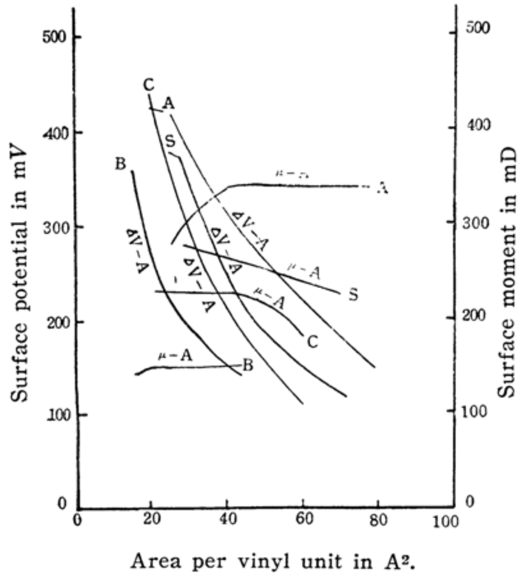

Fig. 6 The ΔV-A and μ-A curves of vinyl polymers by successive injection method.

The fluctuation of surface potential, observed in the region of low surface concentration in the case of the compression technique, is probably caused of inhomogeneity of the surface layer. The compression of the film by the barrier from one side often causes accidental condensation and accompanies the heterogeneity of the film. Consequently, the change does not always follow the course of equilibrium. The instability of the film of copolymers with small content of vinyl stearate may be attributed to this accidental change appearing at the various parts of the film.

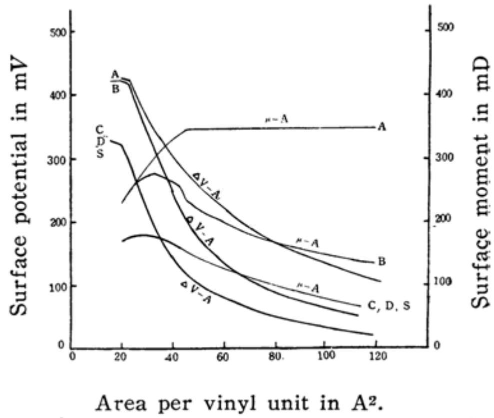

Fig. 7 The ΔV-A and μ-A curves of vinyl polymers by compression method.

Discussion

Polyvinyl acetate gave the film of expanded type with free space between the chains. If stearate groups are substituted for the acetate groups in polyvinyl acetate, the mutual cohesion between side chains is considerably increased and the film tends to condense. With polyvinyl stearate film, the specific area is usually less than with polyvinyl acetate, and the expanded region at low surface pressure is lacking. The limiting area per monomer of the film of copolymer with moderate content of vinyl stearate was found often to be even less than that of polymer containing only vinyl stearate as shown in Fig. 2. It may happen that the attraction of hydrocarbon chains of stearate compresses the vinyl acetate groups from the interface into aqueous phase.

From simple thermodynamic calculations, it may be found that the inclination of the FA—F curve, i.e. α, in

$$\mathrm{FA}=\beta+\alpha\mathrm{F} \quad \text{.................}(3)$$

corresponds to the co-area of the molecule.[9] From these considerations, it was concluded that the co-area of polyvinyl acetate is 60 A^2./monomer and that for polyvinyl stearate is 25 A^2./monomer. The limiting areas per monomer for polyvinyl acetate and stearate were 55 A^2. and 30 A^2. respectively as mentioned above. These areas are nearly equal to the co-areas estimated from equation (3). The co-area of the polyvinyl stearate thus estimated is plausible if we recognize that the stearate side chains project out of the water surface and that they are closely packed. However, the co-area of the polyvinyl acetate is much larger than that estimated from molecular model, even if the side chains are lying flat. In the film of polymer with short side chains such as polyvinyl acetate, the motion of the segment of chain is so violent that the co-area is nearly twice the area per monomer estimated from the molecular model owing to the elimination of the restriction of molecular motion by the attraction between side chains. According to the analogous calculation with b in the van der Waals' equation, the co-area must be twice of actual area in two dimensional gas.

From the surface moment data, it can be concluded that the orientation of the side chains of polymer are not affected very much by the compression up to the area of 40 A^2./monomer with polyvinyl acetate and to 28 A^2./monomer with polyvinyl stearate film. Below 40 A^2./monomer the surface moment of polyvinyl acetate decreased gradually. These results are readily explained using the model of polymer film assumed by us just mentioned above. With the film of polyvinyl acetate the area, where the surface moment begins to decrease, corresponds to the area where the film begins to change to coherent type from an expanded film. For the polyvinyl acetate film is of expanded type having free space between chains, and the film changes to a coherent film if it is compressed to less than 40 A^2./monomer, where the change of μ begins to appear. On the other hand, with the film of polyvinyl stearate, stearate groups in a polymer molecule project out of water phase and mutually interact so that the side chains have definite orientation even if the surface concentration is low. The μ begins to change when the film is compressed after the coherent film is completely formed. The areas where μ deviates from a constant value, are also parallel to the co-areas of the polymers mentioned above.

Surface potential of polyvinyl acetate reached the saturated value of 420 mV below 25 A^2./monomer, and that of polyvinyl stearate 370 mV below 28 A^2./monomer, respectively. Surface potential-area curves change the inclination at these areas. At these points a part of ester groups was probably removed from the interface, and the film was partially collapsed. From F—A curves, however no indication of discontinuity was detected at these points.

The surface potential curves of the copolymers were continuous far below these areas. It seems probable that the attraction between the hydrocarbon chains of stearate groups suppresses the vinyl acetate groups from the interface into aqueous phase if surface pressure is sufficiently high. Consequently the film was gradually changed into so-called "overfilm". The relatively remarkable change of surface pressure with time after every compression and the small values of μ, found with these copolymer films, agree with our views mentioned above.

The F—A curve of polyvinyl stearate showed almost the same feature as that of polyoctadecyl methacrylate studied by Crisp,[5] suggesting that structures and shapes of molecules in both films are almost identical. The limiting area found by Crisp for polyoctadecyl methacrylate was 30.5 A^2./monomer, while that for polyvinyl stearate found by us was 30.0 A^2. However, the surface moment of polyvinyl stearate per monomer was 278 mD, whereas that of polyoctadecyl methacrylate per monomer found by Crisp was 460 mD. This far smaller surface moment of polyvinyl stearate than that of polyoctadecyl methacrylate is readily understood in the light of molecular orientation at the interface. The principal difference between them may be governed by the orientation of C=0 bond as shown in Fig. 8.

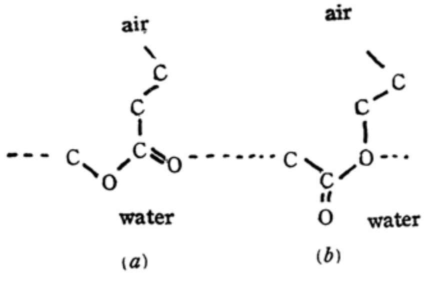

Fig. 8 Orientation of side chain at the air/water interface;
(a) polyvinyl stearate;
(b) polyoctadecyl methacrylate.

As mentioned above, the results obtained

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[9] H.B. Bull, *J. Biochem.*, **185**, 27 (1950).

by two different methods of changing surface concentration of the polymer did not agree with each other, especially, in high surface concentration. Unlike the compression method, the spread molecules would not be in the unusually forced orientation, if the surface concentration of the film was changed by successive injection method. However, the injected polymer would not be spread at the interface as a monolayer when the surface concentration exceeded a certain value and the film was closely packed by its own spreading pressure. For these reasons, the area per monomer shown in Figs. 5 and 7 are only apparent. On the other hand, the orientation of the molecule spread by this method may be more natural than that studied by the compression method. Recently, B.D. Powell and A.E. Alexander[10] studied the monolayers of copolymers between vinylpyridine and styrene with the two different methods. They found smaller surface potential by the successive injection method than by the compression method. They attributed this to the "edge effect." In our opinion, however, this phenomenon may be closely connected with the difference of the facility of spreading of the film by these two methods. Surface potential-area curves with polyvinyl acetate film obtained by these two methods coincided with each other. The F—A curves, however, did not coincide with each other, especially, in high surface concentration. The F—A curve obtained by the compression method was almost consistent with that obtained at the oil/water interface, on which we will report in the following paper. These results are all comprehended in the light of the molecular flexibility which will be discussed also in the following paper in some details. The discrepancy between the F—A curves observed by two different methods may be caused by the fact that the surface concentration near the ring can not only reach an equilibrium value within relatively short time interval after every injection, but also can reach it after formation of a fresh surface by raising the ring. That may be the essential difficulty inherent in the study of surface film of polymer by means of the ring method.

Summary

The surface films of some linear non-electrolytic polymers such as polyvinyl acetate, polyvinyl stearate and copolymers between them were studied at the air/water interface by measuring surface pressure, and surface potential in relation to the area occupied per monomer.

The surface concentration was changed by two different methods, namely by the compression with barrier and by the successive addition by injection with micrometer syringe.

Polyvinyl acetate gave the film of expanded type and was hardly affected by its degree of polymerization. Polyvinyl stearate gave the film of coherent type and its F—A curve resembled that of polyoctadecyl methacrylate. The copolymer with moderate content of vinyl stearate showed the smaller limiting area per monomer than polymers of its constituents.

The results were discussed in relation to the molecular model and to the methods adopted to change the surface concentration.

In conclusion, the authors express their hearty thanks to Prof. S. Murahashi and Mr. S. Otsuka in our institute who kindly supplied copolymers to them. The cost of this research has been partly defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the authors' thanks are due.

The Institute of Scientific and
Industrial Research, Osaka
University, Sakai, Osaka

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[10] B.D. Powell and A.E. Alexander, *J. Colloid Sci.* **7**, 432 (1952).