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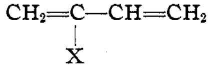
Acetylene Polymers and their Derivatives. V. The Polymerization of Bromoprene (Third Paper on New Synthetic Rubbers)

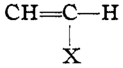
BY WALLACE H. CAROTHERS, JAMES E. KIRBY AND ARNOLD M. COLLINS

Chloroprene (I, X = Cl) polymerizes spontaneously to yield a rubber-like product,[1] and the speed of this transformation is roughly 700 times greater than the analogous transformation of isoprene. The present paper deals with the behavior of bromoprene[2] (I, X = Br), and the results may be summarized in the statement that it shows no significant qualitative differences from chloroprene, although its speed of polymerization under most conditions appears to be somewhat greater.



$CH_2{=}\underset{X}{\underset{|}{C}}{-}CH{=}CH_2$

I



$CH{=}\underset{X}{\underset{|}{C}}{-}H$

II

In connection with the behavior of these materials the following analogies are of interest. Vinyl chloride and vinyl bromide (II, X = Cl and Br) polymerize spontaneously yielding products of very high molecular weight,[3] but this behavior is not shown by propylene, which polymerizes only in the presence of special catalysts or under drastic conditions and then yields products having only moderately high molecular weights. The haloprenes (I) bear the same structural relationship to isoprene that the vinyl halides bear to propylene. Thus the very powerful activating effect of a single halogen atom on ethylene is also manifested in butadiene (when the halogen atom is on the β-carbon). The rate of polymerization is of great importance in studying the behavior of dienes since a high rate not only makes it possible to obtain experimental results in a reasonable length of time, but it permits one to extend the observations over a wide range of conditions. It becomes possible then to recognize the different types of reactions involved in the spontaneous polymerization and to obtain data on the way in which these different types of reactions are affected by changes in the conditions. Data of this type on chloroprene have already been presented, and it will be useful to review them briefly (with some extensions) and to make comparisons with those now available for bromoprene and for other dienes.

The polymerization of chloroprene leads to the four well defined and qualitatively distinct types of polymers shown in the chart.

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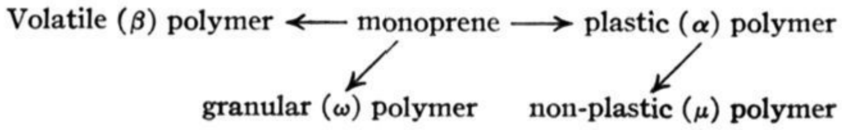
(1) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).

(2) Carothers, Collins and Kirby, *ibid.*, **55**, 786 (1933).

(3) Staudinger, Brunner, and Feisst, *Helv. Chim. Acta*, **13**, 805 (1930).



The influence of various conditions on each of these reactions is indicated in Table I.

TABLE I

INFLUENCE OF CONDITIONS ON THE POLYMERIZATION OF CHLOROPRENE

Condition	Monoprene to β-polymer	Monoprene to α-polyprene	α-Polyprene to μ-polyprene	Monoprene to ω-polyprene
Temperature	+++	+	+	Autocatalytic, initiated by strong ultraviolet light and by metal surfaces
Pressure	+	++	+?	
Light	0	++	0?	
Oxygen	0	+++	++?	
Antioxidants	0	− − −	±[a]	

[a] Certain substances commonly classified as antioxidants (*e. g.*, phenyl-β-naphthylamine) act as inhibitors; others (*e. g.*, benzidine) act as accelerators: + accelerates, 0 no effect, − inhibits.

Of these different types of polymers the most important are the α- and the μ-polyprenes since the former corresponds to unvulcanized rubber and the latter corresponds to vulcanized rubber.

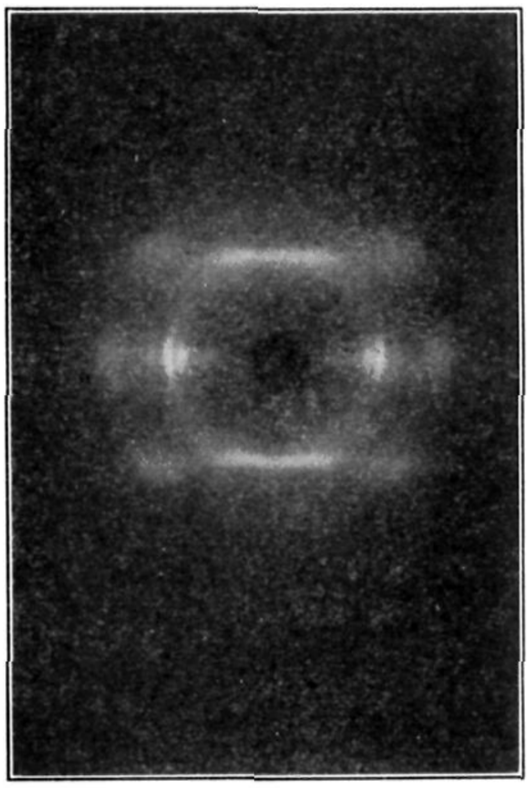


Fig. 1.—x-Ray diffraction pattern of μ-polybromoprene (from latex) stretched 500%.

The μ-polyprene is the final product of the spontaneous polymerization of chloroprene; the α-polyprene is an intermediate step in the formation of the μ-product. Isolation of the α-polymer free of μ-polymer is possible only when the reaction is conducted under certain conditions: the temperature must not be too high, since elevated temperature accelerates the transformation of α-polymer to μ-polymer more than it accelerates the formation of α-polymer from monomer; the reaction must not be too slow, since most inhibiting influences have a greater decelerating effect on the formation of the α- than on the μ-product; moreover, very slow reaction frequently leads to the formation of the ω-polymer. Light and pressure both appear to have a greater accelerating effect on the formation of the α-polyprene than on the transformation of this into the μ-polyprene.

The β-polymer, a terpene-like material, is an undesirable by-product in the rubber synthesis. In the chloroprene polymerization the production of β-polymer becomes appreciable only at temperatures higher than are necessary to bring about a rapid formation of α-polyprene. Butadiene, isoprene and dimethylbutadiene polymerize very slowly; to get the transformation to proceed at a reasonable rate, elevated temperatures are generally used, and this results in the formation of relatively large amounts of β-polymer.

The ω-polychloroprene is also a useless product; it is made up of discrete rubber-like particles (irregular globules) which are non-plastic and not even swelled by rubber solvents. The formation of this polymer is autocatalytic. When a speck of the ω-polymer appears (or is introduced) in a specimen of incompletely polymerized chloroprene, the entire specimen is soon more or less completely converted into the ω-polymer. The formation of nuclei of the ω-polyprene is favored by strong ultraviolet light and by metal surfaces (*e. g.*, sodium, potassium, mercury, iron, copper and aluminum). The opportunities for the formation of such nuclei are also increased by a long reaction time under any particular set of conditions. Similar polymers, frequently described as cauliflower-like masses, have been obtained from isoprene, butadiene and dimethylbutadiene, and one suspects that they may be the forms in which the polymers of these dienes are most frequently obtained. The very slow rate of the polymerization of these dienes would be especially favorable to the formation of ω-polymer.

The term rubber-like is vaguely used to cover a multitude of the most diverse properties, and the literature of synthetic rubber is exceedingly obscure. Most of the agencies that are available to hasten the very slow polymerization of isoprene and butadiene are such as have been found in the case of chloroprene to affect more strongly the conversion of the α- into the μ-polymer than the formation of the α-polymer. One may expect therefore that the isolation of a true α-polyprene[4] from the isoprene and butadiene products will present especial difficulties. So far as we are aware no clear disclosure has ever been made of an α-polyprene from isoprene or from butadiene. However, when isoprene is subjected to a pressure of 12,000 atmospheres until 30% of the isoprene has polymerized, the polymer is at least 90% soluble in ether.[5] If the reaction is allowed to proceed further until 80% of the isoprene has polymerized, the product is completely insoluble.[5,6] Thus the formation of a completely vulcanized

(4) With the aid of swelling agents, softeners, and lubricants it is possible to confer a certain amount of plasticity on μ-polychloroprene. It is also possible to obtain from chloroprene plastic polymers that, on being heated, lose their plastic properties very incompletely or not at all. The material that we refer to as α-polychloroprene is an inherently plastic, *polymerizable* polymer; its plastic properties are completely lost and its elastic properties become fully developed when it stands or is heated.

(5) Conant and Tongberg, THIS JOURNAL, **52**, 1667 (1930).

(6) According to observations made by Dr. H. W. Starkweather in this Laboratory, isoprene polymers prepared in this manner are also completely non-plastic.

rubber-like product without the aid of sulfur is by no means peculiar to chloroprene. In fact the differences between the behavior of chloroprene and the behavior of other dienes appear to be differences of degree rather than differences of kind.

The Spontaneous Polymerization of Bromoprene.—A sample of bromoprene when allowed to stand at the ordinary laboratory conditions in a stoppered flask containing a small amount of air becomes noticeably more viscous after twelve to fifteen hours. As the reaction proceeds, the viscosity increases; after about five days the sample sets to a stiff, elastic jelly containing a considerable amount of unchanged bromoprene. Usually after eight to ten days all of the bromoprene has reacted, but the time required varies considerably in different experiments. The product has a density of about 1.74, and this is 24% greater than the density of the bromoprene. (The increase in density in the formation of μ-polychloroprene is about 28%.)

This product, μ-polybromoprene, corresponds in its properties with the μ-polychloroprene already described. It is tough, resilient, and elastic but harder than the analogous product from chloroprene. On standing it gradually undergoes further change: it becomes still harder and less extensible and the resemblance to soft vulcanized rubber pretty largely disappears although it still remains very tough and retains considerable elasticity and resiliency. These changes in the nature of the product are due, at least in part, to a progressive action of air and they can be retarded by the application of antioxidants to the surface of the sample. μ-Polybromoprene is similar to μ-polychloroprene in its behavior toward solvents. It is greatly swelled by chloroform, carbon tetrachloride and aromatic hydrocarbons but remains practically unchanged after prolonged immersion in alcohol, ether, or aliphatic hydrocarbons such as gasoline.

α-Polybromoprene.—The preparation of an α-polybromoprene (plastic polymer) presents no difficulties. A sample of bromoprene was exposed to light from a Cooper–Hewitt lamp at 25°. After twenty-four hours 50% of the material had been converted into polymer. (This rate is about 40% greater than that usually obtained with chloroprene under the same conditions.) The product was an exceedingly viscous, yellow sirup. When it was mixed with a large volume of alcohol the α-polybromoprene was precipitated as a soft, plastic mass. This product showed no tendency to resist permanent deformation and sheeted out very readily on cold rolls. Two per cent. of phenyl-β-naphthylamine was worked into the plastic mass to prevent spontaneous conversion into an elastic polymer.[7] The sample was compounded with about 5% of its weight of zinc oxide and heated in a mold at 120 to 125° for twenty minutes. The product was non-plastic, strong, resilient and extensible (500 to 700%). However,

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[7] Ref. 1, p. 4219.

compared with a similar product from chloroprene it was somewhat lacking in snap, and its permanent set was rather high. It also showed a greater tendency to "freeze." After about two hours at ordinary temperatures it became very stiff, but the original pliability was restored when it was heated to 80° for a few minutes.

The Polymerization of Bromoprene in Aqueous Emulsion.—Like chloroprene, bromoprene is readily dispersed in water and the resulting smooth emulsion polymerizes with great rapidity to form a stable latex. The preparation and polymerization of such an emulsion is illustrated in the following example.

Twenty-five cubic centimeters of 2% aqueous sodium oleate in a wide-mouthed bottle was surrounded by a bath of ice and water. Two drops of triethanolamine was added to the solution, and then, with vigorous stirring, 25 g. of bromoprene. A smooth, milk-like emulsion resulted. After the mixture had stood in the ice-bath for five hours an aliquot portion was removed and poured into a large volume of alcohol. The weight of the precipitate thus obtained indicated that 78% of the bromoprene had polymerized. Under the same conditions chloroprene is only about 20–30% polymerized. The bromoprene emulsion described above was transferred to a refrigerator. After seventeen hours, more than 95% of the bromoprene had polymerized. Five cubic centimeters of 3% ammonium hydroxide was added to stabilize the emulsion and a small amount of an aqueous dispersion of phenyl-β-naphthylamine (2% on the rubber content) added to function as an antioxidant. The resulting latex was very stable.

As in the case of polychloroprene, the dispersed particles in the synthetic latex derived from bromoprene correspond more closely to the μ- than to the α-polymer. Nevertheless, when the latex is coagulated by the addition of acids, the particles coalesce and cohere very firmly. The coagulum is at first soft and plastic, but it quickly becomes tough, elastic and non-plastic. Homogeneous, coherent films are obtained by allowing the water to evaporate from a thin layer of the fluid latex on a plate of porous porcelain. The films are readily stripped from the plate and the removal of the water can be completed by drying them for a few hours in an oven at 80°. Such films are exceedingly tough and more resistant to tearing than analogous films prepared from chloroprene latices. A typical specimen had a breaking strength of 160 kg./sq. cm. and an elongation at break of 740%. (The elongation of similar polychloroprene films is usually about 800%.) The films exhibited the high permanent set and the tendency to freeze or stiffen already referred to in connection with the vulcanized α-polybromoprene. Like the latter, they were non-plastic and did not dissolve but merely swelled in chloroform and benzene.

β-Polybromoprene.—The conversion of bromoprene into a volatile liquid polymer (β-polybromoprene) occurs under conditions similar to those already described for chloroprene.[8] A sample of bromoprene containing about 5% of thiodiphenylamine, a substance which powerfully inhibits the conversion of the haloprenes to rubber-like polymers, was

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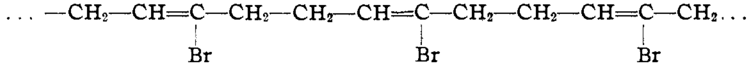
(8) Ref. 1, p. 4211.

heated in a sealed tube at 80° for five days. When the resulting black oil was poured into alcohol a small amount of a black tar separated. From the alcohol there was obtained by distillation a small amount (about 15%) of a yellow oil boiling at 104 to 110° at 11 mm. It had a fragrant, terpene-like odor very similar to that of β-polychloroprene and was a mild lachrymator. It showed no tendency to polymerize further.

ω-Polybromoprene.—The formation of ω-polybromoprene, like the formation of ω-polychloroprene, occurs under conditions which result in very slow polymerization. For example, samples of bromoprene containing 0.2% of phenyl-β-naphthylamine or 0.5% of tetramethylthiuram disulfide and 0.3% of sulfur slowly became more viscous and, after two to six weeks, a white deposit having a crystalline appearance began to form. After formation of this substance had started, conversion of the whole mass was complete in a few days. The product turned dark brown in color on standing in air. ω-Polybromoprene is soft, opaque and noncoherent, while ω-polychloroprene is a mass of glistening, hard, rubbery granules. Like ω-polychloroprene, it is not swelled by benzene.

The Structure of Polybromoprene.—Evidence has already been presented for concluding that α-polychloroprene is precisely analogous to natural rubber in its chemical structure. The analogies between polychloroprene and polybromoprene are sufficiently close to justify the assumption of a similar structure (III) for the latter compound. The x-ray evidence is especially interesting. The fact that μ-polychloroprene when stretched furnishes a fiber diffraction pattern has already been disclosed.[1] Polybromoprene shows a similar behavior, but it furnishes an even sharper pattern (Fig. 1).[9] So far as we are aware, it has not been possible to obtain fiber diagrams from any other synthetic rubbers, and this fact perhaps justifies the conclusion that polychloroprene and polybromoprene are more regular in their molecular structure than any other known synthetic rubbers.

(III)


$$\ldots\text{—CH}_2\text{—CH=}\underset{\underset{\text{Br}}{|}}{\text{C}}\text{—CH}_2\text{—CH}_2\text{—CH=}\underset{\underset{\text{Br}}{|}}{\text{C}}\text{—CH}_2\text{—CH}_2\text{—CH=}\underset{\underset{\text{Br}}{|}}{\text{C}}\text{—CH}_2\ldots$$

Summary

The polymerization of bromoprene is closely analogous to that of chloroprene, but somewhat more rapid. Spontaneous polymerization yields as the final product μ-polybromoprene, which resembles vulcanized rubber but is more dense than rubber or μ-polychloroprene. A plastic (α) polybromoprene is readily isolated from partially polymerized bromoprene, and it is converted to the μ-product by the action of heat. At elevated temperatures in the presence of inhibitors a volatile liquid (β) polymer is

(9) The x-ray data will be discussed in more detail in a future paper by Dr. A. W. Kenney.

formed. ω-Polybromoprene, a granular, insoluble, rubber-like mass, is produced under conditions that lead to very slow polymerization.

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Studies in the Chlorophyll Series. IX. Transformations Establishing the Nature of the Nucleus

BY J. B. CONANT AND C. F. BAILEY

In previous papers of this series, the view has been put forward that the fundamental nucleus of chlorophyll *a* and the related phaeophorbides and chlorins is a reduced porphyrin ring. Such a formulation was largely based on spectroscopic data obtained at low temperatures.[1] We have now been able to obtain very convincing evidence of the correctness of this hypothesis by showing that a typical chlorin (chlorin *f*) can be oxidized to a porphyrin.

The dehydrogenation of chlorin *f* can be brought about either by the action of potassium ferricyanide on an alkaline solution at room temperature (the reaction is very rapid) or by the action of air on a hot alkaline solution of the complex metal salts of the chlorin. The latter method of converting chlorins to porphyrins has been used by Fischer in reoxidizing the "synthetic chlorins" prepared by reduction of the porphyrins.[2] It is clear that chlorin *f* is entirely analogous and is a reduced porphyrin. Since in chlorin *f* the side chain attached to the bridge has been removed, the failure of chlorin *e* to be so readily oxidized to a porphyrin can be attributed to the presence of the other functional groups. The number of hydrogen atoms present in chlorin *f* in excess of a porphyrin can be taken quite definitely as two, since one or three is excluded by valency considerations and four seems excluded by the analyses of chlorin *f* and its ester. The found and calculated percentages of hydrogen in the dimethyl ester and the free chlorin are as follows (paper IV): ester, found 7.05, 6.9, calcd. dihydro 7.04, tetrahydro 7.37; free chlorin, found 6.3, 6.6, calcd. dihydro 6.67, tetrahydro 7.02.

Chlorin *f* is a dibasic acid containing no group on a bridge atom, since it is readily converted to rhodoporphyrin by reduction with hydrogen iodide and reoxidation. However, the porphyrin which is formed from it by direct dehydrogenation is not rhodoporphyrin but an isomeric porphyrin which we shall designate as isorhodoporphyrin. It is identical with the

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[1] Conant and Kamerling, THIS JOURNAL, **53**, 3522 (1931). Since the publication of this paper, the measurements of Kistiakowsky and Arnold there referred to have been published [*ibid.*, **54**, 1713 (1932)]. A comparison of the ultraviolet absorption spectra at low temperature of benzene and cyclohexadiene (Fig. 2, K. and A.) with the absorption spectra of aetioporphyrin and chlorin *e* (Figs. 1 and 3, C. and K.) also at low temperature shows in a very striking way the resemblance of the porphyrin-chlorin relationship to that of benzene *vs.* cyclohexadiene.

[2] Fischer and Helberger, *Ann.*, **471**, 285 (1929).