chloro compound and to supply the water escaped together with the ligroin. The reaction mixture was heated now under an upward condenser for additional three hours at 95–98° and extracted with benzene. Fractional distillation of the product gave 4.3 g. of semi-solid mass boiling at 185–205° and 10 mm. This was recrystallized from methanol–ligroin and colorless prisms melting at 132.5–133.5° resulted. Mixtures of the product with a known sample of 2,3-dianisylbutane, which we had prepared[9] from 2,3-dianisyl-1,3-butadiene, melted without depression. As 2,3-dianisylbutane described by Dodds, *et al.*,[10] is said to have the m. p. 87–88°, our substance seems to be an isomeric compound, probably of the *meso* form.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.87; H, 8.46.

2,3-bis-(*p*-Methoxy-*o*-tolyl)-butane.—A solution of 10 g. of *p*-vinyl-*m*-methylanisole[7] in 50 cc. of ligroin was saturated with dry hydrogen chloride at −18 to −10° and treated with 5 g. of iron powder in 60 cc. of water as above. After recrystallization from alcohol 1.6 g. or 16% yield of pure colorless plates of the m. p. 142° was obtained.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.91; H, 8.79.

The demethylation of the product with methylmagnesium iodide[5] yielded a free phenolic substance of m. p. 188–189° and the acetylation of the latter compound gave colorless plates of diacetate melting at 164°.

Anal. Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.40. Found: C, 74.67; H, 7.56.

The melting points and other properties of these substances were found to be in accord with those reported by the Hungarian investigators.[6]

3,4-Dianisylhexane.—Twenty-five grams of anethole dissolved in 110 cc. of ligroin was saturated with dry hydrogen chloride. Upon working up the product with 15 g. of iron powder in 150 cc. of water as above, 8 g. of a distillate at 180–210° and 4 mm. was obtained. The first fraction of this vacuum distillation consisted of about 12 g. of anethole which could be employed in the next batch. The product crystallized out from methanol–ligroin and recrystallizations from petroleum ether gave 2.4 g. of colorless plates, m. p. 144°, in accord with the m. p. of the *meso* compound reported in the literature.

When the same procedure was repeated with hydrogen bromide instead of the chloride, the yield of 3.8 g. was obtained.

Anal. Calcd. for $C_{20}H_{26}O_2$: C, 80.50; H, 8.78. Found: C, 80.12; H, 8.51.

3,4-bis-(*p*-Hydroxyphenyl)-hexane (Hexestrol).—Demethylation of 3,4-dianisylhexane with a Grignard reagent yielded colorless plates, m. p. 186°, which value agreed with that of the literature.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.70; H, 8.32.

On acetylation the diacetate was obtained, m. p. 140–141°.

Acknowledgment.—In preparing these reports I and II we are indebted to the Editorial Board of This Journal for the courtesy of checking the literature references since 1941 (except those of Japan) which we are not able to obtain even now in our city.

Summary

Hexestrol and 2,3-bis-(*p*-hydroxy-*o*-tolyl)-butane were prepared by the condensation of hydrochlorides (or hydrobromide) of anethole and *p*-vinyl-*m*-methylanisole, respectively, by the action of metallic iron powder in a water suspension followed by the demethylation.

Kyôto, Japan Received March 24, 1947

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[9] Unpublished result.

[10] Dodds, *et al.*, *Proc. Roy. Soc.* (*London*), **B132**, 83 (1944).

[Contribution from Chemical and Physical Research Laboratories, The Firestone Tire and Rubber Co.]

X-Ray Diffraction Study of Some Synthetic Rubbers at Low Temperatures

By E. E. Hanson and G. Halverson

The use of the powerful X-ray diffraction method for the study of high polymers had its inception in 1925 with the experiments of Katz[1] on natural rubber. He observed that the X-ray diffraction pattern of stretched rubber consisted of a broad halo with a superposed set of discrete spots characteristic of crystallites oriented in the direction of stretching. Hauser and Rosbaud[2] observed that the diffraction pattern of frozen unstretched rubber consisted of sharp concentric rings characteristic of a randomly oriented polycrystalline material. From such X-ray data have been determined the unit cell of the rubber crystallite,[3–7] the arrangement and the shape of the molecular segments in the unit cell and the size and shape of the rubber crystallites.[8,9] In addition, the X-ray diffraction method has yielded important information regarding the structures of a host of other polymers,[10] particularly those of the plastics and fibers, most of which give well developed fiber diagrams. Examples of synthetic rubber polymers which crystallize upon stretching are neoprene,[11] polyisobutylene,[12] and thiokol.[13] However, it is unfortunate that the majority of the synthetic rubber polymers give only an amorphous halo and therefore the X-ray diffraction method can give correspondingly little information regarding the structures of these polymers.

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[1] J. R. Katz, *Naturwissenshaften*, **13**, 37 (1925).

[2] E. A. Hauser and P. Rosbaud, *Kautschuk*, **3**, 17 (1927).

[3] E. A. Hauser and H. Mark, *Kolloid Chem. Beihefte*, **22**, 63 (1926).

[4] H. Mark and G. von Susich, *Kolloid-Z.*, **46**, 11 (1928).

[5] W. Lotmer and V. H. Meyer, *Monatsh.*, **69**, 115 (1936).

[6] E. Sauter, *Z. physik. Chem.*, **B36**, 405 (1937).

[7] A. A. Morss, This Journal, **60**, 237 (1938).

[8] S. D. Gehman and J. E. Field, *J. Applied Phys.*, **15**, 371 (1944).

[9] Review articles covering the field are: S. D. Gehman, *Chem. Rev.*, **26**, 203 (1940); C. W. Bunn, "Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946.

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[11] C. J. B. Clews, *Proc. Roy. Soc.* (*London*), **A180**, 100 (1942).

[12] C. S. Fuller, C. J. Frosch and N. R. Pape, This Journal, **62**, 1905 (1940).

[13] J. J. Trillat and R. Tertran, *Compt. rend.*, **219**, 395 (1944); *R. Chem. Tech.*, **19**, 1090 (1946).

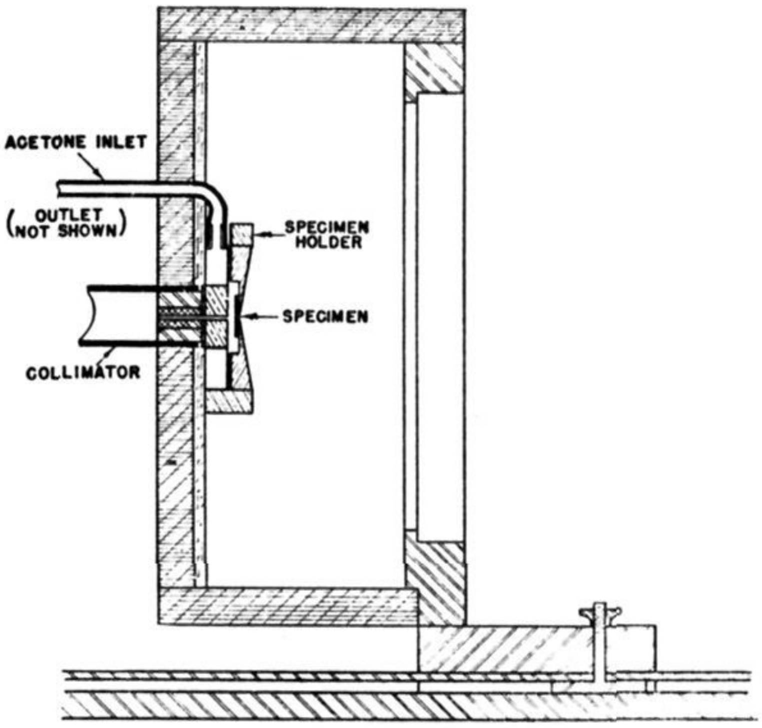

Fig. 1.—Low temperature X-ray camera.

The work to be discussed was an attempt to cause whatever regularity was present in some "non-crystalline" synthetic rubber polymers to show up in the X-ray diffraction experiment. The raw polymers were used because they can be elongated to a greater extent than the vulcanizates and because the cross-linking of molecular chains by vulcanization probably interferes with crystallization. Since the thermal motions of the molecular segments tend to prevent the relatively weak intermolecular forces from forming aggregates, the temperature of the polymer was reduced as much as possible prior to stretching. G. von Susich[14] found that the fibering of natural rubber upon stretching depended upon temperature, the amorphous fraction being favored by raising the temperature. Hauser and Mark[3] suggested freezing stretched natural rubber. In order to prevent relaxation of the elongated specimen during X-ray exposure, the specimen was frozen in an alcohol–Dry Ice bath immediately after stretching and the specimen was maintained at a temperature of −65 to −70° during the X-ray exposure. Essentially the same technique had been used in 1928 by Hock and Barth[15] in their study of polydimethylbutadiene, but their data did not permit calculations of the Bragg spacings of the diffraction lines.

The following steps were used in the manipulation of the specimens. 1. Cool the specimen to a temperature at which it may still be readily elongated. 2. Quickly stretch the sample to as high an elongation as possible. 3. Immediately freeze it at a temperature of −70° in an alcohol–Dry Ice bath, and 4. Obtain the X-ray exposure at a temperature of −65 to −70° in a special camera.

At the temperature of −65°, all of the polymers except emulsion polymerized butadiene were stiff enough to remain in their extended condition without clamping. To determine the elongation of the specimen, the length at −70° was measured, the specimen was allowed to warm up to room temperature, and the length of the relaxed sample was again measured. Conceivably, a small amount of permanent set was present in the relaxed state, and so the percentage of elongation recorded in the present data may be somewhat low.

Apparatus

A General Electric X-ray diffraction unit was used with either a copper target or a molybdenum target tube. The copper radiation was filtered by nickel foil, and the molybdenum radiation was filtered with a commercial zirconium oxide filter.

A sketch of the low temperature camera is shown in Fig. 1.

A box was made from 0.25-inch bakelite plates. One side was clamped firmly to the post supporting the collimating pinhole assembly. The film holder and the other four sides were mounted separately on a post which could be moved along the track. The five sides of the box were constructed to telescope over the sixth side (clamped to collimator assembly). Thus the specimen-to-film distance could be varied at will from 0 to 15 cm. The specimen holder consisted of a copper block with a recess cut away to receive a removable copper disc to which the specimen was clamped. The copper block was constructed with a 0.25-inch square channel, through which chilled acetone was pumped. The acetone circulating and cooling system is shown in Fig. 2. It consists of an automobile fuel pump, which was run continuously, a copper coil immersed in a Dry Ice–acetone-bath, a manually controlled needle valve for rough adjustment of the flow through the tubing by-passing the cooling coil, a second needle valve which was driven by a reversible motor controlled by a Micromax controller–recorder, and in the line a bimetallic spiral thermostat which acted as a limit switch. In this study, the automatic controls were not used because the specimen tempera-

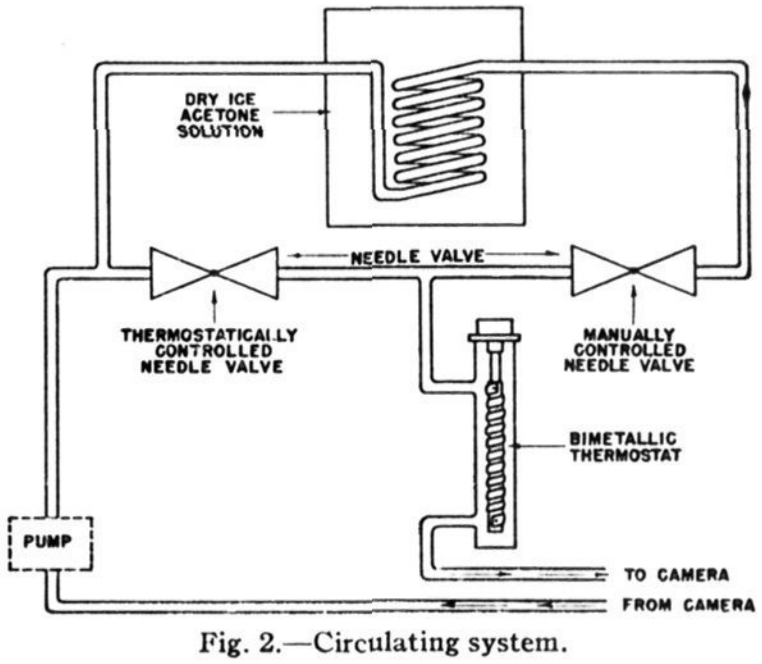

Fig. 2.—Circulating system.

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(14) G. von Susich, *Naturwissenshaften*, **18**, 915 (1930).

(15) L. Hock and W. Barth, *Z. Physik. Chem.*, **134**, 271 (1928).

ture was kept as low as possible. The specimen temperature was measured with a thermocouple clamped in the copper block close to the path of the X-ray beam.

Results

The following polymers were studied: emulsion and sodium polymerized butadiene, emulsion polymerized 75/25 butadiene–styrene copolymer, emulsion and sodium polymerized isoprene and emulsion polymerized dimethylbutadiene. Morris and Jordon[16] found that a tread-type vulcanizate of GR-S produced weak maxima on the equator of the X-ray diagram. Hock and Barth[15] observed a crystallization of polydimethylbutadiene when the raw polymer was stretched at a low temperature, but their patterns were incomplete and no spacings were given. Evidence for the crystallization of polydimethylbutadiene was also found by Katz and van Campen.[17] They observed that the X-ray pattern of a stretched sample of an especially prepared methyl rubber vulcanizate contained a single pair of equatorial spots (*d* = 4.3 Å.) and two elongated arcs on the meridian (*d* = 3.2 and 2.3 A., respectively). No evidence has been found in the literature[18,19] to indicate that any of the other polymers listed above show any ordering in the stretched condition.[20]

Polybutadiene-emulsion Polymerized.—Figure 3 is an X-ray diffraction pattern of emulsion polymerized butadiene elongated 500% at a temperature of −70°. The very intense equatorial arcs occur at a Bragg distance of 4.06 Å. and the second pair of weak equatorial arcs at 2.33 Å. On the meridian two very weak arcs are observed at 2.26 and 1.16 Å., respectively. The two arcs were interpreted as second and fourth order reflections, respectively. The arc at 2.26 Å. could possibly be due to two unresolved spots near the meridianal axis. The limiting values for the spacings of hyperbolic layer lines that can be drawn through the arc are 4.58 and 4.8 Å. The arc at 1.16 Å. lies close to the axis and the corresponding layer line of fourth order gave an identity period of 4.8 Å. which agrees with the largest calculated value derived from the 2.26 Å. arc. Since the planar zig-zag *trans* chain has an identity period of 5.05 Å., this constitutes evidence for the *trans* structure of polybutadiene in accordance with the statements of Meyer[21] and of Mark.[22]

The equatorial spacings are interpreted as the distances between the extended molecules. Now, the equatorial spot corresponding to the larger intermolecular distance is by far the more intense of the two. The degree of this difference is indicated in Figure 4 which is an X-ray pattern taken under similar conditions but with a shorter exposure time and a greater specimen to film distance. The second equatorial arcs and the meridianal arcs would be too weak to be registered by this exposure. Therefore, it seems likely that the extended frozen polymer is composed of an appreciable percentage of amorphous material and a larger percentage of molecules which are divided into two categories of ordering: 1. By far the most numerous of the ordered molecules are lined up in the direction of stretching without forming a three-dimensional lattice. Fuller and Baker[23] refer to this type of ordering as mesomorphic. The very intense equatorial spots are due to scattering from these molecules. 2. The weak equatorial arc at 2.33 Å. and possibly another obscured by the 4.06 Å. intense arc, and the two weak meridianal arcs are due to relatively few crystallites formed of chain segments composed of all 1,4-addition butadiene presumably in the *trans* form.

X-Ray diffraction photographs were also obtained for specimens at zero elongation. At room temperature, the Bragg spacing for the point of maximum intensity of the single amorphous halo was 4.58 Å., which agrees well with Katz[24] value of 4.6 Å. for liquid butadiene. The X-ray diffraction pattern of the unstretched polymer obtained at minus 70° is shown in Fig. 5. Besides the amorphous halo, a sharper ring occurs at a distance of 4.01 Å. which agrees fairly well with the spacing observed for the most intense of the equatorial spots for the stretched specimen. (The ring survived on extraction of the specimen.) It is apparent, therefore, that at the lower temperature there are groupings of parallel molecular segments reminiscent of the smectic state in certain liquids.[21] The amorphous halo has shifted to a lower value, 4.31 Å., as would be expected from the positive coefficient of linear expansion of the polymer.

Polybutadiene—Sodium Polymerized.—A. Saffer and B. L. Johnson[25] using the perbenzoic acid addition method have determined the percentages of 1,4 groups occurring in the polymers referred to in this paper.

They found that the sodium polymer of butadiene contained 40% of 1,4 units as compared with 75% of 1,4 units for the emulsion polymer. Since side groups presumably occur at random along the chain, it is to be expected that the sodium polymer would exhibit much less ordering than the emulsion polymer. That this is true may be seen from Fig. 6 which is the X-ray diagram of the sodium

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(16) R. E. Morris and C. B. Jordan, *Rubber Age* (*N. Y.*), **55**, 161 (1944).

(17) J. R. Katz and P. van Campen, *Chem. Ztg.*, **51**, 53 (1927).

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(19) L. B. Sebrell and A. P. Dinsmore, *R. Chem. Tech.*, **16**, 857 (1941).

(20) L. A. Wood, "Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1946, p. 57.

(21) K. H. Meyer, "High Polymers. Natural and Synthetic High Polymers," Vol. IV, Interscience Publishers, Inc., New York, N. Y., 1942, p. 183.

(22) H. Mark, "The Chemistry of Large Molecules." Interscience Publishers, Inc., New York, N. Y., 1943, p. 61.

(23) C. S. Fuller and W. O. Baker, *Ann. N. Y. Acad. Sci.*, **44**, 329 (1943).

(24) J. R. Katz, *Trans. Faraday Soc.*, **32**, 77 (1936).

(25) A. Saffer and B. L. Johnson, to be published in *Ind. Eng. Chem.*

polymer elongated 470% at −40°. A slight amount of alignment of molecules is observed from the pair of very weak and very extended equatorial arcs. The equatorial arcs occur at a Bragg spacing of 5.85 Å. as contrasted to the main equatorial spacing of 4.06 Å. for the emulsion polymer. The larger interchain distance for the sodium polymer would be expected from the larger amount of side groups present.

The Bragg spacing of the maximum intensity in the halo obtained from the unstretched polymer at room temperature was 5.92 Å. which is considerably higher than the value of 4.6 Å. given by Katz for the liquid monomer. This discrepancy is presumably due to the larger percentage of side groups present in the polymer.

Butadiene–Styrene Copolymer.—Figure 7 is the X-ray pattern of GR-S elongated 600% at minus 50°. The arc at the equator and the arc on the meridian appear at the same distances as for emulsion polymerized butadiene. The inference is, therefore, that polybutadiene crystallites occur in GR-S. Whether the molecules participating in the formation of these crystallites also contain styrene units outside of the crystallites is a question. No other evidence of regularity was found in the polymer.

It was found that milling the polymer tended to destroy the fiber pattern. A milling time of twelve minutes reduced the X-ray pattern to only the amorphous halo with only a slight enhancement at the equator. This may indicate that essentially pure chains of polybutadiene occur in the copolymer and that the milling process disperses them so thoroughly in the copolymer that they can no longer become associated in ordered aggregates.

Polyisoprene.—An additional factor promoting disorder in the polymer chains has been added in the case of polyisoprene, namely, the possibility of heterogeneous mixtures of head-to-head and head-to-tail additions of the monomer units. There is also the possibility of 3,4 addition. Therefore, it would be expected that these polymers would show less ordering than polybutadiene.

Figure 8 is the X-ray diffraction pattern of emulsion polymerized isoprene stretched 580% at −55°. The only sign of ordering is the weak pair of extended arcs appearing at 4.86 Å.

Figure 9 is the diffraction pattern of the sodium polymer stretched 600% at +10°. Here, too, only a weak equatorial arc appears at 6.53 Å.

The emulsion polymer contains 90% of 1,4 units and the sodium polymer 45% of 1,4 units. The inter-chain distances, therefore, increase with increasing percentages of side groups.

The room temperature X-ray patterns of the unstretched sodium and emulsion polymers consist of halos occurring at 5.95 and at 5.10 Å., respectively. The value given by Katz for the liquid isoprene halo is 4.9 Å. The agreement between the values for the monomer and for the polymer, therefore, is seen to be improved by a higher proportion of 1,4 additions in the polymer.

Polydimethylbutadiene (Emulsion).—Since polydimethylbutadiene is constructed of structurally symmetrical monomer units, the only hindrances to its regularity of structure are the presence of side groups and the possibility of mixtures of *cis* and *trans* forms. The emulsion polymer is known to be composed of about 85% 1,4 addition units. Therefore, it should exhibit a regularity of structure comparable with that of emulsion polymerized butadiene.

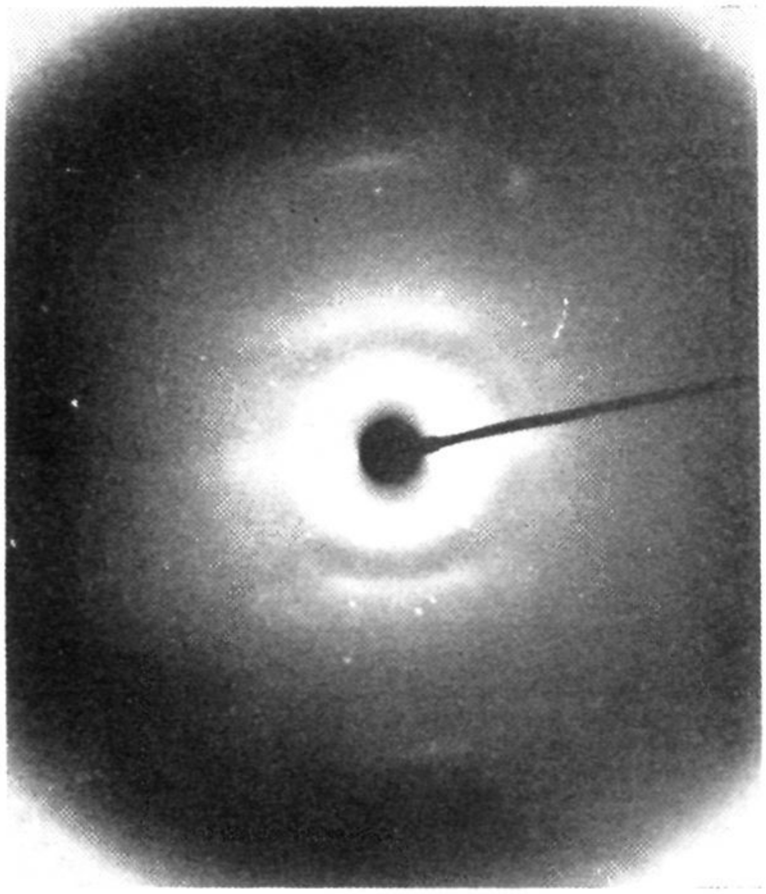
Figure 10 is the X-ray pattern for emulsion polydimethylbutadiene stretched 670% at 0°. A single strong arc is present at 5.3 Å. on the equator and three weak arcs on the meridian at 3.30, 2.24 and 1.17 Å. The 1.17 Å. arc is extremely weak and is not reproducible on a photographic print. Katz and van Campen's[17] values of 2.3 and 3.2 Å. for meridianal arcs correspond quite well with the above values, but their value of 4.3 Å. for the equatorial spot is in disagreement. Our value of 5.3 Å. for the equatorial spot agrees well with their value of 5.4 Å. for the amorphous halo.

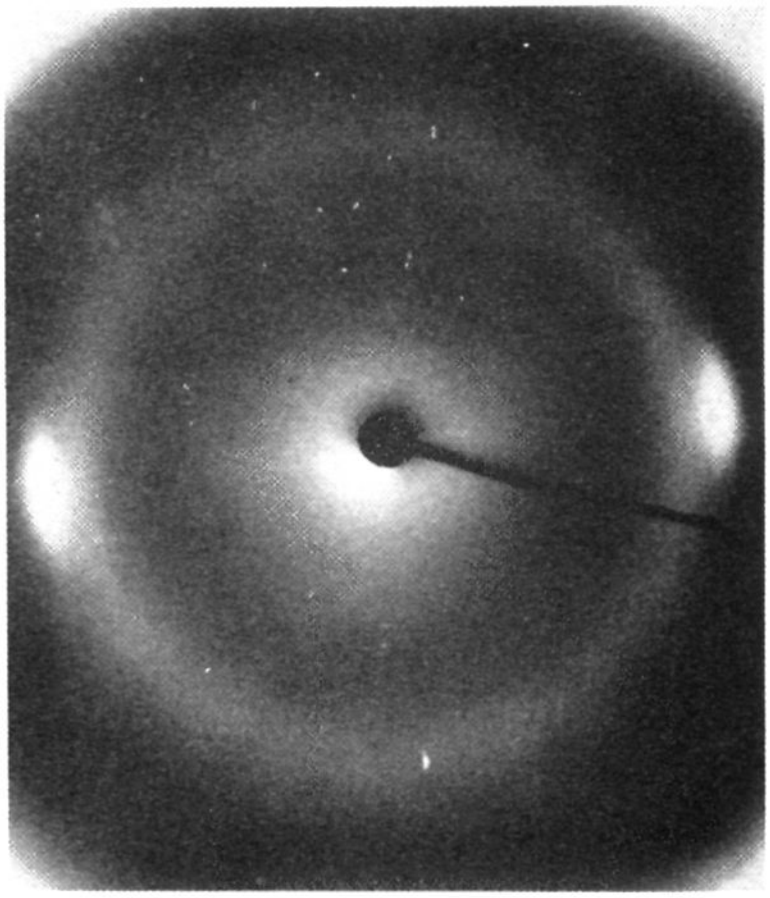
It was found that when the polymer was kept at 0° for one hundred and forty-four hours and elongated 650% the equatorial spot at 5.3 Å. was partially resolved into two spots at 4.8 and 5.8 Å. and a third extremely weak arc appeared on the equator at 3.9 Å. The same pattern could also be obtained after three or more cycles of retraction and elongation at 0° without prolonged storage at this temperature.

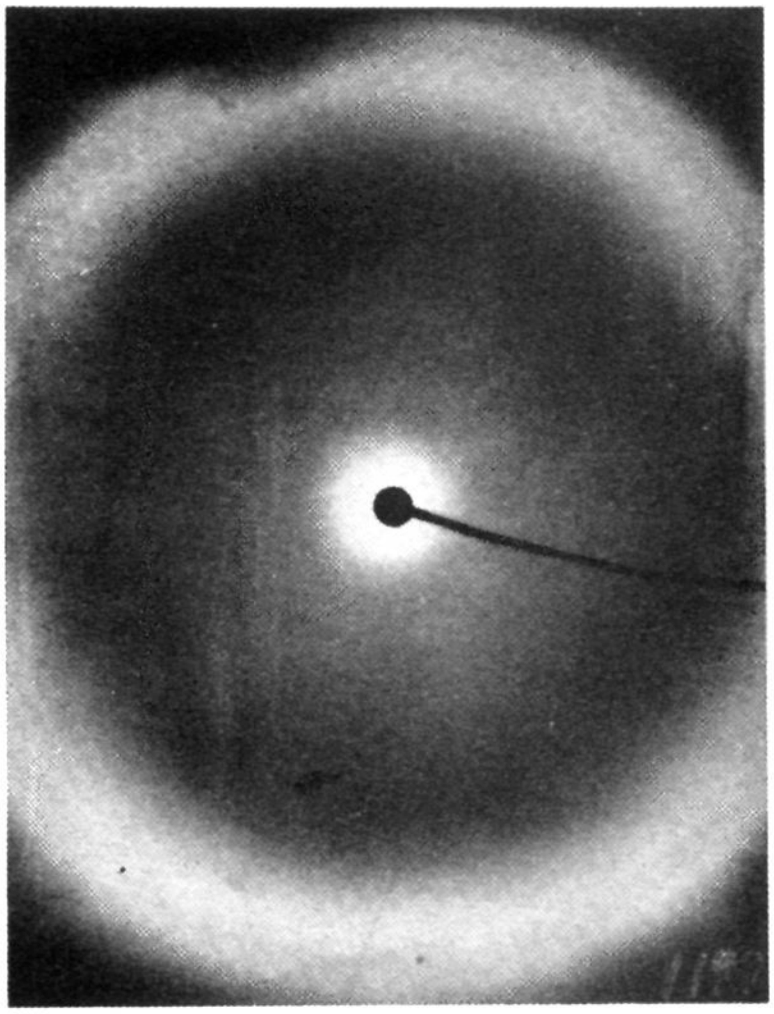
A tentative interpretation may be made of the meridianal arcs in terms of the identity period of the molecule. If the arcs occurring at the Bragg spacings of 3.30, 2.24 and 1.17 Å. are interpreted as reflections of order 2, 3 and 6, respectively, and if the possible layer-line hyperbolae are drawn through the arcs, the possible identity periods are 6.75 to 8.16, 6.72 to 8.26 and 7.38 to 9.0 Å., respectively. Therefore the values which are common to all three arcs lie between 8.16 and 7.38 Å. This would correspond to a *cis* structure for the polymer.

Since the equatorial spots are very intense, we can draw the same conclusions as we did for emulsion polybutadiene. A relatively small number of crystallites of 1,4 addition, polydimethylbutadiene, probably with a *cis* structure, exist together with a relatively large number of molecules containing side groups and which are lined up in the direction of stretch, but exhibit no other characteristics of regularity. In addition there is quite a large amount of the polymer which is amorphous in character.

The maximum in the halo obtained from the unstretched polymer at room temperature corresponds to a Bragg spacing of 5.76 Å. The value given by Katz for the liquid monomer is 5.3 A.







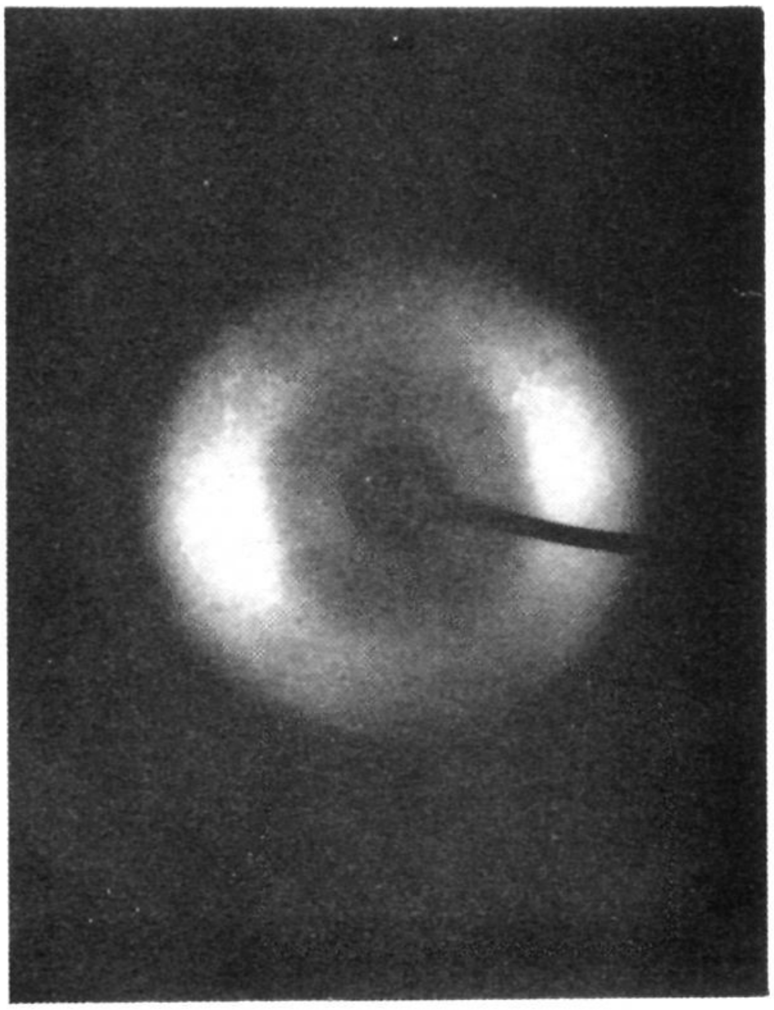
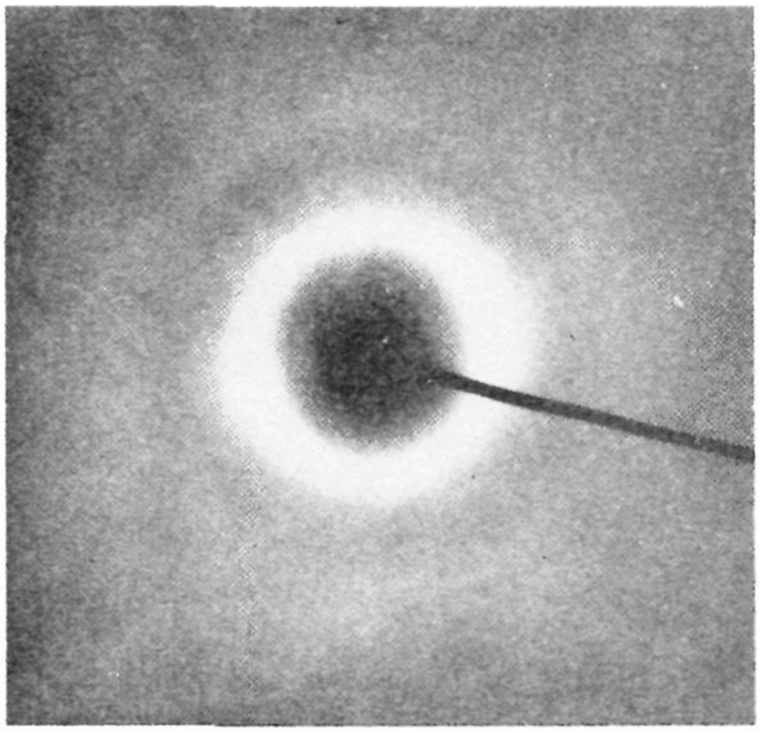
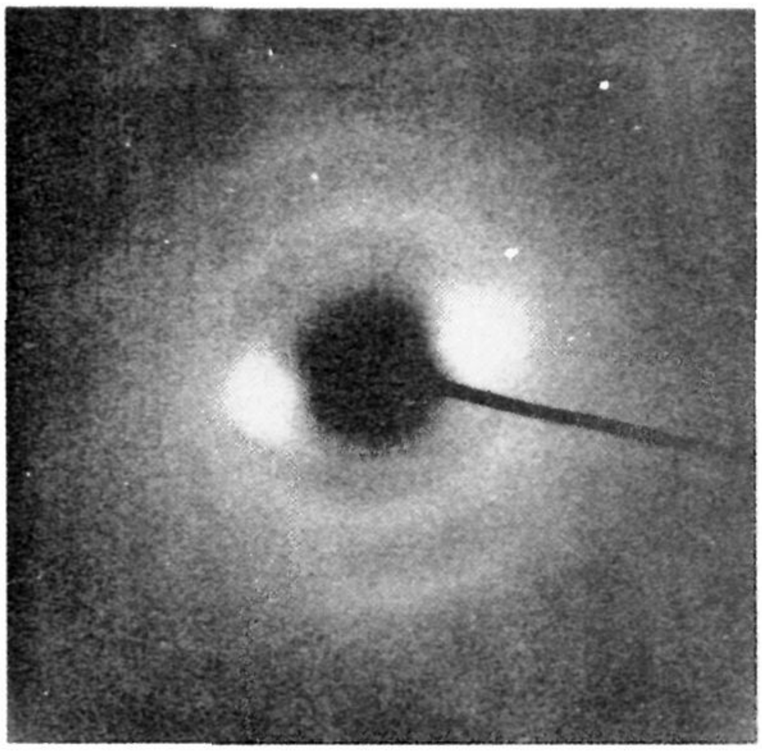
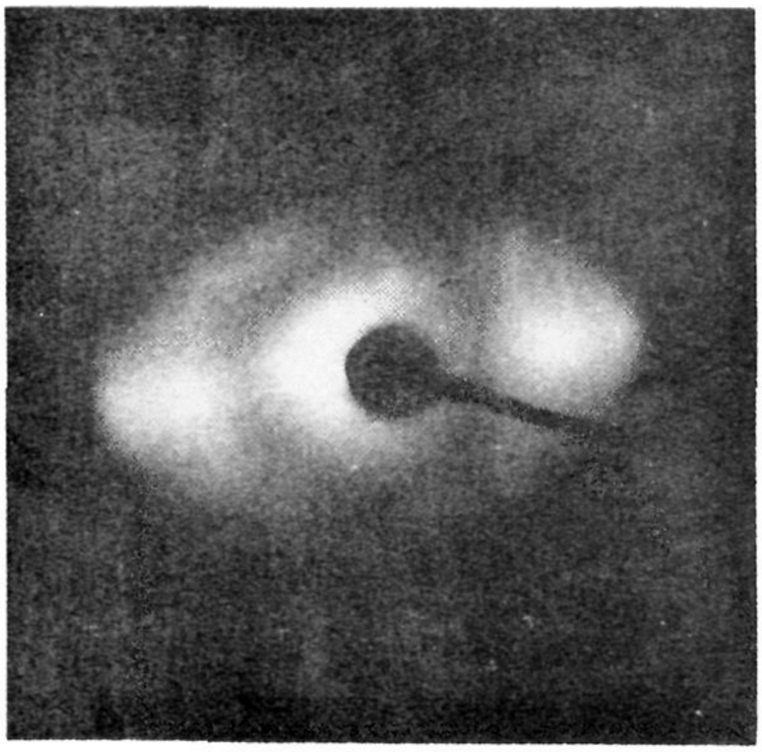
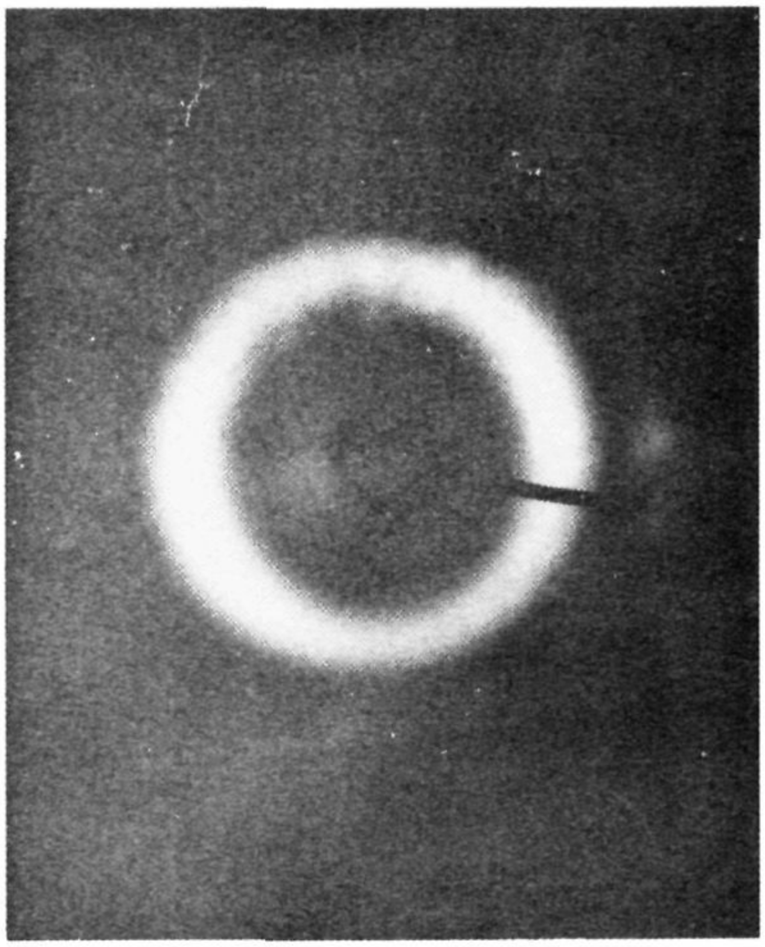


Fig. 3 (*top left*).—Emulsion polybutadiene stretched 500% at −70°. Fig. 4 (*top right*).—Emulsion polybutadiene stretched 600% at −30°. Fig. 5 (*bottom left*).—Emulsion polybutadiene—0% elongation, −70°. Fig. 6 (*bottom right*).—Sodium polybutadiene stretched 470% at −40°.









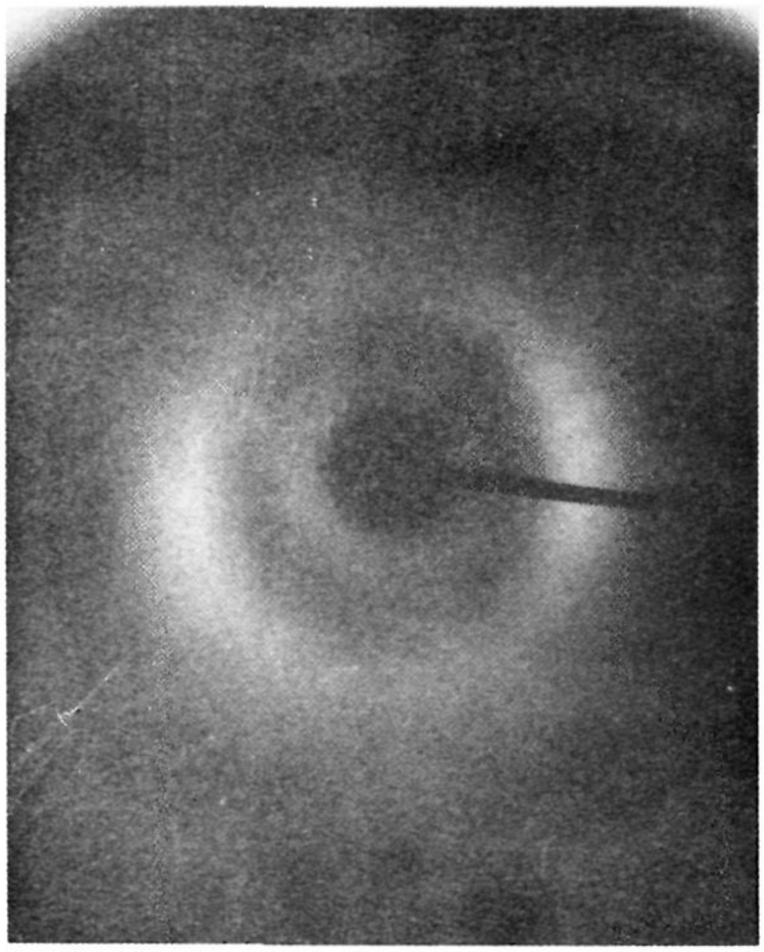


Fig. 7 (*top left*).—GR-S stretched 600% at −50°. Fig. 8 (*top right*).—Emulsion polyisoprene stretched 550% at −55°. Fig. 9 (*bottom right*).—Sodium polyisoprene—600% elongation and 10°. Fig. 10 (*center left*).—Emulsion polydimethylbutadiene—extended 670% at 0.0°. Fig. 11 (*bottom left*).—Emulsion polydimethylbutadiene, elongated 650% at 0°. Stored at 0° for one hundred and forty-four hours.

The difference is probably due to the presence of the side groups in the polymer.

Discussion

The above X-ray diagrams were not necessarily obtained under the most ideal conditions. Long, Singer and Davey[26] have shown that there is a lag in the fibering of rubber after stretching. Since the specimens were elongated by hand, it is not likely that the optimum conditions for fibering prevailed. The effects of temperature and of time will also need to be studied more thoroughly than we could in this preliminary report. However, the results obtained with the technique indicate that it has value in the study of "non-crystalline" high polymers.

The observation was made that the Bragg spacing of the halo obtained from the relaxed specimen at room temperature depended upon the quantity of side groups in the molecules. Similarly, the spacings of the equatorial arc for the stretched specimens increased with increasing percentages of side groups. These values are tabulated in Table I. It may be possible to develop a method for calculating the percentages of side groups present in the polymer from such X-ray data.

TABLE I

CORRELATION OF SIDE GROUPS WITH INTERMOLECULAR SPACING

Polymer	1,4-addition, %	Amorphous halo, Å.		Principal equatorial arc, Å.
		Polymer	Monomer	
Emulsion–butadiene	75	4.6	4.6	4.06
Sodium–butadiene	40	5.9		5.85
Emulsion–isoprene	90	5.1	4.9	4.86
Sodium–isoprene	45	6.6		6.53
Emulsion–dimethylbutadiene	85	5.7	5.3	5.30

It is not the purpose of this paper to discuss the correlation of physical properties and structures. However, it was observed that emulsion polybutadiene retained its rubber-like extensibility down to −70°, but that sodium polybutadiene was rigid at −70° and barely extensible at −60°. This constitutes evidence that increasing the side groups (and probably branching) would seem to raise the brittle point temperature. It would seem, from comparisons of the brittle points of rubber (*cis* structure), and balata (*trans* structure), that the *cis* structure should have the better cold properties. However, emulsion polybutadiene with a probable *trans* configuration has the lowest brittle point of all the rubbers.

Acknowledgments.—It is a pleasure to thank the Synthetic Rubber Group, especially Dr. R. L. Bebb, for supplying us with polymers, Dr. M. J. Brock for having the samples extracted, and Drs. B. L. Johnson, A. Saffer, F. W. Stavely and J. W. Liska for discussions of the problem.

Summary

A certain amount of ordering has been found in the "noncrystalline" synthetic rubbers which were studied by the use of the technique of cooling the raw polymer before it is elongated and freezing it immediately after stretching to prevent relaxation. Polybutadiene and polydimethylbutadiene whose monomer units were structurally symmetrical displayed the greatest degree of ordering. The presence of a high percentage of 1,2 units in sodium polymerized butadiene destroyed almost all of the ordering observed in the emulsion polymer. GR-S and emulsion polybutadiene showed the presence of small amounts of crystallites presumably of 1,4 addition polybutadiene, probably the *trans* form. Polydimethylbutadiene showed the presence of crystallites presumably of 1,4 addition in the *cis* form. The intermolecular distance between the extended chains increased with increasing amounts of side groups. The departure of the Bragg angle spacing of the amorphous halo from the corresponding quantity for the liquid monomer increased with increasing amounts of side groups.

AKRON, OHIO RECEIVED MAY 28, 1947

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[26] J. D. Long, W. E. Singer and W. P. Davey, *Ind. Eng. Chem.*, **26**, 543 (1934).