Surface Chemistry of High Polymers. VI. The Monolayer of Polyethylene Terephthalate and Poly-N-vinyl Pyrrolidone

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(Received August 10, 1954)

Although we studied the monolayer of various linear polymers up to the preceding paper, these polymers consist of chains alone either in the main chain or in the side chain.[1-5] In order to obtain some information in respect to the contribution of the ring group in the side chain as well as in the main chain to the behavior of surface film, we studied the monolayer of polyethylene terephthalate and poly-N-vinyl pyrrolidone by the measurements of interfacial pressure and potential at the air/water and oil/water interfaces. It was found as the results of the present investigation that the ring groups in the main chain make the polymer molecule rigid even at the oil/water interface, while that in the side chain is not essentially different from the chain groups. Further more the study of the hydrolysis of poly-N-vinyl pyrrolidone by the monolayer technique provides a useful inference concerning it.

Experimental

Polyethylene terephthalate was spread from the solution of the mixture of benzene and cresol (1: 1) at the air/water and benzene/water interfaces using a micrometer syringe. The distilled water was used as the water phase.

Poly-N-vinyl pyrrolidone, whose molecular weight is 13,400, was spread from the aqueous solution containing 20% pyridine at the air/water and petroleum ether/water interfaces. The pH of the substrate was adjusted with hydrochloric acid or sodium hydroxide as in the previous papers[4,5] to investigate the effect of hydrolysis.

Both materials were kindly supplied from Prof. S. Murahashi of our Institute.

The interfacial pressures at the air/water and oil/water interfaces were measured by the hanging plate method[1] and ring method[2], respectively, as in the previous papers. The interfacial potential at both interfaces was measured by the vibrating electrode method.[1,5] The detailed descriptions of spreading technique and of measurements were already given in the previous papers. The only different technique adopted in the present investigation is that the area at the air/water interface was changed by the successive injection method for poly-N-vinyl pyrrolidone, which was already reported in the first paper.[1] The surface moment-area curve, shown by dotted lines and denoted with prime in Figs. 1 and 4, was calculated from observed surface potential using the Helmholtz's formula as usual.[1]

Results and Discussion

A. Polyethylene Terephthalate.—The surface potential and moment at the air/water interface (15°C) plotted against area per residue are shown in Fig. 1. The reliable value of surface potential was obtained at a smaller area than 115 Å^2 per residue, and became

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

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

[3] H. Hotta, ibid., 27, 80 (1954).

[4] T. Isemura, H. Hotta and S. Otsuka, ibid., 27, 93 (1954).

[5] H. Hotta, ibid. 27, 412 (1954).

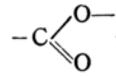
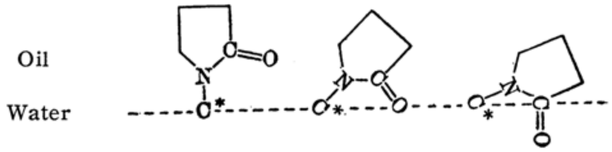
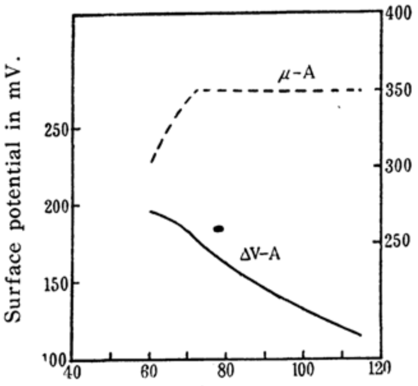
constant at 62 A² per residue. The corresponding surface moment was kept constant to 350 mD. up to about 72 Å² per residue Therefore, the surface moment of 175 mD. might be attributed to a single group of  $-\mathrm{C}(=\mathrm{O})\mathrm{O}-$ in this constant range. When we consider the magnitude and direction of each polar bond in this group,[6] the model proposed in Fig. 2 is entirely consistent with Table I in the third paper[3] showing the relationship between the value of surface moment and the inclination of C=O bond at the surface. Thus, this table would be useful for estimating the inclination of C=O bond at the surface for an unknown polymer.

TABLE I

THE STATE OF POLY-N-VINYL PYRROLIDONE AT THE OIL/WATER INTERFACE

Model			
Most compact area estimated from Fig. 4 in Å² per residue	18	25	35
Surface moment in mD.	210	290	350



Area in Å² per residue

Fig. 1. The surface potential (ΔV) (or moment (μ))-area curve of polyethylene terephthalate at the air/water interface.

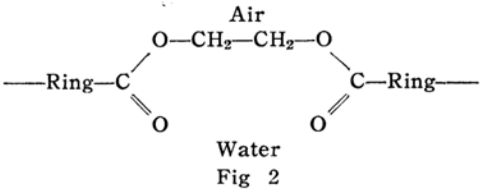
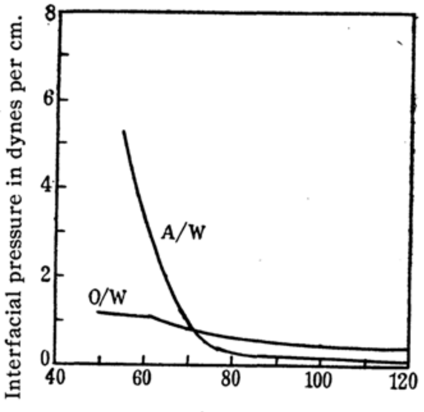


Fig 2

Although the surface pressure at the air/water interface was measured by the hanging plate method using a glass barrier for compression, the film was so gelatinous that a hanging plate, which was once raised with compression, did not return to an equilibrium position during moderate experimental time. Especially, it was recognized that the plate was considerably displaced horizontally as the area of the film was decreased to less than about 72 Å² per residue, from which the surface moment begins to decrease. Therefore, since the true surface pressure could not be obtained, a tentative curve for it is shown in Fig. 3 (15°C).



Area in Å² per residue

Fig. 3. The interfacial pressure of polyethylene terephthalate at the air/water (A/W) and benzene/water (O/W) interfaces.

Although the attempt was made at first the interfacial pressure to measure at the petroleum ether/water interface, we failed to measure it due to the slow desorption of cresol in the spreading solution from the surface. Then, it was measured at the benzene/water interface (15°C) as shown in Fig. 3. The kink point of this curve (62 Å² per residue) corresponds to the area where the surface potential at the air/water interface attained a constant value. This area may be very plausible as the area occupied by the model proposed in Fig. 2. By using the extrapolated value of the product of interfacial pressure and area to infinite area as

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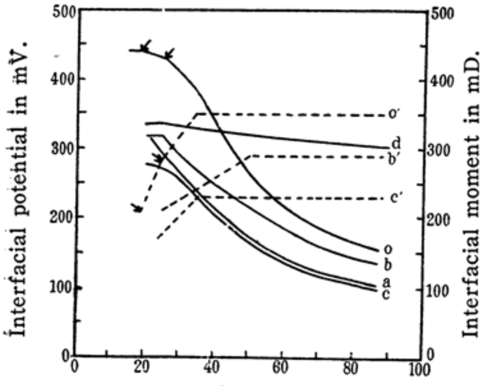
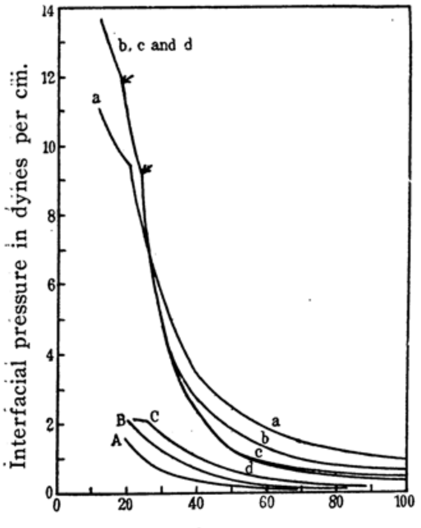
6) C.P. Smyth, *J. Am. Chem. Soc.*, **60**, 183 (1938).

already reported,[2,3] the degree of polymerization for the segment as a statistical kinetic unit at the oil/water interface is estimated to be 13. Although the detailed interpretation for this value will be given elsewhere with other polymers,[7] it is concluded that the ring groups in the main chain make the polymer molecule rigid and should be interpreted in the light of a different base from the chain groups.



Area in Å² per residue

Fig. 4. The interfacial potential (—) (or moment (...))-area curve of poly-N-vinyl pyrrolidone (curve a, pH 0.3, 0.8, curve b, pH 1.4, 3.8, 4.5, and curve c, pH 5.6 –11.4) by successive injection method, (curve d, pH 3.8, 5.6) by compression of glass barrier at the air/water interface, and (curve o, pH 0.4–9.0) at the petroleum ether/water interface.

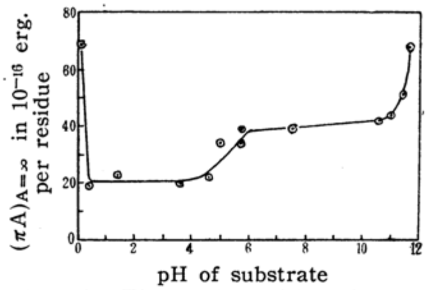


Area in Å² per residue

Fig. 5. The interfacial pressure of poly-N-vinyl pyrrolidone at the air/water interface (curve A, pH<0.8, curve B, pH 1.4−7.4 and curve C, pH 11.0) and at the petroleum ether/water interface (curve a, pH 0, curve b, pH 0.4, 1.4, 3.6, 4.6, curve c, pH 5.7, 7.5, 11.0, and curve d, pH 11.6).

B. Poly-N-vinyl Pyrrolidone.—When the film was compressed, for the measurement at the air/water interface, by using a glass barrier as usual, the obtained surface potential was very abnormal as shown as curve d in Fig. 4. It is presumably because the molecules are not spread or compressed uniformly all over the surface. Therefore, the successive injection method using a micrometer syringe was adopted instead of compression by barrier, for, in this case, the film is spread in a small place so as to avoid to some extent the lack of uniformity as mentioned above. The obtained results of surface potential (or moment) and pressure (19±1°C) were grouped as shown in Figs. 4 and 5, respectively.

The interfacial potential (or moment) (20±1°C) and pressure (8±1°C) at the petroleum ether/water interface were also shown in Figs. 4 and 5, respectively. The interfacial potential at the pH between 0.4 and 9.0 lay on a single curve o in Fig. 4. Those at pH 10.0 and 11.0 were somewhat lower than that shown by this curve at the larger area than about 70 Å² per residue. That on pH 11.8 was furthermore lower at the larger area than about 50 Å² per residue, but identical at the smaller area. However, we had to wait for a long time to obtain the equilibrium value at the higher pH than 9. This fact and the trend of some fluctuation for observed value show that there may be some lack of uniformity even at the oil/water interface. The values of the product of interfacial pressure and area per residue extrapolated to infinite area are shown in Fig. 6 as the function of the pH of substrate.



pH of substrate

Fig. 6. The product of interfacial pressure (π) and area per residue (A) of poly-N-vinyl pyrrolidone extrapolated to infinite area plotted against the pH of substrate.

From these facts, it is concluded that the behavior of this film is different according to the acidity or alkalinity of the substrate, and affected more sensitively by alkali than acid. However, the evidence of this difference is somewhat obscured by the non-uniformity of compression as mentioned above.

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

This non-uniformity is so considerable in the pH range to show the effect of the substrate that we could not confirm the extent of change with the pH sufficiently accurately. On the other hand, Frank had found on studying the lactam-amino acid equilibrium at 100°C that this polymer is more labile in the alkaline solution in contrast with the acidified solution[8]. His result is also qualitatively consistent to the present result.

The trend shown in Fig. 6 gives another evidence of the above conclusion. The value on the acidified substrate is almost identical to that of polyvinyl acetate[2], which has the massive side chains lying at the interface similar to this polymer. The value on the alkaline substrate does not show any serious change of structure, but only a small change such as hydration. Such a hydration is conceivable when we consider the instability in the alkaline solution mentioned above[8]. The high value at both the extremes of pH in Fig. 6 is presumably owing to the partial hydrolysis, but its extent in the pH range shown in Fig. 6 should be very small in the light of the value of interfacial potential at these pH especially at the smaller area. Such a fact was previously reported in the case of polymethacrylic acid[4].

The interfacial moment at the oil/water interface in Fig. 4 is kept constant to 350 mD. up to 35 Å^2, decreases rapidly to 290 mD. at 25 Å^2 and furthermore to 210 mD. at 18 Å^2 per residue, namely, at the collapse point. The latter two kink points shown by arrows in Fig 4 appear also in the interfacial pressure curve at the same areas as shown by arrows in Fig. 5, respectively. Therefore, the film is considered to be transformed at these areas with the fair change of hydrophility of polar groups. Furthermore, since the bond moment of C$-$N bond as well as C$-$O bond in vacuo is small compared with C$=$O bond[6], the inclination of C$=$O bond for each state of this polymer at the oil/water interface can be estimated from Table I of the third paper[3]. The models proposed in Table I in the present paper are considered to be consistent with the previous table[3] and also with the corresponding area shown in this table taking into account the behaviour of other polymers previously investigated[1-5]. In this table carbon atom of main chain is represented by C*.

Although the surface moment at the air/water interface is somewhat uncertain due to the non-uniformity as mentioned above, the valus of curves b′ and c′ in the constant moment range at the larger area in Fig. 4 are almost identical with those at the areas of the first and second kink points of curve o, respectively. Furthermore, the largest area of maximum surface potential is also identical with the area at the first kink point of curve o. It is considered from these facts that the configuration under the above respective condition corresponds to that for the same value of surface moment in Table I. That is, as mentioned above, the difference between their respective condition is not caused by the serious change of structure, but by the small change of hydration of polar groups as shown in Table I. The model of most condensed type corresponding to curve c′ is consistent with the trend of observed value already mentioned, but apparently inconsistent with the lability of the film on alkaline substrate. Such an inconsistency is not clarified at present.

Summary

As the result of the measurements of the interfacial pressure and potential of polyethylene terephthalate and poly-N-vinyl pyrrolidone at the air/water and oil/water interfaces, it is concluded that the ring groups in the main chain make the polymer molecule rigid even at the oil/water interface, while that in the side chain is not essentially different from the chain groups. The film of poly-N-vinyl pyrrolidone is relatively labile on the alkaline substrate.

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 of our Institute who kindly supplied valuable samples to him. The cost of this research has partly defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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[8] H. P. Frank, *J. Polymer Sci.*, **12**, 565 (1954).