Studies on Monomolecular Films. VI. On the Surface Films of Diphenylsiloxane Polymers

By Ryôhei MATUURA

(Received June 14, 1951)

Introduction

Recently the studies on organosiloxane polymers have become very active and extensive because of their practical importance and structural chemical interests. A great many compounds have been synthesized and their physical and chemical properties have been discussed. As to the surface chemical properties of organosiloxane polymers, the elaborate works have been performed by Hunter *et al.*,(1) Zisman *et al.*(2), and Newing(3). They studied the surface tension, spreading and monolayer formation on the surface of water and the built-up film and the lubricating property of silicones, but the substances used in these experiments were chiefly the linear polymers. It is hoped to elucidate the surface chemical properties of the cyclic polymers as well. So it is attempted in the present work to investigate the surface films of the cyclic diphenylsiloxane trimer on water and compare their properties with those of the linear one.

Experimental

Apparatus.—The film balance used in this experiment is the same as described already.(4)

Material.—Diphenylsiloxane polymers were prepared with the method of Kipping.(5) That is, diphenyldichlorosilane (B. P. 200—210° at 45mm. Hg), prepared by the Grignard method from pure silicon tetrachloride and monobromobenzene, was hydrolysed with ice water and the resulting white solid was washed repeatedly with chloroform and petroleum ether. Then it was dissolved in the 5% potassium hydroxide solution and neutralized with acetic acid. Diphenylsilandiol thus obtained was recrystallized from acetone solution several times. For the purpose of preparing polymers of diphenylsilandiol the crystal was heated to the temperature above its melting point (132°). The polymers of various molecular structure were obtained by controlling the temperature and the period of heating, but by the suitable choice of the condition the polymers of

---

(1) M. J. Hunter, M. S. Gordon, A. J. Barry, J. F. Hyde and R. D. Heidenreich, *Ind. Eng. Chem.*, **39**, 1389 (1947).

(2) H. W. Fox, P. W. Taylor and W. A. Zisman, *ibid.*, **39**, 1401 (1947).

(3) M. J. Newing, *Trans. Faraday Soc.*, **46**, 755 (1950).

(4) T. Sasaki, *J. Chem. Soc. Japan*, **62**, 796 (1941); R. Matuura and I. Hayasi. *Memoris of the Faculty of Science, Kyushu University, Ser. C*, Vol. 1, 31 (1948).

(5) F. S. Kipping, *J. Chem. Soc.*, **101**, 2108, 2125 (1912); F. S. Kipping and R. Robinson, *ibid.*, **105**, 484 (1914).

rather simple and definite construction could be obtained. The film experiments were carried out with these simple polymers by spreading from benzene solution on the surface of water. The variety of samples studied are tabulated in Table 1.

Results

In Fig. 1 pressure∼area curves of nine samples obtained by the procedure mentioned above are shown. The substrate is fresh distilled water (pH 5.4) and the temperature of experiment is 14—15°. The numeral in parentheses for the curve in Fig. 1 corresponds to that in Table 1. When the polymers of diphenylsilandiol are prepared by heating the monomer above its melting point, the dehydration takes place during the process and, therefore, the weight decreases by the amount of water lost. This decrease is shown in Table 1 as a loss of weight (in percentage). The molecular weight of each sample was determined cryoscopically in benzene solution.

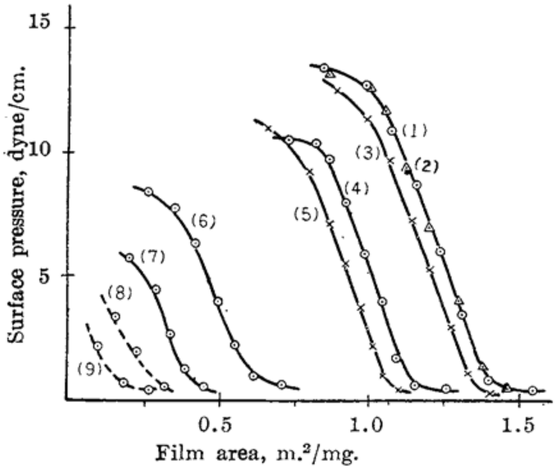


Fig. 1.—Pressure∼area relations of surface films of diphenylsiloxane trimers.

Table 1

Experimental Data of Linear and Cyclic Trimers of Diphenylsilandiol and their Mixtures

No. of sample	Loss of weight, %	Molecular weight	Film area	
			in m.²/mg.	in Å.²/molec.
(1)	5.61	601	1.40	139
(2)	5.73	610	1.40	140
(3)	6.01	618	1.35	138
(4)	6.93	620	1.15	118
(5)	7.02	605	1.09	109
(6)	7.91	681	0.61	69
(7)	8.16	630	0.38	40
(8)	8.47	622	0.30	31
(9)	8.28	590	0.20	20

The samples (1) and (2) spread well and form the stable monolayers on water but the samples (3) to (7) spread with less easiness and form more and more unstable surface films as the loss of weight increases until at last in the case of samples (8) and (9) a surface film can hardly be obtained and the agglomeration readily occurs resulting in the formation of the three-dimensional crystals. The dotted lines shown in Fig. 1 represent the temporary pressure∼area curves obtained by the rapid compression.

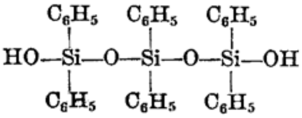
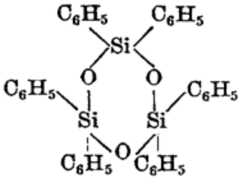
Discussion

Kipping reported several linear and two cyclic polymers obtained by the condensation of diphenylsilandiol. When diphenylsilandiol is heated above its melting point, it seems to condense first to the linear polymers and then to the cyclic ones if the chain grows long enough. The final product is, according to Kipping, mainly hexaphenylcyclotrisiloxane. In the present experiment the samples (1) and (2) consist mainly of a linear trimer and (8) and (9) of a cyclic trimer, as are confirmed by comparing the data of weight loss by the dehydration and the molecular weight observed as shown in Table 1 with those expected from the structural formulas shown in Table 2. It seems probable that a linear trimer is readily produced by heating diphenylsilandiol above its melting point for a short period and by further heating it turns to a cyclic trimer by the dehydration between hydroxyl groups at both ends of the chain. Each of the samples (3) to (7) in this experiment is considered to be a mixture of these two compounds. This is also confirmed by the result of the molecular weight determination. Since the molecular weight of the linear trimer and the cyclic one is approximately the same, about 600, the mixture of these two is expected also to have nearly the same molecular weight as above, irrespective of the composition. This is really the case as shown in Table 1. The content of the cyclic trimer in the mixture will become larger as the loss of weight in Table 1 increases.

The monolayer of the linear trimer is very stable and occupies 1.40 m.²/mg. which corresponds to 140 Å.² per molecule, while the cyclic trimer forms no stable surface films on water, readily forming large aggregates of molecules. This difference should be accounted for from the stereochemical point of view with

Table 2

Comparison of the Observed Data with the Theoretical Ones

	Structural formula	Loss of weight, %		Molecular weight	
		Theor.	Obs.	Theor.	Obs.
Linear trimer	 $HO{-}Si(C_6H_5)_2{-}O{-}Si(C_6H_5)_2{-}O{-}Si(C_6H_5)_2{-}OH$	5.56	5.61 (1) 5.73 (2)	613	601 (1) 610 (2)
Cyclic trimer		8.33	8.47 (8) 8.28 (9)	594	622 (8) 590 (9)

these two polymers. In the linear trimer, six phenyl groups can be arranged on one side of siloxane chain so that this surface is wholly nonpolar while the opposite surface, consisting of siloxane chain, is polar. That is, the molecule is clearly separated into polar part of siloxane chain and nonpolar part of phenyl groups. This polar-nonpolar character of the linear trimer is essential for it to form a stable monolayer on the surface of water. Here, of course, two hydroxyl groups attached to both ends of the chain will play a role in the film formation by anchoring to the surface of water. On the other hand, in the cyclic trimer the polar siloxane chain is almost completely concealed among six phenyl groups with no anchoring groups appearing on the surface of molecule. This leads to the lack of formation of the stable surface films on water.

The difference in the molecular structure mentioned above can also be confirmed by the experiment on the stabilization of emulsion. Namely, the benzene∼water emulsion of a suitable composition was remarkably stabilized by the linear trimer but little by the cyclic trimer. This is interpreted in such a manner that the molecule of the linear trimer which has a decided polar-nonpolar structure plays an important role in stabilizing benzene∼water emulsion, while that of the cyclic trimer which lacks such a structure does not. It is natural that the samples (3) to (7), being presumably the mixture of these two compounds, should be intermediate in the surface chemical properties. In fact, as mentioned already, the mixture becomes less and less spreadable as the content of the cyclic trimer increases.

Adam⁽⁶⁾ reported that the area per phenyl group attached to the end of the hydrocarbon chain is 24 Å.^{2} Assuming this value also in the present experiment, six phenyl groups of the diphenylsiloxane trimer should occupy the area of 144 Å.^{2}, if the area of each phenyl group takes part in the area of the molecule as a whole. This is very close to the molecular area (140 Å.^{2}) of the linear trimer obtained in this experiment. Therefore it is allowed to assume that six phenyl groups are packed compactly in the film, rendering the upper film surface completely hydrophobic. This also explains the remarkably water repellent nature of the silicon film as pointed out by many workers⁽⁷⁾. On the other hand in the cyclic trimer, the molecular area should not be less than 72 Å.^{2}, the area of three phenyl groups, no matter how the molecule may orient itself. The reason is that, since the siloxane ring in the cyclic trimer has been confirmed to be planar⁽⁸⁾, two phenyl groups attached to every silicon atom may overlap when projected on a horizontal plane if the molecule is oriented in such a way that the plane of the siloxane ring is horizontal, and it is impossible for the molecule to be oriented in any other way to occupy the area smaller than this. The molecular area of the cyclic trimer observed in this experiment is far smaller than this, *i. e.*, 20Å.^{2}, showing again that the molecule is not arranged in a monomolecular way, but forms large aggregates owing to its lack of polar-nonpolar balance.

Summary

The surface films of diphenylsiloxane polymers obtained by heating the monomer above its melting point were formed on the surface

---

(6) N. K. Adam, *Proc. Roy. Soc.*, **A 103**, 676 (1923); N. K. Adam, W. A. Berry and H. A. Turner, *ibid.*, **117**, 532 (1928).

(7) C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Revs.*, **41**, 97 (1947).

(8) L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945); E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).

of water and their properties were discussed in connection with their molecular structure. The linear trimer formed a very stable monolayer on water and its molecular area was approximately equal to the area of six phenyl groups, while the cyclic trimer formed no surface film, readily aggregating into three-dimensional crystals. This difference was explained by the difference in molecular structure; the former has a decided polar-nonpolar structure, while the latter lacks such a structure. This was also confirmed by the experiment on emulsion stabilization.

In conclusion, the author wishes to express his sincere thanks to Prof. Tunetaka Sasaki for his guidance and encouragement given to the author during this experiment.

Chemical Institute, Faculty of Science,
Kyûshû University, Fukuoka