Nature of Stark Rubber [1]

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The melting behavior and X-ray diffraction patterns of four different samples of "stark rubber" have been investigated. The melting temperatures, 39° to 45.5° C, are substantially higher than that observed for natural rubber crystallized by cooling. The X-ray diffraction patterns indicate that the crystallites in stark rubber are oriented. This observation can explain the higher melting temperatures. Thus, the previous assignment of an equilibrium melting temperature, 28° ±1° C, to unoriented crystalline natural rubber is shown to be appropriate. Several different methods that have been used successfully in preparing stark rubber under controlled conditions in the laboratory are outlined.

1. Introduction

Long-chain molecules that possess a sufficient amount of chain regularity are capable of crystallizing under favorable conditions. The crystallization and the subsequent melting are similar to the processes that occur in monomeric materials of low molecular weight. The existence of an equilibrium melting temperature in polymers has been demonstrated [1]; [2] it has also been shown that this temperature is systematically depressed by low molecular weight diluents in a manner quantitatively describable by the application of the thermodynamics of phase equilibria [1,2]. Similarly, the kinetics of crystallization of polymers can be satisfactorily accounted for by the assumption of the concurrence of nucleation and growth, with the magnitude of the nucleation rate dependent mainly on the difference between the equilibrium melting temperature and the temperature of the crystallization [3]. The success achieved in describing both the melting process and the crystallization kinetics gives additional evidence for the existence of an equilibrium melting temperature, and adds to its significance in the understanding of the crystallization behavior of polymers. This temperature is defined as the one at which the most perfect crystallites are unstable relative to the undeformed, unoriented liquid state.

For many polymers, including natural rubber, it has been observed that the melting temperature, T_m, depends on the crystallization temperature when the heating rate is relatively rapid [4,5,6,7]. However, for polyesters [5], polyamides [6], and more recently for natural rubber [8], it has been demonstrated that when slow heating rates are employed the melting temperature observed is independent of previous thermal history and then the equilibrium melting temperature is approached. This heating schedule is presumably conducive to the formation of more perfect crystallites, which are stable at higher temperatures. For natural rubber the equilibrium melting temperature has been found to be 28° ±1° C [7]. Melting temperatures appreciably higher than 28° C have also been reported for natural rubber. Considerable confusion has arisen due to the apparent variability of its melting point. Since the melting temperatures below 28° C have been demonstrated to be solely a result of the heating rates used in their determinations, the occurrence of melting temperatures above 28° C also requires explanation.

The natural rubber samples that have been observed to be high melting can be divided into two types, "racked" rubber and "stark" rubber. If unvulcanized natural rubber is repeatedly extended at an elevated temperature and then cooled, it can be given a rather enormous pseudopermanent extension without any applied force being maintained [9]. Extensions as great as 10,000 percent have been reported. Rubber thus treated has been termed "racked" rubber, and its mechanical properties are similar to those of a hard inelastic material. The racking process is accompanied by increase in density of the rubber, and its X-ray diffraction pattern gives a very intense fiber-type diagram, indicating not only that crystallization is occurring, but that the crystallites thus formed are highly oriented in the direction of the stretching. On heating, racked rubber retracts and the X-ray pattern disappears, indicating that fusion is occurring. The melting temperature, which depends on the extent of racking, occurs in the range 35° to 50° C, substantially higher than the equilibrium melting temperature assigned to natural rubber. However, as the crystallites are highly oriented in racked rubber, the connecting amorphous regions must be deformed from their statistically more probable configuration, and so the crystallites will be expected to be stable at higher temperatures than crystallites in an undeformed system.

When natural rubber is stored in temperate climates it is occasionally found to be hard and inelastic, because of the development of appreciable amounts of crystallinity. Many of these samples also exhibit high melting points on initial heating and this type of rubber has been designated as "stark" rubber because it is hard and rather rigid at room temperature. Stark rubber has not heretofore been prepared

under controlled conditions, and the reasons for its higher melting temperature cannot be ascertained from existing information, as in the case of racked rubber.

In an effort to understand the nature of stark rubber and the reasons for its high melting temperature, the melting behavior and X-ray diffraction patterns of four stark rubber samples, from widely different sources, have been investigated. As a result of this study some conclusions have been reached both as to the reasons for its high melting temperature and as to how it is formed. As a further consequence of these studies, methods have been devised for the laboratory preparation of stark rubber under controlled conditions.

2. Experimental Procedure

The specific volume-temperature relations and the melting temperatures were determined, using dilatometric techniques. Descriptions of the volume dilatometers employed and the procedures followed have been published [6, 10]. The dilatometers were immersed in constant-temperature baths controlled within ±0.1 deg C. The thermal histories of the samples and the times held at the various temperatures are detailed below. The absolute densities of the stark rubber specimens were determined at 25° C by the method of hydrostatic weighings [11].

The samples for the X-ray diffraction studies were cut from the sheets of stark rubber into rectangular strips about 1 mm thick. The X-ray diffraction photographs were taken in a flat plate camera, using copper radiation (Kα) and operating at 40 kv and 20 ma. The sample-to-film distance was 10 cm, the aperture of the sample holder was 0.025 in., and the exposure time was 5½ hours. The variation in intensity of the diffraction around the circumference of a ring was determined by the manual use of a densitometer.

3. Samples

Sample I was received from G. S. Whitby about 1936. It was a sample of smoked sheet, identified by the year of its preparation, 1913, and appeared to be similar to a specimen referred to in the literature [9, p. 105]. Sample II was also a smoked sheet and had been highly milled, with the intention of using it as a rubber cement. It was stored in the basement of the Geophysical Laboratory of the Carnegie Institution of Washington from 1936 until 1951, when it was discovered to have become stark. Sample III was received in 1929. It had been tapped and smoked on the Upper Amazon River and washed and dried at Belem (Para). The sample was firm when received but not so stiff as it had become by 1952, when it was reexamined. Sample IV was from a bale of smoked sheet that had been stored in the NBS Rubber Section for several years; a portion of this bale was found to be stark, whereas other portions, including regions contiguous to the stark portion, were completely amorphous.

4. Results

4.1. Chemical Analyses

The results of chemical analyses for major constituents, which were performed on three of the stark rubber samples, are given in table 1.[3] The amounts of the major constituents found are typical of the composition of unpurified raw rubber. Hence the behavior of stark rubber cannot be attributed to any major chemical differences from the usual, or normal, raw rubber.

TABLE 1. *Chemical analyses of stark rubbers*

Major constituent	Sample		
	I	II	III
	%	%	%
Rubber hydrocarbon [a]	94.1	94.7	94.8
Acetone extract	3.3	3.5	2.6
Benzene insolubles	1.2	0.9	1.1
Protein [b]	2.1	2.3	2.5

[a] Chromic acid oxidation method.
[b] Boric acid method.

4.2. Melting Behavior

The melting behavior of the four stark rubber samples was investigated. Because of time effects above 35° C, a revision was required in the heating schedule that has been used with ordinary natural rubber [8] and other polymers [2, 6, 10]. The observations were initiated at about 15° C, and the temperature was raised at the rate of 1 deg each 12 to 24 hours. Up to temperatures of about 35° C, volume equilibrium appeared to be attained simultaneously with temperature equilibrium, and the specific volume varied linearly with temperature. This is in marked contrast to other polymers [2, 6, 8, 10], in which partial melting and recrystallization always occur in the temperature range below the equilibrium melting temperature. At a given temperature above 35° C the volume of the stark rubber samples no longer remained invariant with time, but was observed to increase slowly. These slow increases in the volume of stark rubber in this temperature region have also been observed by Whitby [9, p. 105]. Although the rate of volume increase was slow, the total volume change at a given temperature was significant. A typical example of this phenomenon is that for sample I after 500 hours at 37° C the specific volume had increased 0.0135 cm^3/g. After the temperature was raised to 38° C and held there for 240 hours, the specific volume had increased 0.00318 cm^3/g. Similarly, after 600 hours at 39° C it had increased 0.0030 cm^3/g, and after 500 hours at 39.5° C it had increased 0.0008 cm^3/g. These observations are also in marked contrast to the behavior of other polymers for which, in the vicinity of T_m, only very slight increases in volume with time are observed. These observations for stark

rubber necessitated that the samples be held for exceptionally long periods of time in the temperature interval between 35° C and T_m. In this interval the temperature was raised in 1-deg increments, and the sample was held at a given temperature until there was no perceptible increase in volume for about 5 to 7 days. Thus, the total heating process for a typical determination of T_m was of the order of 50 to 100 days. The melting temperature was then taken as the temperature at which the last trace of crystallinity disappeared, following the typical heating schedule just described.

Possible reasons for this rather unusual melting behavior will be discussed in more detail in connection with the X-ray diffraction analysis of the structure of stark rubber. It is apparent that the value observed for T_m will depend on the over-all rate of heating and on the total time held at specified temperatures just below T_m. For example, sample II was initially held in the temperature range of 37° to 41° C for 26 days; T_m was found to be 41° C, and the total volume change in melting was 0.0250 cm³/g. Another specimen of sample II was brought from 30° to 38° C in 7 days, and up to the present has been held at 38° C for a little over a year. A steady increase of the volume has been observed, and 60 percent of the total volume change occurring on melting the first specimen has already occurred. There is thus the distinct likelihood that if a sample of stark rubber is held at a temperature below the reported T_m for a sufficiently long time, a lower melting temperature will be observed [9, p. 105].

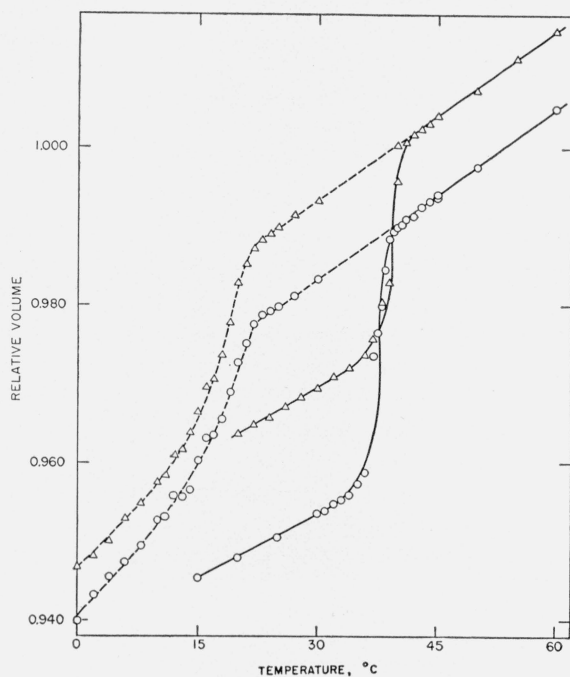Plots of the relative volume as a function of temperature are given in figure 1 for samples I and II.

FIGURE 1. *Relative volume-temperature plot for stark rubber.*

Solid lines, original heating; dashed lines, heating after initial melting and then crystallizing at 0° C; ○, sample I; △, sample II.

This figure also shows the curves that are obtained for the same samples after they were first melted and then recrystallized at 0° C. For the latter case the melting behavior is similar in all respects to that usually observed for natural rubber. If stark rubber is first dissolved, and the solvent is sublimed or evaporated off, and if the sample is recrystallized at 0° C and slowly heated, the usual type of behavior is also found [8]. Thus, if the crystallites originally present in stark rubber once disappear, subsequent crystallization induced by cooling is identical with that which occurs in ordinary amorphous natural rubber.

4.3. Melting Temperatures and Densities

In table 2 the densities of the semicrystalline rubber, ρ_{sc}; the completely amorphous rubber after melting the same samples, ρ_a; and their differences at 25° C are given, as well as their respective melting temperatures, T_m, which were determined from the specific volume–temperature studies. As the stark rubber samples are almost identical in chemical composition, the variations in the density differences must reflect variations in the degree of crystallinity. The fact that the samples, when arranged in order of decreasing density differences, as in table 2, are also in order of increasing melting temperatures may be regarded as fortuitous because the range of melting temperatures is only a little larger than the precision of determination. Therefore, the authors are of the opinion that the melting temperature does not depend on the amount of crystallinity.

TABLE 2. *Densities at 25° C and melting temperatures of stark rubbers*

Sample	ρ_{sc}	ρ_a	$\Delta\rho$	T_m
				° C
I	0.9405	0.9129	0.0276	39.5 to 40
II	.9302	.9094	.0208	41
IV	.9270	.9092	.0178	42.0
III	.9114	.8945	.0169	45.5

4.4. X-Ray Diffraction

Typical X-ray diffraction patterns are illustrated in figures 2 and 3. The positions of the four most intense rings correspond to the d-spacings given in table 3 and confirm the values given by Barnes [12] for stark rubber and that given by Clark, Wolthuis, and Smith [13] for rubber crystallized by either stretching or cooling. Thus, the crystalline form present in stark rubber is the same as that obtained on cooling amorphous natural rubber.

TABLE 3. *Spacings for stark rubber*

d-spacing	Indices [a]
6.30	200
5.00	201
4.24	120
3.77	{ $\overline{1}21$
	121

[a] For a unit cell of dimensions a, b, and c, the direction of the chains (the fiber axis) is the c axis in the above.
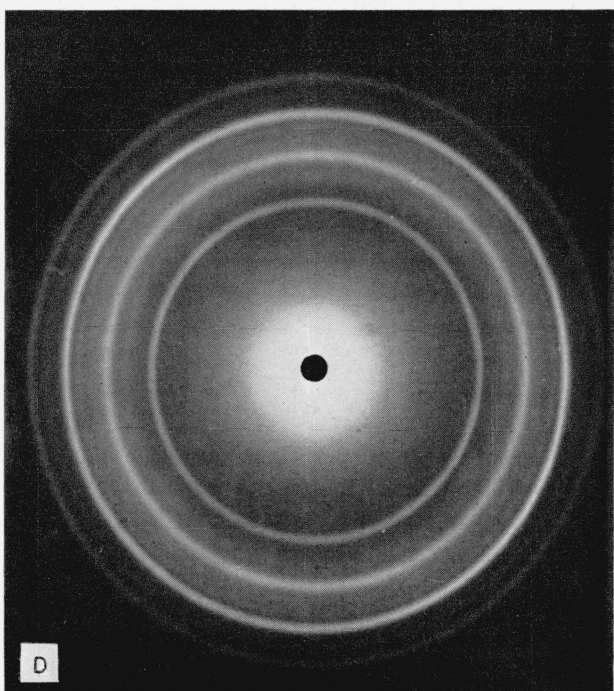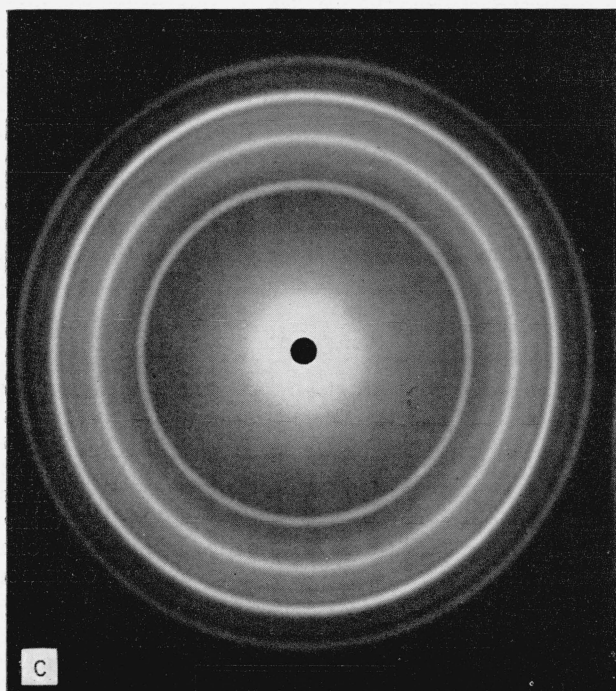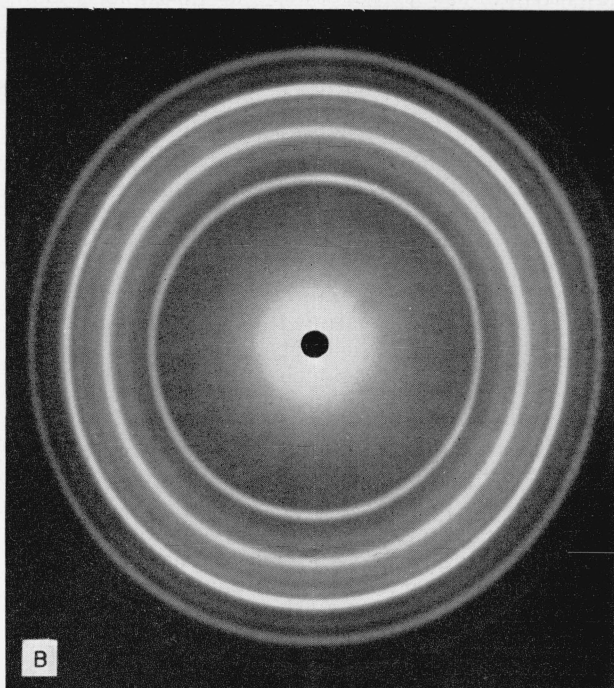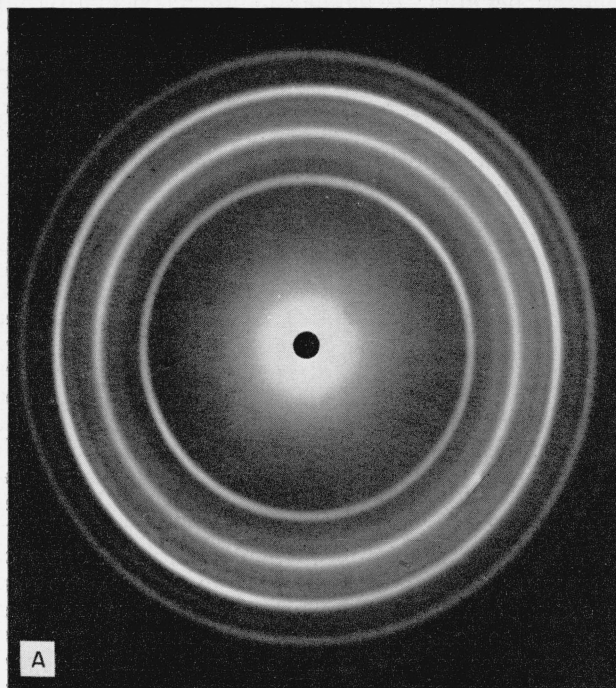
FIGURE 2. *X-ray diffraction photographs of stark rubber.*

A and B, Sample I, with position of X-ray beam parallel and normal, respectively, to plane of rubber sheet; C and D, sample II, with position of X-ray beam parallel and normal, respectively, to plane of rubber sheet.
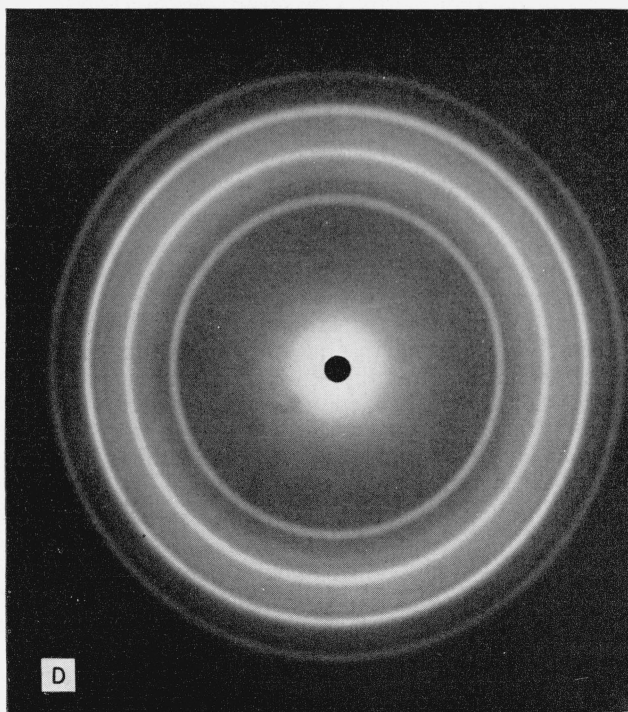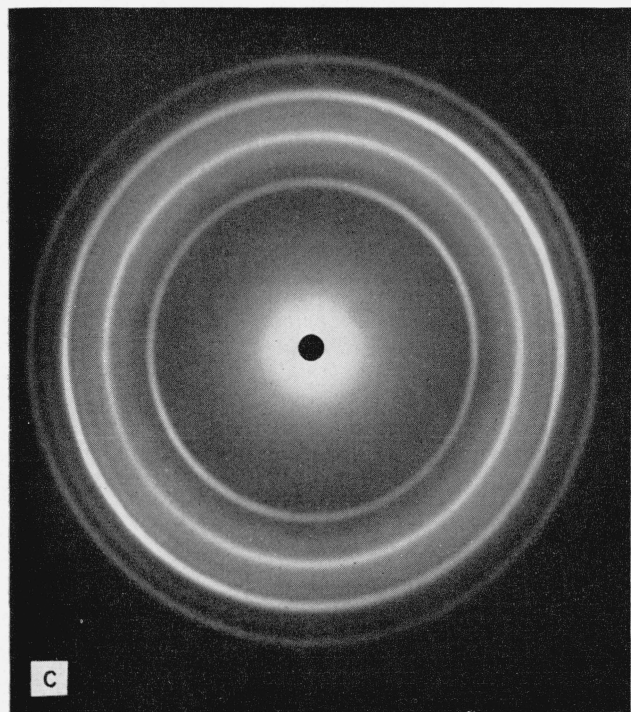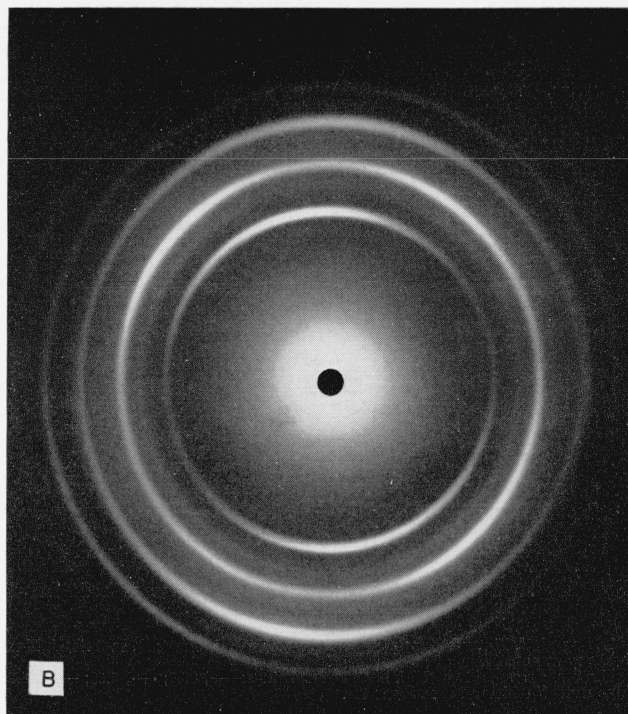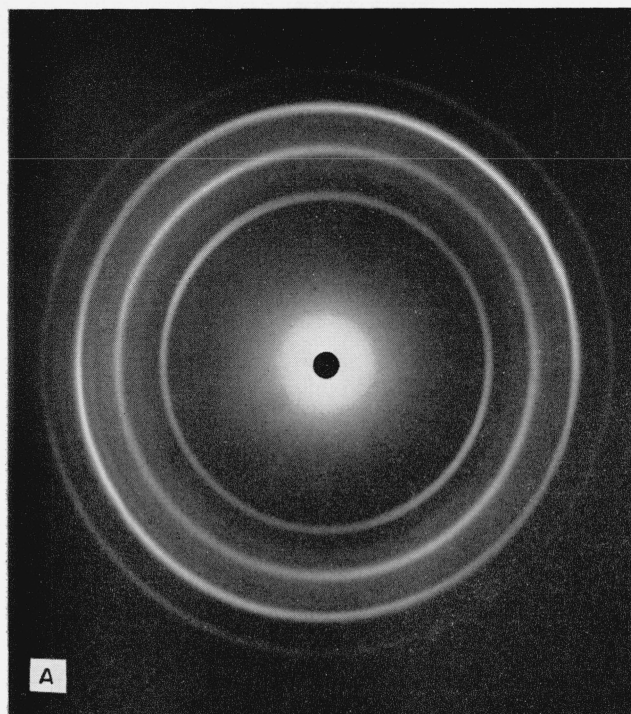
FIGURE 3. *X-ray diffraction photographs of stark rubber.*

A and B, Sample III, with position of X-ray beam parallel and normal, respectively, to plane of rubber sheet; C and D, sample IV, with position of X-ray beam parallel and normal, respectively, to plane of rubber sheet.
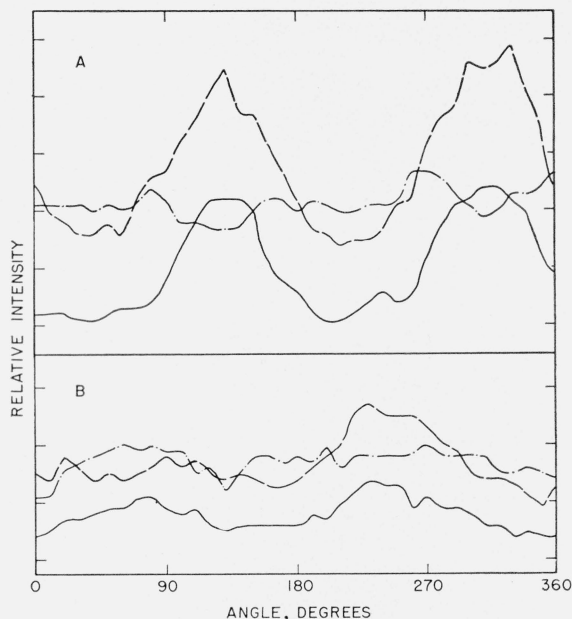
FIGURE 4. *Relative intensity of diffraction around circumference of rings.*

A, Sample I, X-ray beam parallel to plane of rubber sheet; B, sample II, X-ray beam normal to plane of rubber sheet.
Curves correspond to the following *d*-spacings:———, 6.30; •——, 5.00; — —, 4.24. The unit of relative intensity is 0.1.
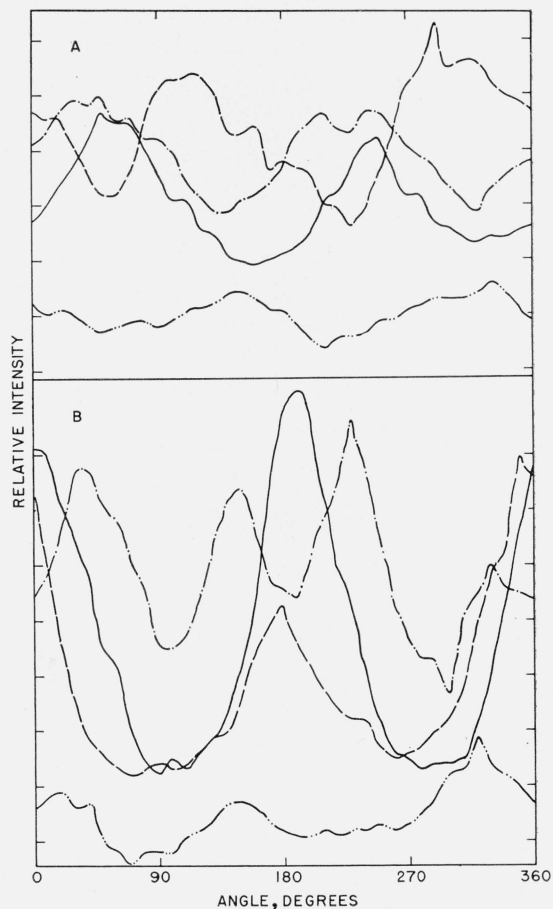

FIGURE 5. *Relative intensity of diffraction around circumference of rings for sample III.*

A, X-ray beam parallel to plane of rubber sheet; B, X-ray beam normal to plane of rubber sheet.
Curves correspond to the following *d*-spacings: ——, 6.30; ·——, 5.00; — —, 4.24; ·· —, 3.77. The unit of relative intensity is 0.1.

An inspection of the X-ray patterns indicates that around certain of the rings the intensity of the diffracted X-ray is not uniform. This is seen most clearly in the patterns for samples III and IV (fig. 3). If the crystallites were randomly oriented with respect to a fixed direction in the sample, then the intensity of the diffraction should be uniform around the circumference of any given ring. The non-uniformity of the rings indicates that the crystallites have a preferred orientation in the sample. To further confirm the reality of the orientation, a direction in the sample was fixed as reference, and the diffraction photographs were taken with the X-ray beam successively normal to and parallel to this direction. The results shown in figures 2 and 3 indicate that the diffraction patterns depend on the position of the beam relative to the sample, and hence the non-uniformity of the rings is caused by diffraction from oriented crystalline planes.

To further illustrate these observations, the variations of the relative intensity around the circumferences of the diffraction rings of interest are plotted in figures 4, 5, and 6. For all the samples the major variation in intensity occurs in the rings corresponding to reflections from the 200 and 120 planes which are the only diffracting planes parallel to the direction of the chain axis. In sample II the effect is smaller than in the other samples, but the results are reproducible and well within the experimental limits of the photometering procedure. Figures 5 and 6 indicate quite clearly the non-uniformity of the rings and the changes in intensity that occur when the position of the X-ray beam

relative to the sample is altered. More than two diffraction photographs for each sample are required to establish the detailed nature of the orientation. It is hoped that an analysis of the more detailed X-ray work now in progress will lead to a more quantitative description of the orientation. For present purposes, the establishment of the fact that the crystallites in stark rubber are oriented suffices.

5. Discussion

It has been suggested that there are two forms of crystalline natural rubber and that one of these forms is the higher-melting stark rubber [14,15]. However, the X-ray analyses of a sample of stark rubber by Barnes [12], the results of which are corroborated by the present work, indicate that the structure of the crystals in stark rubber is identical in all major respects with the structure of crystals induced by either stretching or cooling the amorphous rubber. Hence, polymorphism does not appear to be an explanation of the nature of stark rubber.
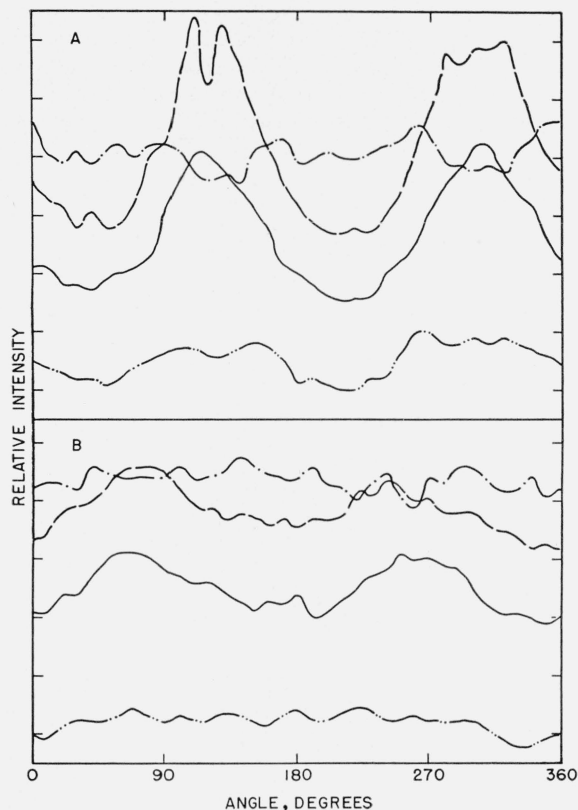
FIGURE 6. *Relative intensity of diffraction around circumference of rings for sample IV.*

A, X-ray beam parallel to plane sheet; B, X-ray beam normal to plane of sheet. Curves correspond to the following d-spacings: —, 6.30; ·—·, 5.00; — —, 4.24; ·· —, 3.77. The unit of relative intensity is 0.1.

Wood and Bekkedahl [4] observed that when natural rubber is crystallized by cooling, the melting temperature depends very markedly on the temperature of crystallization if rapid heating rates are employed. This led them to make the suggestion that the melting temperature observed in stark rubber is caused by a relatively high crystallization temperature. The validity of this suggestion is difficult to establish directly from experiment. Natural rubber crystallized at 14° C has a melting temperature of 28° C; to accomplish the crystallization at this temperature requires about 200 days. Crystallization at any higher temperature takes such an unduly long time as to make the necessary experiments a practical impossibility. However, in this temperature range the crystallization rate is governed mainly by the steady-state nucleation rate [3]. The extreme slowness of the rate of production of stable nuclei indicates that the difference between the crystallization temperature and the equilibrium melting temperature must be small, so that the equilibrium melting temperature is being approached. From studies of the crystallization rates of other polymers in this region [3], it is thought unlikely that the assigned value of the equilibrium melting temperature of undeformed natural rubber can be raised more than a few degrees. Thus the possibility that the high melting temperature of stark rubber results solely from a high temperature of crystallization seems somewhat remote.

Pickles [16] noted some years ago that under the same conditions of storage certain bales of natural rubber seemed more prone to become hard than others. This led him to believe that some factor in the previous history of the material, particularly the plantation processing, might be causing the observed effect. The X-ray diffraction patterns indicate quite clearly that a characteristic of stark rubber is the orientation of its crystallites. It is not difficult to envisage how the plantation processing might eventually cause the presence of oriented crystallites. After coagulation of the latex, the amorphous rubber is rolled into sheets, and the sheets are then stacked one upon another in an irregular manner. The bale of rubber is then subjected to a rather large simple compressional stress, which is eventually removed. It is likely that this process can cause the amorphous segments to be preferentially oriented, and because of the high viscosity of natural rubber, this orientation can persist for long periods of time at the usual storage temperatures when the external stresses are removed. Orientation of the chain segments will facilitate the rate of crystallization at temperatures where the crystallization rate is prohibitively slow for undeformed rubber.

Because the crystallites are oriented, the amorphous regions that connect them can also be oriented to some extent. If this orientation were maintained during the fusion process, then a crystalline segment would gain less entropy on melting than in the case where the amorphous region was completely random. Then for an oriented system the fusion would have to occur at a higher temperature than in an unoriented system. If the orientation were maintained, this could explain the higher melting temperatures observed for both stark and racked rubber. However, it does not explain the observed peculiarities of the melting process nor the fact that all the stark rubbers have melting temperatures in approximately the same range. Furthermore, if unvulcanized natural rubber is crystallized by stretching and the external force maintained during the subsequent heating (thus maintaining the orientation during the fusion), much higher melting points are observed [17].

After stark rubber has been melted and then recrystallized by cooling, the melting temperatures that one subsequently observes are the same as for normal natural rubber. Thus the initial heating of the stark rubber samples to temperatures slightly above the tabulated T_m causes the orientation to disappear. During the heating process, and within the time scale of the experiments, a temperature may be reached where the segmental motions of the amorphous rubber become sufficiently great to cause a return to their more probable configurations. If this temperature is greater than the equilibrium melting temperature of the unoriented semicrystalline polymer, T_m°, then crystallites that were thermodynamically stable above T_m° due to the orientation will now become unstable and will melt. Because

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the fusion process causes an increase of the specific volume, the uniqueness of the melting behavior of stark rubber can be explained by the fact that at a temperature several degrees below the assigned T_m, but above T_m°, the relatively large volume changes with time are a manifestation of the slow rearrangement of the amorphous regions. Because the increases of the volume with time occur at all temperatures between 35° C and T_m, the rearrangement process is extremely temperature sensitive. It would then be expected that as long as no external forces are maintained, melting will occur in approximately the same temperature interval, irrespective of the amount and type of orientation.

It is interesting to note that in their study of the dimensional changes of unvulcanized natural rubber, using interferometric techniques, Wood, Bekkedahl, and Peters [18] observed that plastic flow occurred in the vicinity of 40° C. Similarly, Smith and Saylor [19] noted that the birefringence in natural rubber caused by induced strains (not crystallites) disappeared in the range 40° to 55° C. With the observation that the crystallites in stark rubber are oriented and with the above explanation for the melting behavior, it is clear that the assigned values of T_m are not thermodynamically significant. The assignment of an equilibrium melting temperature to the unoriented semicrystalline natural rubber would thus appear to be justified [8].

In principle, other crystalline polymers should display this behavior. Its common observation in natural rubber is due to a combination of circumstances. The high viscosity of amorphous natural rubber allows the orientation of the chain segments to be maintained for relatively long periods of time in the temperature range of interest. The lower limit of this temperature range is set by T_m°. As long as T_m° is sufficiently low, as in the case of natural rubber, for the rate of amorphous segmental rearrangement to be slow, this phenomenon should be observed.

6. Stark Rubber Prepared in a Laboratory

As stark rubber has not been prepared heretofore under controlled conditions, it is now thought possible to prepare it in the laboratory. One should seek conditions such that the crystallization occurs while the rubber is being deformed, and that when the external stresses causing the deformation are removed, the orientation will persist at temperatures above T_m°. Carson [20] was able to produce stark rubber by deforming a sample in a rubber-cutting machine and storing under slight pressure for nearly a year at temperatures between 5° and 35° C.

Early attempts in this direction were made by Smith and Saylor [19], who compressed a sample of amorphous natural rubber between aluminum plates for 6 months at −25° C. The resulting crystallites displayed definite orientation, but the melting point was only 10° to 11° C. A further experiment was performed wherein the rubber was compressed in a steel block at a pressure of 1,000 atmospheres and held at −25° C for 2 weeks. Upon removal of the sample and on subsequent heating to room temperature, the rubber remained crystalline, and its melting point was found to be about 33° to 34° C.

About 1934 A. T. McPherson and W. L. Holt, then in the NBS Rubber Section, pressed some smoked sheet between aluminum-faced boards and then wrapped it very tightly with strips of stretched vulcanized rubber. Although the details of the thermal history of the sample are not precisely known, the sample was kept most of the time in the temperature range 0° to 14° C. The sample was examined in May 1954, and found to possess an appreciable amount of crystallinity at 25° C. Dilatometric observations indicate that its melting temperature is greater than 35° C. In figure 7,A, the X-ray diffraction photograph of this sample indicates very marked orientation.

A portion of a bale of sprayed latex, which contained about 95 percent of rubber hydrocarbon and whose X-ray diffraction pattern indicated it to be completely amorphous, was passed through a mill several times and rolled into a tight cylinder. After storage at 25° C for 2 years, it was reexamined and found to have lost some of its rubberlike elasticity. Its X-ray diffraction pattern is given in figure 7,B. Although the intensity of the diffraction pattern is not great, it is evident that the crystallites are oriented. Because of the small amount of crystallinity developed, the melting point could not be determined precisely, but it is in the range 35° to 40° C. A portion of the roll was placed in a vacuum press at 28° C and subjected to a compressive load of 50 tons. The result of this treatment, as illustrated in figure 7,C, was to further increase the amount of both crystallinity and orientation. The melting temperature of this specimen is 42° ±2° C.

A small section of cast-iron pipe, which was closed at the lower end and threaded at the upper end, was completely filled with the amorphous sprayed latex. The upper end of the pipe was closed with a threaded cap and tightened completely, thus subjecting the rubber to a compressive stress with orientation of certain regions brought about in the process of tightening the cap. After storage at 14° C for 18 months, portions of the rubber had crystallized. They maintained their crystallinity after warming to room temperature. The X-ray diffraction pattern is illustrated in figure 7, D, and its high orientation is apparent. The melting temperature was difficult to determine accurately, but it is in the vicinity of 35° C.

Stark rubber can thus be prepared in the laboratory by a variety of methods. Those discussed above are certainly not exhaustive, and other methods should be equally successful. The essential requirement seems to be orientation during the crystallization. This is a necessary, but not a sufficient, condition. In the course of this study several methods that were attempted have not as yet yielded stark rubber. For example, holding samples at 14° C in simple extension at various extension ratios caused crystallization. However, when the tensile
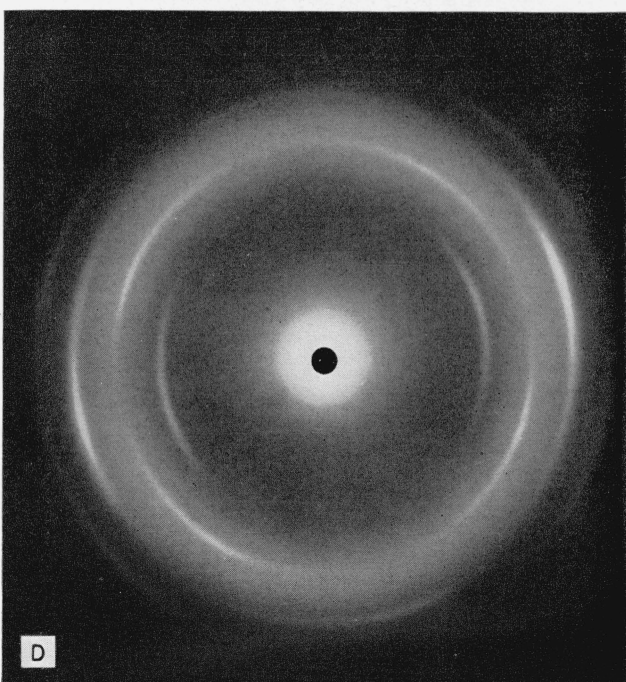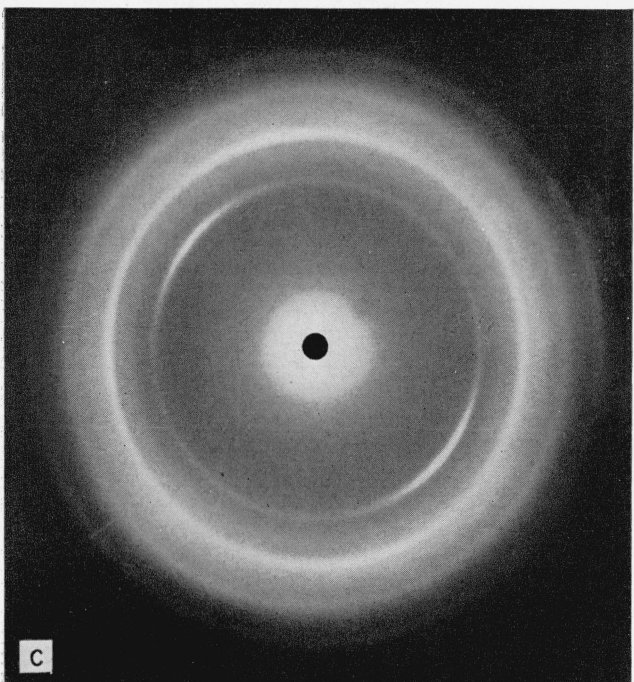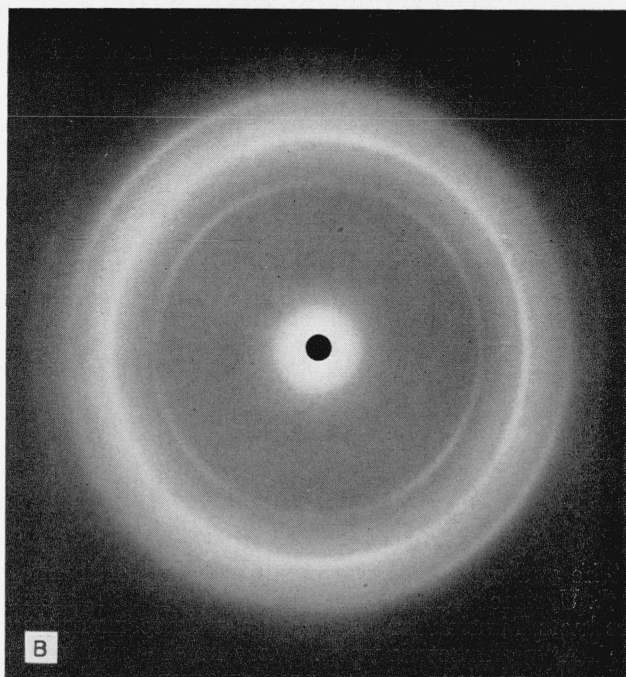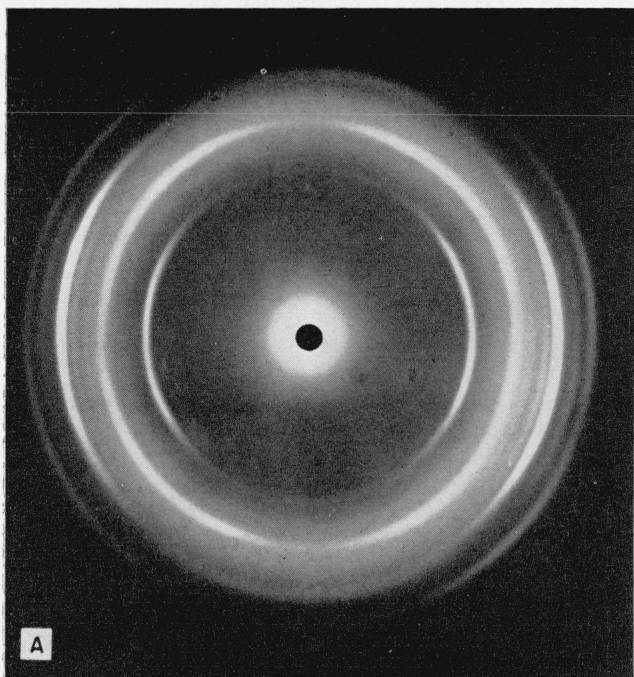
FIGURE 7. *X-ray diffraction photographs of laboratory-prepared stark rubber.*

A, Prepared by McPherson and Holt; B, sprayed latex milled and rolled; C, cold-molding of sample B; D, prepared in cast-iron pipe.

force was removed and the sample heated to 28° C, the crystallinity completely disappeared. Similarly, it is known from the work of Goppel and Van Rossem [21], that calendering rubber causes the crystallites that are formed on cooling to be oriented. However, when these experiments were repeated at the National Bureau of Standards a completely amorphous X-ray diffraction pattern was obtained at 25° C. The difference between these results and those of Goppel and Van Rossem can be attributed to the fact that the diffraction photographs of the latter investigators were taken in the temperature range 17° to 20° C [22]. The apparent failure of the methods just described cannot be taken as final. It is possible that after longer times, when greater amounts of crystallinity have developed, the rubber may become stark by the methods outlined.

Some additional samples of stark rubber are being studied, and other laboratory methods of preparation are being explored. The melting behavior of some of the stark-rubber samples reported in the present paper is being reexamined, using much slower heating rates.

WASHINGTON, November 4, 1954.

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