

On the Crystallization of Crude Rubber

By Chulchai Park (朴哲在)

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Abstract

The identity of crystallization in a stretched smoked sheet of rubber, in pale crepe, and in frozen rubber was established. A small expansion by freezing was found in smoked sheet ribbons of rubber stretched to various degrees. Maximum expansion occurred with the stretching of about 200-300 percent of the original length, and there was no, or almost no expansion in the case of stretching which was higher than about 700 percent. From these facts a new theory was proposed to explain the crystallization of rubber by stretching, milling, freezing and compressing. In this theory long chain molecules of rubber are considered to form large irregular spirals having numerous isoprenes many more than two in one turn of the spirals.

I. Experimental results

(1) Crystallization by various methods

It has already been ascertained that the crystallization of rubber can be induced by various methods, such as stretching, freezing, milling and compressing.

If a narrow ribbon of smoked sheet rubber is stretched extensively, the X-ray diffraction pattern shows a fibrous arrangement of the microcrystals. With a stretching of about 150 percent, a faint fibre diagram was obtained and with 500 percent stretching, the diffraction spots became sharp and intense. The amorphous halo peculiar to unstretched rubber remained unchanged in width and position, but its intensity decreased with an increasing amount of stretching in contrast to the increase of the intensity of the fibrous spots.

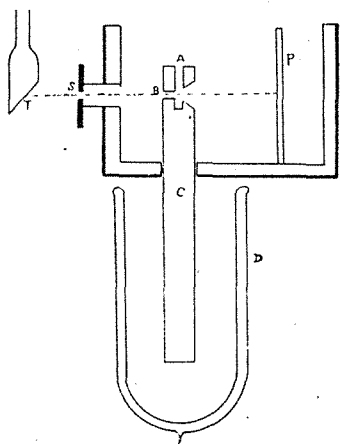
It was already found by Katz and Bing¹ that crepe rubber is crystalline. This point was confirmed by Dr. K. Tanaka and the writer; the Debye-Scherrer rings obtained by them with crepe rubber is shown in Fig. 1 of Plate I. In preparing a sheet of crepe rubber, coagulated strips are passed between rolls 8-12 times, and the coagulated strips are strongly crystallized by such severe rolling. On the other hand, in preparing a smoked sheet, the rolling of coagulated strips is not so severe as in the case of crepe rubber; and some of rubber crystals

1. J. R. Katz and Bing; *Z. angew. Chem.*, **38**, 439 (1925).

formed in the process of rolling, melt on being heated in the process of smoking.

In order to take a photograph of frozen rubber, the specimen must be kept frozen throughout the whole exposure. For this purpose use was made of the simple apparatus shown in Fig. 1, which was devised by U. Yoshida and S. Tsuboi.¹ In this figure C is a copper rod, and a piece of the specimen to be examined is inserted in a small vertical hole A in the upper part of the rod C. The small horizontal hole B

Fig. 1



passing through the upper part of the rod C is a slit for the X-rays. The X-rays, starting from a Cu or Fe target of a Shearer tube, illuminate the specimen in hole A, after passing through the slits S and B; and the pattern of the diffracted X-rays is impressed on the photographic plate P standing perpendicular to the incident X-ray beam. The specimen of rubber is kept frozen by dipping the lower part of the copper rod C in a suitable freezing mixture. The writer used as freezing mixture acetone and dry ice and measured the temperature

of the frozen specimen by inserting a thermometer into hole A. As the specimen of rubber, smoked sheet was used in this case. At -5°C , the writer got the powder diagram shown in Fig. 2 of Plate I; but at 0°C no interference fringe was detected. This means that the smoked rubber does not crystallize at about 0°C , unless it is kept for a long time at that temperature. However when it is kept cooled at 0°C for a long time, for example two weeks, crystallization is detected.

A piece of smoked sheet, $2\text{ cm} \times 4\text{ cm} \times 0.2\text{ cm}$, was put between two bronze plates, $7\text{ cm} \times 7\text{ cm} \times 0.3\text{ cm}$, and pressed at $5-6^{\circ}\text{C}$ for about two weeks by putting the weight of 3.5 kg. upon the upper plate. The specimen was found to be crystallized as appears in the powder diagram shown in Fig. 3 of Plate I.

Very recently, P. A. Thiessen and W. Kirsch² reported an interesting experiment on the crystallization of rubber by compressing.

1. U. Yoshida and S. Tsuboi; *These Memoirs*, **12**, 203 (1929).

2. P. A. Thiessen and W. Kirsch; *Naturwiss.*, **17**, 387 (1938).

Generally the rubber crystallizes at a higher temperature when the degree and duration of compressing are increased.

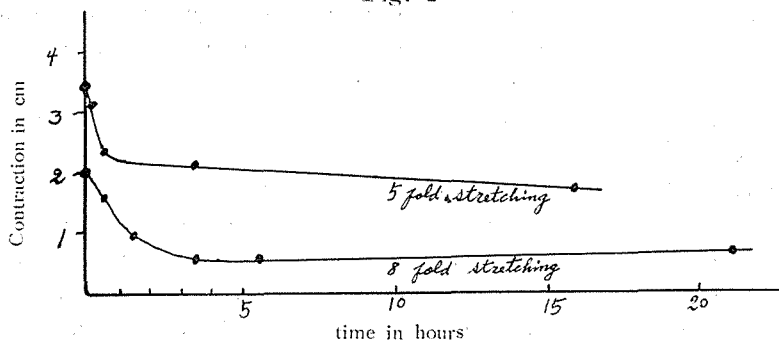
When a ribbon of rubber kept slightly stretched in an uncrystallized degree is frozen, it gives an imperfect fibre diagram consisting of short arcs, as shown in Fig. 4 of Plate I. The fibre axis lies in the direction of stretching. Further, when a sample of rubber inserted in hole A of Figure 1 is frozen by being slightly pressed by placing a thermometer on it, it also gives a fibre diagram consisting of short arcs as shown in Fig. 5 of Plate I. In this case the fibre axis is perpendicular to the direction of pressing.

When a sufficiently stretched ribbon of rubber is released and its contracted length becomes 1.7 times the original length, it produces no crystalline interference at room temperature. But when it is frozen at a temperature lower than about -5°C it gives an imperfect fibre diagram as shown in Fig. 6 of Plate I. The fibre axis is in the direction of stretching. These facts indicate that the rubber when stretched or compressed a little at room temperature is already coming almost to a crystalline state though it is not yet perfectly crystalline, and that such a crystallizing tendency is completed by subsequent freezing.

(2) Contraction when tension is released

The remarkable contraction, when tension is released, is one of the characteristic properties of rubber. When the tension is released immediately after stretching at room temperature, the crude rubber contracts almost though not quite to its original length. When, however, the tension is released after many hours continuous stretching, the contraction decreases greatly. The behavior of contraction of a ribbon of a smoked sheet of rubber in relation to the duration of time of continuous stretching at about 20°C is shown in Fig. 2.

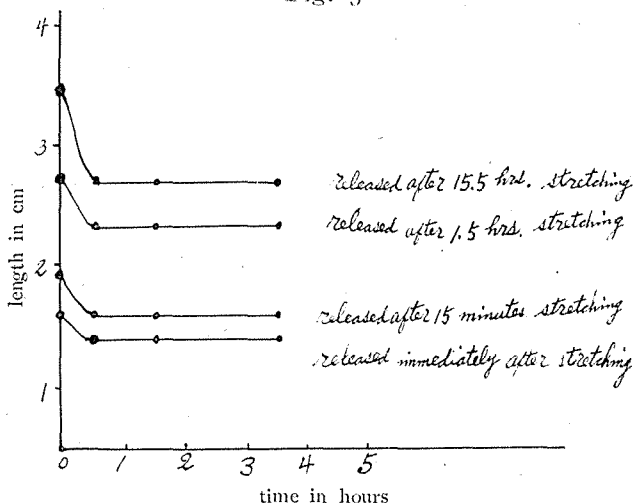
Fig. 2



One cm of a ribbon of smoked sheet is stretched 5 fold or 8 fold and after being stretched for a certain time the tension is released, and its length is measured immediately. The difference of the lengths in the stretched and released state is taken as the amount of contraction in Fig. 2.

Next the writer measured the slow change of contraction of a ribbon of smoked sheet after release of tension which had been applied to the specimen for a certain duration of time. The results obtained at the temperature of about 20°C are shown in Fig. 3. In this case all the specimens were stretched 5 fold and the lengths of the specimens which are represented as ordinates refer to 1 cm of the original length before stretching. As is seen by Fig. 3, the greater part of the

Fig. 3



contraction occurs at the moment when the tension is released, and the remaining contraction is completed within the following 30 minutes. Generally the speed of the contraction of stretched crude rubber after the release of the tension increases with temperature. The contraction proceeds very slowly at a low temperature, but takes place rapidly at a high temperature.

Strongly stretched rubber shows a fibre diagram with sharp spots. When the contraction after the release of the tension is small the sharp spots of the fibre diagram become somewhat diffuse and they extend to form circular arcs. This fact indicates that the parallelism of the crystallites along the fibre axis is somewhat destroyed by the release

of the applied tension, though the fibrous arrangement is still roughly maintained.

When such slightly contracted crude rubber is warmed with faint heat it contracts very slowly, and when it has become about twice its original length before stretching, the arcs of the fibre diagram extend gradually into broad circles and at last they are displaced by the diffuse amorphous halo peculiar to the unstretched original crude rubber.

(3) Identity of the crystals obtained by stretching,
milling and freezing

Barnes¹ examined two samples of frozen crude rubber, which had remained frozen for very long time. His measurements agree closely with those obtained by Lotmar and Meyer² for stretched rubber. Recently, G. L. Clark and others³ reported that the spacings of the crystals in frozen rubber are the same as those in stretched rubber within the limits of experimental errors. This point is also confirmed by the writer. He calculated from the diffraction photographs the spacings corresponding to four intense spots, A_1 , A_2 , I_1 and I_2 with stretched rubber, and compared them with those corresponding to the four intense rings due to pale crepe and frozen rubber. The results are shown in Table I.

Table I

		sin θ/λ			
		Lotmar and Meyer	the Writer		
spot	face hkl	stretched rubber	stretched rubber	pale crepe	frozen rubber
A_1	002*	0.0795	0.080	0.081	0.081
A_2	200*	0.118	0.120	0.118	0.122
I_1	012*	0.100	0.101	0.100	0.103
I_2	013*	0.133	0.134	0.131	0.136

* Indices refer to Lotmar and Meyer's unit cell

From the table, we can recognize that the rubber crystals in stretched rubber, pale crepe and frozen rubber are identical.

1. William H. Barnes; Can. J. Research, **15**, 156 (1937).
2. W. Lotmar and K. H. Meyer; Monatsh. **69**, 115 (1936).
3. G. L. Clark, E. Wolthuis and W. H. Smith; Bureau of Standards, J. of Research **19**, 479 (1937).

(4) Melting of the rubber crystals in stretched crude rubber

As is stated before the crude rubber is still in crystalline state after the release of the tension which was applied to the specimen to transform it to the crystalline state. The melting temperature of such rubber crystals in the state of released tension depends upon the degree of previous stretching and the time elapsed after the release of the tension. But as is revealed by the contraction experiment shown in Fig. 2, the melting temperature seems to attain nearly its maximum value within about three hours after the release of the tension. The writer measured, after one day from the release of the tension, the melting temperatures of smoked sheets which had been stretched to various different degrees. The results are tabulated in Table II.

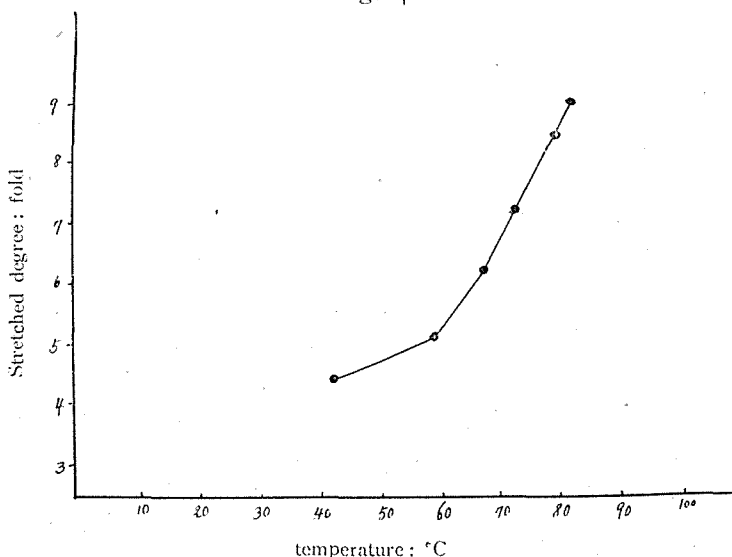
Table II

stretching degree	3.2 fold	4.0	5.1	5.6	6.4	7.2
melting temperature	25°C	26	26	27	27	30

As is seen from the table the melting temperature increases gradually with the increasing degree of stretching.

Next the writer measured, by the X-ray diffraction, the melting temperature of the smoked sheet in the stretched state. The melting

Fig. 4



temperature in this case has a different meaning and is generally much higher than before. The relation between the melting temperature and the degree of stretching is shown in Fig. 4.

The melting temperature of the rubber crystals of a smoked sheet in the frozen state is about $10^{\circ} \pm 1^{\circ}\text{C}$. The melting temperature of the rubber crystals in a smoked sheet which is worked and then frozen, is higher than that of the unworked frozen rubber; in this case the melting temperature is higher with an increasing degree of working.

(5) Slipping between the chain molecules of rubber

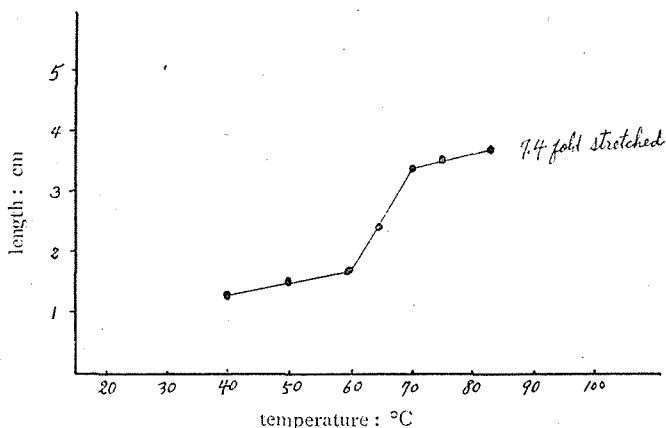
When a rubber ribbon of smoked sheet is stretched to about 7-8 fold its initial length and is simultaneously heated at about 80°C for about one hour, it gives an amorphous halo instead of the fibre diagram peculiar to stretched rubber. To explain this, two suggestions have been made. The first considers that thermal agitation separates the chain molecules from each other and from their position in the crystal lattice. The second accepts this theory and adds the idea that the molecules, slipping on one another, coil up to their original position, restoring the stretched rubber to its original unstretched state.

It produces no crystalline photograph in either case, but the contraction, when the tension is entirely released after heating, is different in the two cases. If the first theory is correct the contraction when tension is entirely released after heating is of the same order as that when tension is entirely released without heating in the stretched state. But if the second explanation is correct the contraction is much smaller than that when tension is entirely released without heating in the stretched state.

When a narrow ribbon of smoked sheet is stretched without special heating to about 7-8 fold its original length for about one hour, and is immersed in boiling water for about ten minutes after the release of its stretching tension, its length shortens to about 1.2 times its initial unstretched length, which may be considered as almost the same as the initial length. But when the same specimen after being stretched to the same amount for about one hour, is heated to its melting point, i. e. 70°C or 80°C in the stretched state, and is immersed in boiling water for about ten minutes after the release of its stretching tension, its length shortens only to about one half of the stretched state, that is 3 or 4 times its initial unstretched length. The results of such an experiment with a ribbon stretched 7.4 fold and heated at various

temperatures are shown by the curve in Fig. 5. In this figure the length of the rubber ribbon when heated in boiling water, referring to one cm of the initial unstretched state, is taken as ordinate, and the heating temperature during stretching is taken as abscissa. This curve shows that heating a piece of rubber in the stretched state above its melting temperature causes, to a remarkable degree though not perfectly, the coiling up and the mutual slipping of the spiral molecules of the rubber.

Fig. 5



II. A theory of crystallization of rubber

The unstretched rubber gives an amorphous ring and the stretched rubber gives a fibre diagram; and various theories have been proposed to explain these facts. Katz¹ believes that the isoprene complex of rubber is chain-like in both states. The stretching merely brings the straight chains into alignment. This theory does not adequately explain the remarkable extension property of rubber. In the discussions already referred to^{2,3}, Astbury shows that the possible maximum extensibility of rubber with such straight chain molecules is only about 57 percent, and it is not possible to explain the enormous extensibility of rubber which amounts to several hundred percent.

Kikentscher and Mark⁴ and others consider that the rubber in unstretched state is composed of isoprene spirals. Two isoprenes make

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1. J. R. Katz; *Naturwiss.* **13**, 411 (1925).
 2. H. Mark; *Trans. Farad. Soc.* **29**, 6 (1933).
 3. M. Mathieu; *Trans. Farad. Soc.* **29**, 122 (1933).
 4. Kikentscher and Mark; *Kautschuk*, **6**, 2 (1930); *Koll. Z. S.* **49**, 135 (1929).

one turn of the spirals, and the stretching straightens the spirals into the chains of von Susich's model. This theory does adequately explain the remarkable extension property of rubber.

Hauser¹ insisted that he had isolated two constituents of rubber, "sol rubber" or "alpha rubber" and "gel rubber" or "beta rubber", and attempted in these terms to explain the cause of the appearance of the interference spots, when rubber is stretched. This theory also seems not to be suitable in explaining the remarkable extension property of rubber.

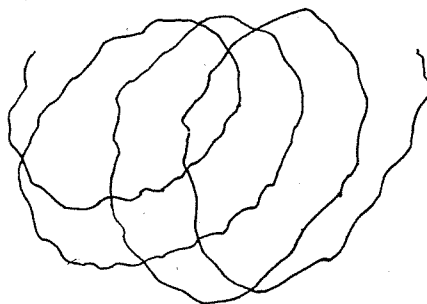
In 1934, E. Mack² proposed an interesting theory of the elasticity of rubber. According to him there appear to be only two reasonable and possible sources of force required to pull extended rubber molecules back to the unstretched positions when tension is released: (I) residual valences of the double bonds and (II) van der Waal's forces between hydrogen atoms on the surface of the molecules. Between the two Mack considers that the available evidence favors the latter.

In the same paper, Mack proposed a zigzag model of the rubber molecules, and succeeded to a considerable extent in explaining the extension and the contraction property of rubber.

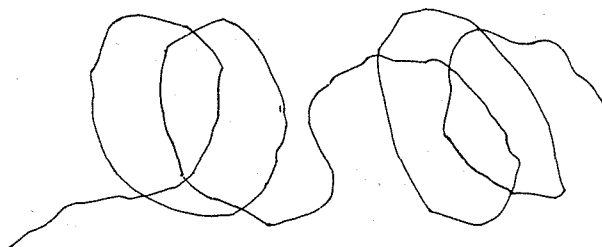
Meyer and others³ tried also to explain the crystallization of crude rubber by stretching by considering long chain molecules; and at the same time the contraction, when tension is released, by thermal agitation of long chain molecules.

Fig. 6

A



B



1. E. A. Hauser; *Ind. Eng. Chem.*, **21**, 249 (1929).

2. E. Mack; *J. Amer. Chem. Soc.* **56**, 2757 (1934).

3. Meyer, Ferri and Hohenemser; *Kautschuk*, **11**, 88 (1935); Meyer, von Susich and Valkó; *K-Z.*, **59**, 208 (1932).

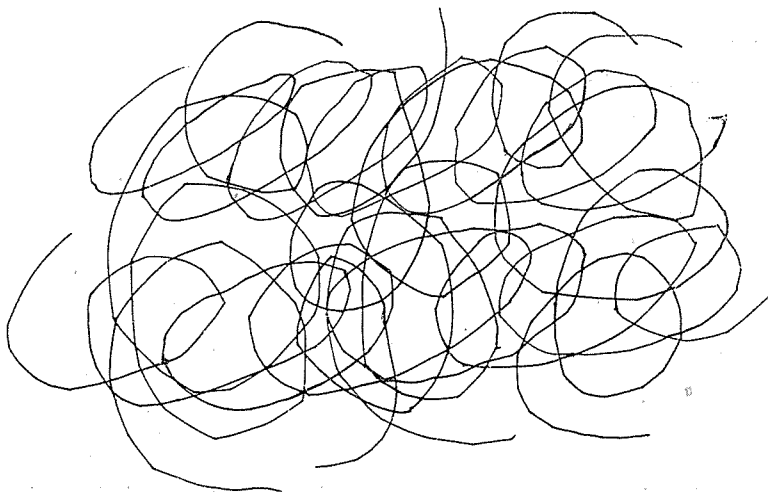
In 1936, a schematic representation of the long chain molecule in unstretched rubber was proposed by Simard and Warren¹.

Very recently Kuhn proposed a "Knäuel" model of the long chain molecule in an elastic solid substance; and tried to explain its elastic property and crystallization by assuming the possibility of free micro-Brownian movement of every small part of a long chain molecule and the impossibility of the macro-Brownian movement of the molecule as a whole.

All the theories cited above concern mainly the crystallization of crude rubber by stretching and milling, but the crystallization to the same lattice form of crude rubber by freezing or compressing must be taken into account with equal weight. Thus it is necessary for the writer to consider another molecular configuration of crude rubber in unstretched state. Let us imagine, as shown in Fig. 6, that a long chain molecule forms a large irregular spiral which contains numerous isoprenes many more than two in one turn, and that the long chain molecules are in thermal agitation corresponding to their temperature.

Fig. 6 represents schematically the configuration of an irregular spiral of a single long chain molecule. In fact, a long chain molecule

Fig. 7



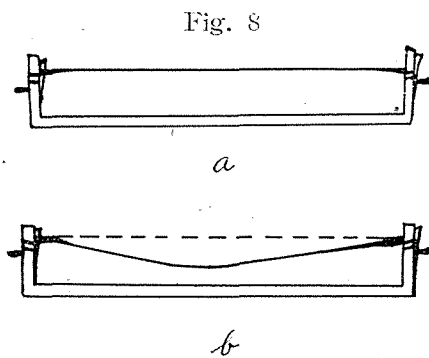
1. Simard and Warren; *J. Amer. Chem. Soc.*, **58**, 509 (1936).
2. W. Kuhn; *Zur Entwicklung der Chemie der hochpolymeren Kuststoff Kautschuk Anstrichmittel Cellulosederivate* (1937);
W. Kuhn; *Angew. Chemie*; **37**, 640 (1938).

may be in the form of an irregular spiral in some parts, but in another part, it may not be so on account of becoming entangled with other spiral groups of long chain molecules; and consequently by assemblage of the spiral groups, may be supposed to lie in a higgledy-piggledy manner as shown in Fig. 7.

When we stretch a piece of rubber, the large irregular spirals of long chain molecules straighten along the stretching direction, and the straightened chain molecules fit together to form the crystal lattice by the van der Waal's force of attraction between chain molecules. Of course, it may be possible that a large irregular spiral contains straight chains in some parts of it. If so, such short straight chains may form a smaller crystal lattice by uniting with those in the neighbouring large irregular spirals before the large irregular spirals are straightened by stretching.

Next when we freeze or hydrostatically compress a piece of rubber, neighbouring chains of the large irregular spirals attract each other and unite to form the crystal lattice by straightening themselves.

Now stretch the ribbons of smoked rubber at various degrees up to 800 percent in the manner shown in Fig. 8 *a*, and cool them in the stretched state at a temperature lower than about 0°C for two or three days; then a small elongation by cooling of about 2-4% occurs with some proper stretching in the manner shown by the curve drawn in full line in Fig. 8 *b*. A ribbon of smoked rubber is stretched to some extent and its ends fastened to the metal frame as shown in Fig. 8 *a* making its length 10 cm, and then it is cooled below 0°C in the stretched



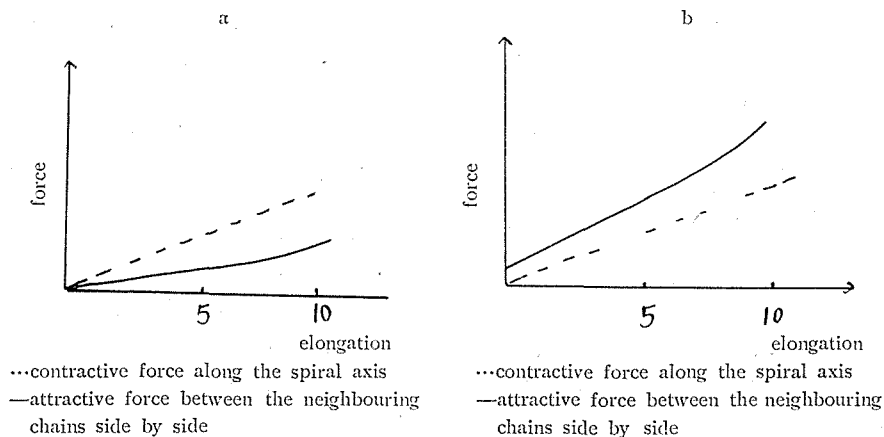
state. The small elongation by cooling of the order stated above occurs with the stretching below about 600 percent, and it is maximum at the stretching of about 200-300 percent. This fact seems to be in accordance with the view that the chains in the large irregular spirals straighten themselves in forming the crystal lattice by freezing. When the stretching exceeds about 600 percent the elongation by cooling as stated above is scarcely discernible.

This seems to be due that the straightening of the chains of the

large irregular spirals in the direction of stretching is already almost completed with such a severe stretching, and that no more straightening of the chains occurs on cooling.

In order to understand the crystallization of rubber, it is helpful to compare the contractive force along the axis of the large irregular spirals with the attractive force side by side between the neighbouring

Fig. 9



chains of the spirals; and this comparison is made schematically by Fig. 9. As is stated before, the crystallization of rubber is due to the attractive force between the neighbouring chains side by side, which may be termed a crystallizing force. At a temperature higher than the room temperature the crystallizing force is suppressed by the contractive force along the spiral axis as is shown by Fig. 9 a. However when rubber is stretched sufficiently the latter force is balanced by the external force applied by stretching, by setting free the former force to cause the crystallization. At a lower temperature, below about 0°C , the attractive force between the neighbouring chains side by side, that is the crystallizing force, becomes predominant and superior to the contractive force along the spiral axis by the decrease of thermal agitation, as is shown by Fig. 9 b, irrespective of the amount of stretching; and the crystallization of rubber occurs without any stretching.

When the tension applied by stretching is released at a temperature higher than the room temperature, the contractive force along the spiral axis is set free, and is stronger than the crystallizing force at that temperature; the curling of the chains into the original large irregular

spirals disjoins the crystalline configuration and makes the stretched specimen contract as a whole.

When rubber crystallized by stretching or freezing is stored for a long time, the melting temperature of its crystals increases. This seems to be due to the fact that the chain molecules of rubber fall more perfectly and more tightly into the crystal lattice by aging, by making it more and more difficult to disjoint it to the original amorphous state.

In conclusion, the writer wishes to express his sincere thanks to Professor U. Yoshida for his kind guidance and invaluable suggestions during the course of his research. His hearty thanks are also due to Dr. K. Tanaka and Mr. S. Shimadzu for the facilities afforded to him during the present experiment.

Chullchai Park

Plate I

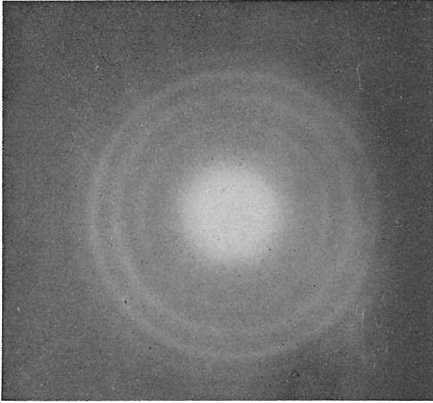


Fig. 1

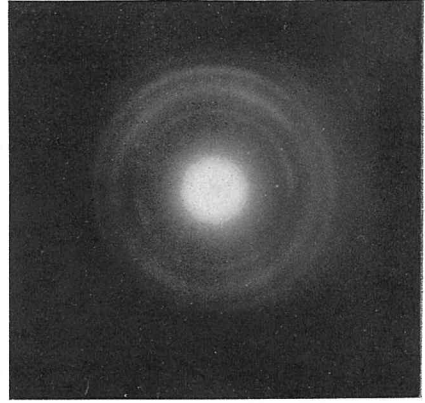


Fig. 2

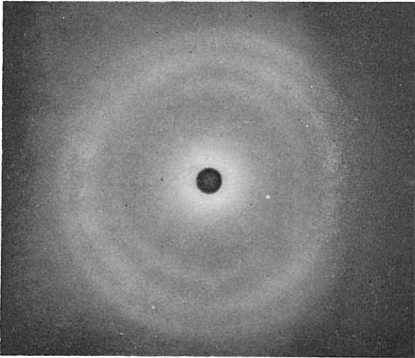


Fig. 3

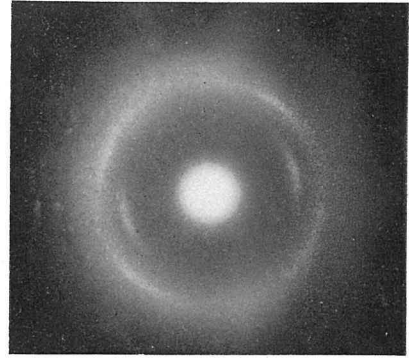


Fig. 4

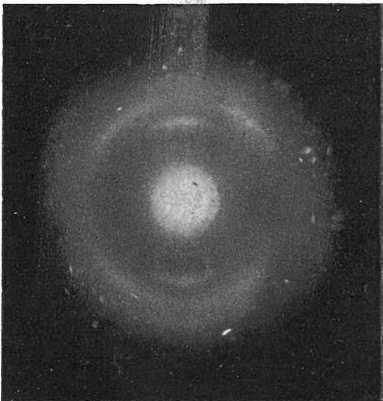


Fig. 5

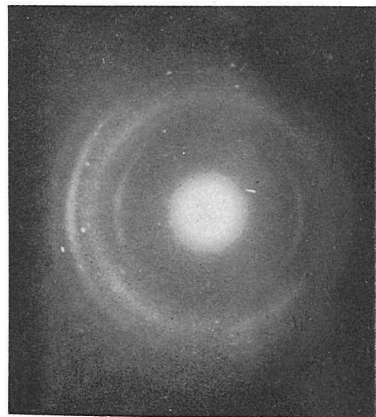


Fig. 6