Surface Chemistry of High Polymers. II. Non-electrolytic Flexible Linear Polymers at Oil/Water Interface

By Hiroshi HOTTA

(Received march 2, 1953)

While the properties and structures of insoluble films at the air/water interface are now known in some detail,[1] there are few investigations at the oil/water interface in spite of emphasis on its necessity.[2,3,4,5,6] In the present investigation the films of amilan and copolymers of vinyl acetate and stearate were studied to obtain informations on the general behaviour of non-electrolytic flexible linear polymer at oil/water interface. The experimental method was similar in principle to that developed by Alexander *et al.*[2,3,4,5]

From the present investigation, it has been concluded that these linear polymer molecules behave freely at the oil/water interface, for the lateral cohesion between them becomes much weaker than at the air/water interface and their non-polar side chains are removed from the interface into the oil phase. The length of the segment of kinetic unit for these polymers at the interface was estimated by adopting the statistical treatment of flexible linear polymer in the bulk solution with some modifications to adapt to the surface film. The results will be given in the following lines in detail.

Since there is the case that the behaviour of monolayer is very different between air water and oil/water interface so far as the side chains are concerned, which was confirmed by our investigation, we cannot always infer the phenomena in the living body from the result of the film at the air/water interface alone. Therefore we need by all means the experiment at the oil/water interface also for this purpose.

Experimental Method

Materials—Amilan (ε-aminocaproic acid polymer) was purified by dissolving in formic acid and reprecipitated by water, and spread from the solution dissolved in a mixture of concentrated sulphuric acid (10 %), isopropyl alcohol (40 %) and water (50 %). Copolymers of vinyl acetate and stearate were spread from benzene solution. Although these copolymers were the same as those which had been used previously at the air/water interface,[7] their compositions, calculated from the analysis, were shown again in Table I for convenience.

Petroleum ether (b.p. = 100~140°C. and *d.* = 0.75) used as the oil phase was purified repeatedly with various agents from commercial Gum Gasoline. The distilled water was used as the water phase.

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
B	20	20.0	130
C	50	58.6	217
D	80	82.6	272
S (Stearate)	100	100	310

Spreading Technique—The oil/water interface was formed and cleaned by the technique developed by Alexander and Teorell.[2] The dimensions of the trough were also almost the same as theirs. The samples were spread from the micrometer-syringe at the interface by adding *ca.* 3×10^{13}

---

[1] N. K. Adam, "The Physics and Chemistry of Surfaces" (1938).

[2] A. E. Alexander and T. Teorell, *Trans. Faraday Soc.*, **35**, 727 (1939).

[3] A. E. Alexander, "Surface Chemistry" (1949), p. 123.

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

[5] A.J.G. Allen and A.E. Alexander, ibid., **46**, 316 (1950).

[6] D. F. Cheesman, *Biochem. J.*, **50**, 667 (1952).

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

monomer units per square centimetre at a time.

Interfacial Tension—The interfacial tension was determined by Alexander's ring method,³⁾ in which the displacement of a ring at maximum pull is read by an optical lever. The ring used was made of platinum-10% iridium wire of a diameter of 0.30 mm, and the diameter of the ring was 2.70 cm. It was cleaned and leveled by Harkins and Jordan's method.⁸⁾ The correction factor of the ring (1.022) was determined experimentally at zero pressure.

On the investigation of insoluble monolayer, one of the sources of error inherent in the ring method is owing to the appreciable extension of interface at both the inside and outside of the ring at breaking point. This effect has been studied experimentally by Alexander and Teorell.²⁾ Nevertheless, it seemed that the effect was slight except at the higher pressure in our present case, as a result of comparison with the other method.

All measurements were made ten minutes after the successive injection of spreading solution, and at room temperature (20~23°C.) without any special temperature regulation, but the variation of temperature during the course of measurement to obtained a single curve never exceeded one degree. The effect of the interval of successive measurements with amilan film was examined, and its result is shown in Fig. 1.

Results and Discussion

Amilan—At first, it was examined how long we must wait before measurement for perfect spreading of the sample after every injection of the polymer solution at the interface. After some preliminary experiments, it was found that ten minutes after every injection was sufficient for perfect spreading. The results are shown in Fig. 1, together with the result at the air/water interface, measured by this method of successive injection used at the oil/water interface.

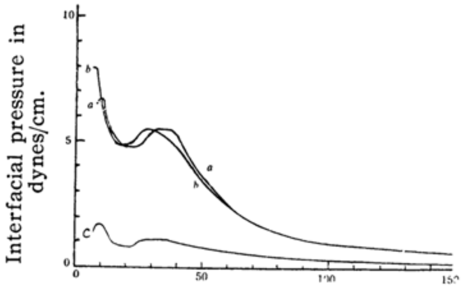

Fig. 1 The π-A curves of amilan: curve a— at petroleum ether/water interface, measured at 10 mins. after injection; curve b— at petroleum ether/water interface, measured at 3 mins. after injection; curve c— at air/water interface, measured at 10 mins. after injection.

In the π-A curve of amilan, it was found the characteristic transition region of van der Waals' type as shown in Fig. 1. Since the appearance of the transition point may be dependent on the strength and distribution of hydrophilic groups, namely, the activation energy transition as discussed later in detail, these conditions may be just optimum for the appearance of such a "superpressed" phenomenon in this case. The first kink point, 38A²., and the again rapidly rising point 18A²., are comprehended in terms of the transition between the flat-in-interface and bent-into-oil phase forms of the hydrocarbon part of the main chain. These dimensions are consistent with that computed by Stuart's model.

Copolymers—The π-A curves of vinyl copolymers at the oil/water interface are shown in Fig. 2., in which the notations of curves are common in Table 1, respectively. The ordinate of the figure is interfacial pressure in dynes/cm., and the abscissa is surface area in A². per vinyl unit, calculated from the mean molecular weight in Table 1.

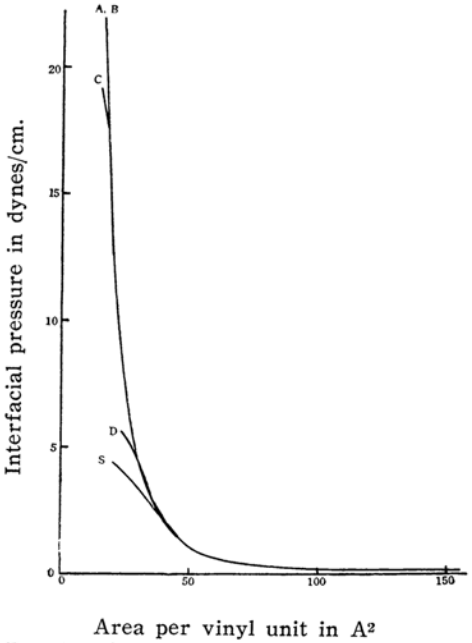

Fig. 2 The π-A curves of vinyl polymers at the petroleum ether/water interface.

All these π-A curves of vinyl copolymers fall on the same curve of polyvinyl acetate independent of the content of stearate in con

---

8) E. D. Harkins and H. F. Jordan, *J. Am. Chem. Soc.*, **52**, 1751 (1930).

trast with much dependence on its content at the air/water interface.[7] However, these curves deviate from this common curve at any wider area with increasing content of vinyl stearate. The areas of deviation are shown in Table 2. These areas can be calculated as the product of the area of vinyl stearate (37 A^2.) and its mole fraction in copolymer as shown in the Table. From these facts it may be concluded that all copolymers at the oil/water interface behave freely, liberating from lateral cohesion, so that the side chains are removed into oil phase. This deviation area of polyvinyl stearate is fairly greater than the limiting area at the air/water interface, obtained in the preceding paper.[7] It is because the free micro-Brownian motion of stearyl group in the oil phase does not permit the neighbouring stearyl group to approach. Upon consideration of the fact that the deviation from the common curve is due to the mutual hindrance of such a micro-Brownian motion, we can understand the proportionality of this area in the films of high stearate content, and the disappearance of this point in those of low stearate content, as shown in the Table 2.

Table 2

Kink Point from Common Curve

Sample	Kink point in A^2. obs.	Kink point in A^2. calc.
A	not found	—
B	not found	—
C	22.6	21.7
D	30.7	30.6
S	37	37

General Behaviour of Film of Non-electrolytic Flexible Linear Polymer

Now, the general behaviour of these non-electrolytic flexible linear polymers at the oil/water interface will be discussed in the light of the above-mentioned facts. On the consideration of such a general problem, we must distinguish between the effect of backbone and that of side chain. Since the latter has remarkably steric factors, the problem becomes very complicated. At the oil/water interface, however, the former effect is essential before the surface concentration is fairly high, for the side chains may be dissolved in the oil phase as mentioned above.

In general the interfacial pressure, π, is expressed thermodynamically as

$$\begin{aligned}\pi &= \gamma_i - \gamma_f \\ &= -\left(\frac{\partial F_i}{\partial A_f}\right)_{T,\Sigma} \\ &= -\left(\frac{\partial H_i}{\partial A_f}\right)_{T,\Sigma} + T\left(\frac{\partial S_i}{\partial A_f}\right)_{T,\Sigma} \qquad \ldots\ldots(1) \\ &\qquad (\Sigma = A_i + A_f),\end{aligned}$$

where A, F, H, S and γ are surface area, free energy, heat content, entropy and interfacial tension, respectively, and the subscripts f and i refer to film and interface, respectively. In equation (1), the first term corresponds to adhesion of polymer to substrate and cohesion between chains, and the second term to kinetics of chain. Therefore, the stronger the hydrophility of the polar group in the chain is, the more distinct the transition point may be. Conversely, when the hydrophility is weak, this polar group cannot already restrain the behaviour of the chain, and the transition point becomes indistinct. It is evidently shown in both our polymers. Sorption of water on these polymers was studied as a measure of extent of hydrophility by some investigators.[9,10] Their results are shown in Table 3 for comparison with the present inference.

Table 3

Moles of Polar Groups per 100 gr. of Polymer Compared with Moles of Water Vapour Sorption at 0.9 Relative Vapour Pressure

Polmer	Moles of polar group	Moles of water vapour
Polyvinyl acetate	1.16	0.17
Polyglycin-DL-alanine	1.56	1.72

Now, the oil/water interface will be compared with the air/water. The polymer molecule behaves generally freely in the former not only by the dissolution of side chain into oil phase as mentioned above, but also by the liberation from lateral cohesion, because the heat of mutual separation of molecules at the interface is scarcely required in such a present case as "like dissolves like." On the other hand, the molecules at the air/water

---

[9] M. Dole and A. D. McLaren, *J. Am. Chem. Soc.*, **69**, 651 (1947).

[10] B. Katchnan and A. D. McLaren, ibid., **73**, 2125 (1951).

interface seem to be frozen in themselves by cohesion even at relatively low surface concentration. Therefore, the change of free energy in respect to surface area should be far greater in the latter. But, in the case when the molecule is free even in the latter, there would be no difference between both interfaces. Such a fact is also shown in the case of polyvinyl acetate as confirmed by our investigation. On the other hand, amilan shows the difference in spite of having no side chain. It may be due to the strong polarity of its polar group, which is also confirmed by Table III. The discussions in the preceding paper⁷⁾ can be also understood only on the ground of these inferences.

As mentioned above, the linear polymer is flexible at the oil/water interface as in organic solvent, and even if the polymer has side chains, its non-polar side chain is removed into oil phase. Therefore, by neglecting the effect of side chain, we may apply the statistical treatment of flexible linear polymer with some modifications to the surface chemistry of the present polymers at the oil/water interface. That is, the relation between the interfacial pressure. π, and the surface area per monomer unit, A, may be expressed in the form as

$$\pi A = \frac{kT}{n}\left(1+\frac{b}{A}\right) \qquad \cdots\cdots(2)$$

The physical meaning of the coefficients, n and b, in this equation will be mentioned below.

Therefore, when we plot the product of πA against the reciprocal of A as shown in Fig. 3, and extrapolate this curve to infinity of area, the length of segment of long chain molecule can be obtained, that is, n-mer is the kinetic unit of these polymers in the interface. The obtained results are listed in Table IV, in which the number of atoms in each unit chain of both polymers is nearly 50 atoms in consideration of the side chain in vinyl copolymer. We must now again remember the extent of error inherent in the ring method as mentioned above. On the other hand, Flory had estimated from the activation energy of flow in viscosity that there are approximately 32 atoms in each segment of flow of polyesters in organic solvent.¹¹⁾

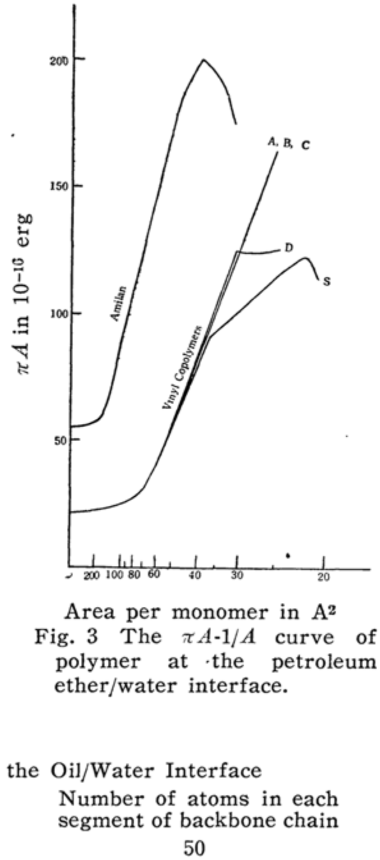

Fig. 3 The πA-$1/A$ curve of polymer at the petroleum ether/water interface.

Table 4

Length of Segment of Linear Polymer at the Oil/Water Interface

Polymer	$(\pi A)_{A=\infty}$	n	Number of atoms in each segment of backbone chain
Amilan	55×10^{-16} erg	7.2	50
Vinyl Copolymer	21×10^{-15}	19	38

The physical meaning of coefficient, b, in the second term of equation (2) in the dilute region may be considered to be analogous to that of bulk solution.¹²⁾

From the curves in Fig. 3, we can readily determine the point, from which the interaction between the chains becomes more predominant, for the kink points appear clearer in these curves. The negative slope appears when some atoms in the backbone chain are removed from interface by either bending or collapsing. The kink points listed in Table II were thus determined. The linear range of the curve corresponds to the range of interaction of the same order. The rapidly rising point in this curve, which may correspond to that of beginning of mutual interaction and of rising of surface viscosity, is

---

11) P. J. Flory, *J. Am. Chem. Soc.*, **62**, 1057 (1940).

12) For example, H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems" (1950), p. 263.

nearly 70 A^2. per vinyl unit for this copolymer, and 150 A^2. per monomer for amilan. On considering an atom unit instead of a monomer unit, these areas are identical on account of the above-mentioned correction of the side chain effect. The π-A curves of both polymers should be also considered on the same universal ground of an atom unit in the interface.

This flexibility phenomenon is observed not only at the oil/water interface. The determination of the molecular weight of high polymers has recently been tried by monolayer method[13,14] among other bulk methods, and it was confirmed by many investigators that the agreement with the molecular weight obtained by other methods is sufficient.[15] On the other hand, it is reported that this method is unsuitable for some polymers such as polyvinyl acetate.[7,16] Especially, it was found in the preceding paper that the molecular weight of polyvinyl acetate obtained by this method is independent of the degree of polymerization, and, as mentioned above, its π-A curves at the air/water and oil/water interface are almost identical. Moreover, its surface potential-area curves at air/water interface, measured by both methods of compression and successive injection, are also entirely identical, as mentioned in the preceding paper.[7] From these phenomena it is clear that we should consider the flexibility of linear polymer also to some extent at the air/water interface. On the other hand, πA-π curve is linear in the case of the rigid molecule such as protein[14] even at the oil/water interface.[5] However, even in the case of protein, it is recently reported that the existence of surface submolecule should be considered in the non-Newtonian region in the experiment of surface viscosity.[17]

In conclusion, the author expresses his hearty thanks to Prof. T. Isemura for his kind guidance throughout the present work, and to Prof. S. Murahashi and Mr S. Otsuka in our institute who kindly supplied copolymers to him. The cost of this research has been partly defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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

---

[13] J. Guastalla, *Compt. rend.*, **208**, 1078 (1939).

[14] For example, H. B. Bull, *J. Biochem.*, **185**, 27 (1952).

[15] For example, M. Abribat and J. Pouradier, *Compt. rend.*, **227**, 1101 (1948).

[16] G. C. Benson and R. L. McIntosh, *J. Colloid Sci.*, **3**, 323 (1948).

[17] M. Joly, "Surface Chemistry" (1949), p. 157.