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## ACETYLENE POLYMERS AND THEIR DERIVATIVES. II. A NEW SYNTHETIC RUBBER: CHLOROPRENE AND ITS POLYMERS

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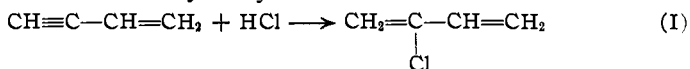
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Study of the reactions of vinylacetylene, a compound which has become available through discoveries described in the preceding paper,<sup>1</sup> has led to the synthesis of a series of new analogs and homologs of isoprene. The present paper is concerned with one of the simplest of these, namely, chloro-2-butadiene-1,3 (I). This compound is especially interesting for the following reasons. It is easily prepared in quantity in a state of purity; it differs structurally from isoprene only in having a chlorine atom instead of a methyl group; like isoprene it reacts with itself to yield a synthetic rubber; but the transformation occurs with much greater velocity than in the case of isoprene; and the product is distinctly superior to natural rubber in some of its properties.

In order to recognize the analogy in structure and behavior which exists between isoprene and chloro-2-butadiene-1,3, we call the latter compound *chloroprene*, and this name also serves to distinguish it from other chlorobutadienes that will be described in future papers.

**Preparation of Chloroprene.**—Chloroprene is obtained by the addition of hydrogen chloride to vinylacetylene



Other products, which will be described in future papers, are also formed by the action of hydrogen chloride on vinylacetylene under certain conditions; but under the conditions indicated in the following example, chloroprene is practically the only product.

Fifty grams of cold vinylacetylene is placed in a pressure bottle containing a thoroughly chilled mixture composed of 175 g. of concd. hydrochloric acid (sp. gr. 1.19), 25 g. of cuprous chloride, and 10 g. of ammonium chloride. The bottle is placed in a water-bath the temperature of which is held at approximately 30°, where it is shaken for a period of four hours. The contents of the bottle are placed in a separatory funnel, the lower aqueous layer is drawn off, and the oily layer is washed with water, dried with calcium chloride, mixed with a small amount of catechol or pyrogallol and distilled *in vacuo* through an efficient column provided with a refrigerated dephlegmator and receiver. Pure chloroprene is thus obtained in yields of about 65% of the theoretical based on the vinylacetylene applied. Some vinylacetylene is recovered in the

<sup>1</sup> Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, 53, 4197 (1931).

distillation. The yields can be considerably improved if the chloroprene is separated from the reaction mixture by steam distillation *in vacuo* (100–250 mm.).

**Physical Properties and Analysis.**—Chloroprene is a colorless liquid with a characteristic ethereal odor, somewhat resembling ethyl bromide. It is miscible with most of the common organic solvents, but only slightly soluble in water. Some of its other properties are boiling point,<sup>2</sup> 59.4° at 760 mm., 46.9° at 500 mm., 40.5° at 400 mm., 32.8° at 300 mm., 6.4° at 100 mm.; vapor pressure,  $\log_{10} v. p. (\text{mm. Hg}) = -1545.3/T(\text{abs}) + 7.527$ ; calculated molal latent heat of evaporation, 7,090 cal.; density,  $d_{20}^{20}$  0.9583; refractive index,  $n_c^{20}$ , 1.4540,  $n_D^{20}$ , 1.4583,  $n_F^{20}$ , 1.4690.

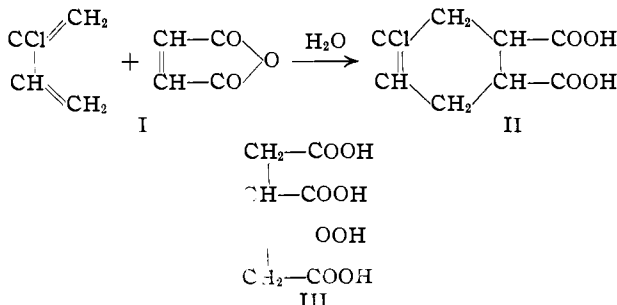
Found	M <sub>c</sub> 25.06	M <sub>D</sub> 25.26
Calcd.	24.67	24.66
Difference	0.39	0.60

Viscosity at 25°, 0.394 centipoise.

*Anal.* Calcd. for C<sub>4</sub>H<sub>3</sub>Cl: C, 54.25; H, 5.69; Cl, 40.06; mol. wt., 88.5. Found: C, 54.37; H, 5.95; Cl, 39.51, 38.81; mol. wt. (in freezing benzene), 89.0, 89.0.

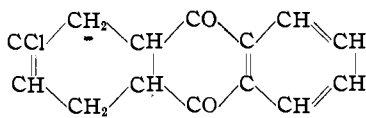
**Chemical Properties and Proof of Structure.**—The structure of chloroprene as chloro-2-butadiene-1,3 is established by its analytical composition and by the following reactions.

It reacts readily with maleic anhydride and yields, after hydrolysis with water, a crystalline product to which we assign the structure chloro-4-tetrahydro-1,2,3,6-phthalic acid (II). The chlorine atom of this product, in accordance with its assumed structure, is very resistant to the action of concentrated boiling alkali, and oxidation with boiling nitric acid yields a crystalline compound identical in melting point and composition with the known acid, butane- $\alpha, \beta, \gamma, \delta$ -tetracarboxylic acid (III).

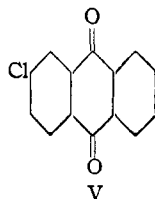


Chloroprene further reacts readily with naphthoquinone, and the primary product, which presumably has the structure chloro-2-tetrahydro-1,4,4a,9a-anthraquinone-9,10 (IV), is smoothly oxidized by air in the presence of alkali to  $\beta$ -chloroanthraquinone (V). The identity of this is established by the method of mixed melting point.

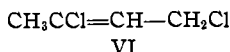
<sup>2</sup> These data are based on vapor pressure measurements made with an isoteniscope by Dr. H. W. Starkweather.



IV



V



VI

In view of the recent studies of Diels and Alder<sup>3</sup> this result decisively demonstrates the presence in chloroprene of a pair of conjugated double bonds, and it fixes unequivocally the position of the chlorine atom.

In chloroform solution chloroprene readily adds approximately two atoms of bromine before substitution begins. It rapidly decolorizes alkaline permanganate solution. In the presence of cuprous chloride it reacts with aqueous hydrochloric acid. The reaction consists in 1,4-addition and the product is dichloro-1,3-butene-2 (VI), which will be described in a future paper. The chlorine atom of chloroprene is very firmly bound. Only traces of chloride ion appear on boiling with alcoholic silver nitrate, alcoholic sodium hydroxide, or pyridine.

**Reaction of Chloroprene with Maleic Anhydride. Preparation of Chloro-4-tetrahydro-1,2,3,6-phthalic Acid (II).**—21.2 g. of chloroprene was warmed with 19.6 g. of maleic anhydride. The anhydride dissolved readily and when 50° was reached sufficient heat was developed from the reaction to maintain this temperature for some time. After standing overnight the reaction product was boiled with 200 cc. of water to remove unchanged chloroprene and filtered. On cooling stout rectangular plates separated; yield 31.5 g. or 77% of the theoretical; m. p. 171–172° (corr.). Recrystallization from water raised the melting point to 173–175°.

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{O}_4\text{Cl}$ : C, 46.94; H, 4.43; Cl, 17.34; neutral equivalent, 102.3. Found: C, 47.54; H, 4.78; Cl, 17.24, 17.71; neutral equivalent, 103.5.

The acid was boiled with 25% potassium hydroxide for three hours. No significant quantity of chloride ion was produced. This indicates that the chlorine is attached to a double-bonded carbon atom.

**Oxidation to Butane- $\alpha,\beta,\gamma,\delta$ -tetracarboxylic Acid (III).**—A sample (8.2 g.) of the above-described acid was warmed with 30 g. of 70% nitric acid until a rather violent reaction took place with the evolution of nitrogen oxides. The unused nitric acid was removed *in vacuo* and the partly crystalline residue taken up in a small volume of hot water. On cooling a thick mass of flat needles with square ends separated. After a second crystallization, the product melted at 192–193° with effervescence.

*Anal.* Calcd. for  $\text{C}_8\text{H}_6\text{O}_8$ : C, 41.05; H, 4.27; neutral equivalent, 58.5. Found: C, 41.32, 41.46; H, 4.66, 4.67; neutral equivalent, 58.8.

This acid has already been described by Auwers and Jacob<sup>4</sup> and also by Farmer and Warren.<sup>5</sup>

<sup>3</sup> Diels and Alder, *Ber.*, **62**, 2337 (1929).

<sup>4</sup> Auwers and Jacob, *ibid.*, **27**, 1114 (1894).

<sup>5</sup> Farmer and Warren, *J. Chem. Soc.*, 897 (1929).

**Action of  $\alpha$ -Naphthoquinone on Chloroprene. Conversion to  $\beta$ -Chloroanthraquinone.**—To 10 g. of naphthoquinone dissolved in benzene 12 g. of chloroprene was added. The mixture was refluxed for three hours and then allowed to stand overnight. The benzene was removed under reduced pressure, and the residual mass was dissolved in warm alcohol and cooled. A considerable amount of unchanged naphthoquinone separated. This was filtered off. Dilution of the mother liquor with water gave a solid which separated from alcohol in fine needles melting at  $76^{\circ}$ . It was still contaminated with naphthoquinone. It was suspended in alcohol containing a little sodium hydroxide, and air was bubbled through the suspension for twenty minutes. The suspended solid was crystallized three times from amyl alcohol; small needles, m. p.  $209.5^{\circ}$ ; mixed melting point with  $\beta$ -chloroanthraquinone,  $209.5^{\circ}$ .

**Spontaneous Polymerization of Chloroprene.**—The following example is typical of the spontaneous polymerization of chloroprene.

About 40 cc. of chloroprene is placed in a 50-cc. bottle of soda glass, closed with a cork stopper, and allowed to stand at the laboratory temperature (about  $25^{\circ}$ ) in the absence of direct light. After twenty-four hours the viscosity of the sample has considerably increased; after four days it has set to a stiff, colorless, transparent jelly, which still contains a considerable amount of unchanged chloroprene. As the polymerization proceeds further this jelly contracts in volume and becomes more tough and dense. After ten days all the chloroprene has polymerized. We call this product  $\mu$ -polychloroprene to distinguish it from other chloroprene polymers that will be described later in this paper.

**Properties of  $\mu$ -Polychloroprene.**—The product of the above described reaction is a colorless or pale yellow, transparent, resilient, elastic mass resembling a completely vulcanized soft rubber. Its density at  $20^{\circ}$  is about 1.23, and its refractive index ( $n_D^{20}$ ) is about 1.5512. It has a tensile strength of about 140 kg./sq. cm. and an elongation at break of about 800%. It is not plastic; that is, it does not sheet out smoothly on the rolls of the rubber mill nor break down on continued milling. It is not thermoplastic. It swells strongly but does not dissolve in carbon tetrachloride, carbon disulfide, benzene, nitrobenzene, pyridine, aniline, ethyl acetate and ether. Compared with natural rubber the tendency of this material to imbibe gasoline and lubricating oil is very slight. When a stretched sample is immersed in liquid air for a moment and then struck with a hammer it shatters into fibrous fragments.<sup>6</sup>

The properties of the  $\mu$ -polymer vary somewhat depending upon the conditions under which it is formed. When the chloroprene has access to large amounts of air or oxygen during the polymerization the product is dark in color and harder and stiffer than otherwise. The polymer formed at elevated temperature is inclined to be soft and it has a distinct terpene-like odor. This is due to the presence of the volatile  $\beta$ -polymer, which will be described in a subsequent paragraph.

<sup>6</sup> The same behavior has already been observed in rubber by Hock, *Gummi-Ztg.*, **39**, 1740 (1925).



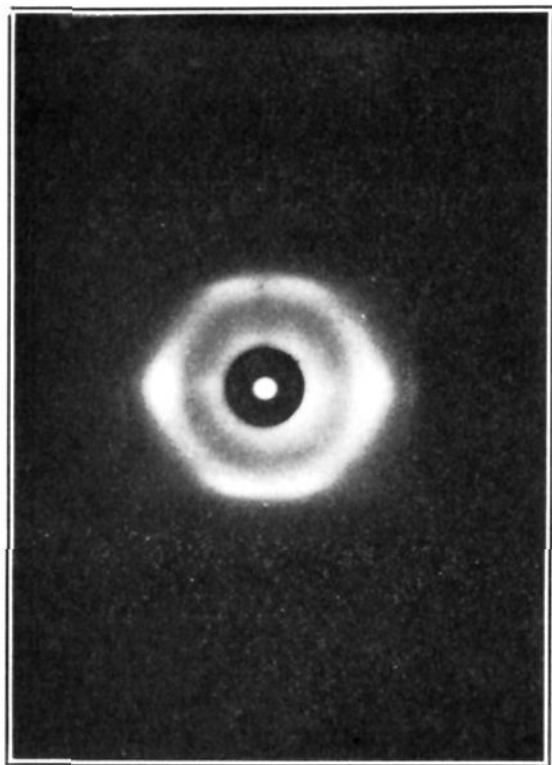


Fig. 1.—x-Ray diffraction pattern of  $\mu$ -polychloroprene (from latex) stretched 500%.

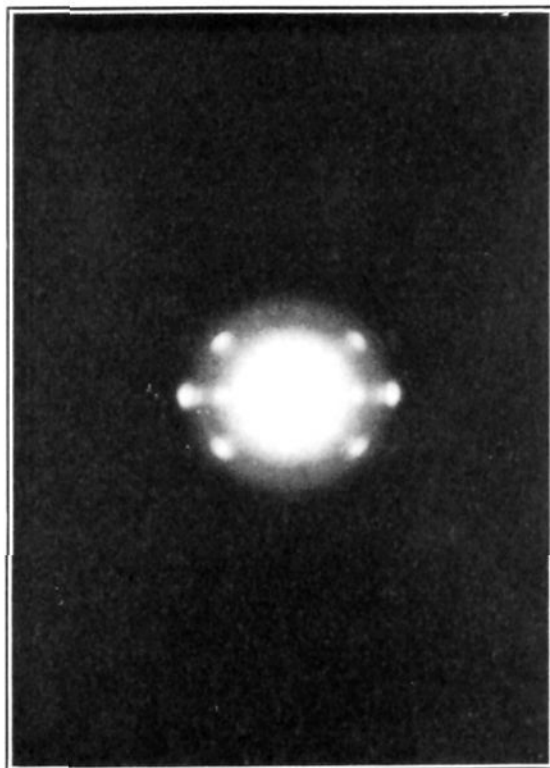


Fig. 2.—x-Ray diffraction pattern of lightly cured smoked sheet rubber stretched 500%.

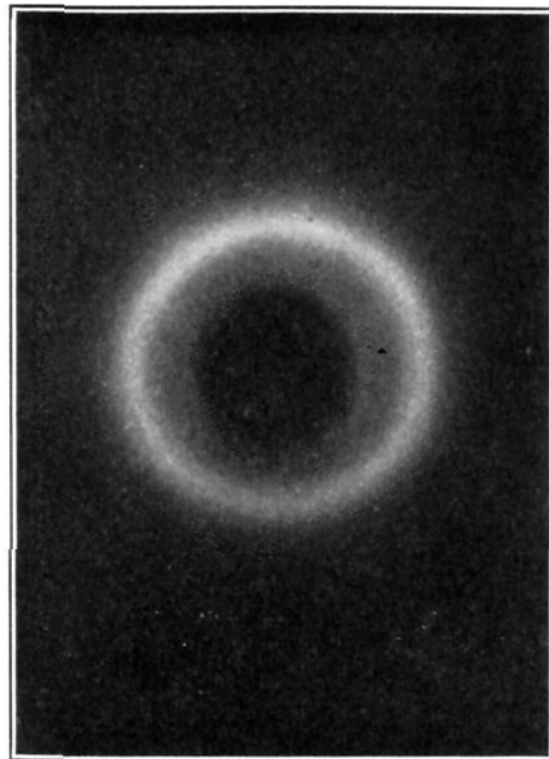


Fig. 3.—x-Ray diffraction pattern of  $\alpha$ -polychloroprene (unstretched).

**x-Ray Diffraction Pattern.**—Although the x-ray diffraction pattern of unstretched rubber shows only a single diffuse ring, characteristic of a liquid or an amorphous solid, stretched rubber shows a point diagram.<sup>7</sup> On the other hand, according to Mark,<sup>8</sup> all synthetic, polymerized products from isoprene or other unsaturated hydrocarbons so far investigated have given, even when stretched, a diffraction pattern analogous to that of a liquid.

It is therefore a matter of considerable interest that the  $\mu$ -polychloroprene described above (as well as the cured plastic polymer described in a later paragraph), when stretched about 500%, exhibits a fully developed fiber diagram showing a number of definite layer lines. One of these diffraction patterns is reproduced in Fig. 1, together with a diagram of stretched rubber (Fig. 2). The identity period along the fiber axis is 4.8 Å. This length corresponds rather closely with the calculated length for one chloroprene unit. The agreement is better if one assumes a *trans* instead of a *cis* configuration since the calculated identity period in a *cis* polypropylene chain is about  $2 \times 4.1$  Å., whereas in a *trans* chain it is about 4.8 Å.<sup>9</sup> Incidentally, 4.8 Å. is exactly the identity period observed for  $\beta$ -gutta percha by Hauser and v. Susich.<sup>10</sup> Unstretched samples of polychloroprene give an amorphous ring (Fig. 3) entirely like natural rubber. The spacing corresponding to this ring is 4.86 Å. We are indebted to Dr. A. W. Kenney for these observations.

**Chemical Properties of  $\mu$ -Polychloroprene.**—The  $\mu$ -product has the composition required for an addition polymer of chloroprene.

*Anal.* Calcd. for  $(C_4H_6Cl)_x$ : C, 54.25; H, 5.69; Cl, 40.06. Found: C, 53.74, 54.83; H, 5.70, 5.93; Cl, 40.06, 39.32.

Molecular weight determinations are not possible on account of its lack of solubility.

The  $\mu$ -polymer is unsaturated toward bromine but no quantitative data on this point are yet available. The chlorine atoms are very firmly bound. Only slight traces of chloride ion are liberated when the compound is heated for six hours in boiling alcoholic potash or boiling pyridine. This fact suggests that the chlorine atoms of the polymer are still attached to carbon atoms bearing double bonds.

The oxidation of the  $\mu$ -polymer with hot nitric acid leads to the isolation of succinic acid.

No attempts have yet been made to degrade the  $\mu$ -polymer with ozone

<sup>7</sup> Katz, *Chem.-Ztg.*, **49**, 353 (1925); Meyer and Mark, *Ber.*, **61**, 1939 (1928).

<sup>8</sup> "Die Röntgentechnik in der Materialprüfung," Eggert and Schiebold, Akademische Verlagsgesellschaft, Leipzig, 1930, p. 142.

<sup>9</sup> Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930.

<sup>10</sup> Hauser and v. Susich, *Kautschuk*, **7**, 145 (1931).

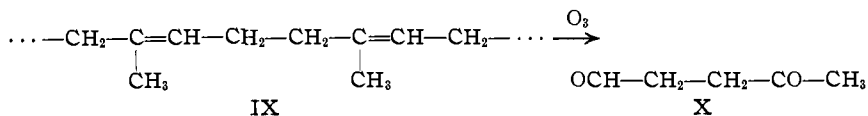
completely, but when stretched it is much more resistant than natural rubber to the deteriorating effect of ozone-containing air.

It is well known that purified rubber hydrocarbon is very susceptible to autoxidation. A similar and perhaps more exaggerated sensitivity is characteristic of synthetic rubbers derived from diene hydrocarbons. In this respect  $\mu$ -polychloroprene appears to be considerably more resistant. Nevertheless it does not long remain completely unaltered when freely exposed to air and light. It gradually becomes darker in color and finally after two or three weeks is dark brown. At the same time, it becomes harder, especially on the surface. These changes are accompanied by the liberation of traces of hydrogen chloride. The autoxidation can be suppressed by treating the polymer with small amounts of antioxidants.

**Chemical Structure of  $\mu$ -Polychloroprene.**—The molecules of natural rubber are long chains built up from the unit (VII) derived (formally) from isoprene (VIII). This structure follows from the fact that the ozoni-



zation of rubber (IX) leads to levulinic acid and levulinic aldehyde (X) as the principal products.<sup>11</sup>

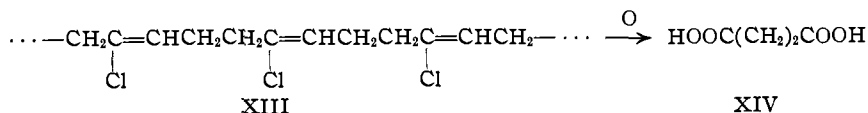


In their behavior toward ozone the so-called *normal* synthetic rubbers from isoprene very closely resemble the natural products,<sup>12</sup> and their molecules must therefore for the most part be built up on the same general plan.

Analogy suggests that the molecules of the chloroprene polymer are similarly built up from the units (XI) derived from chloroprene (XII).



The resulting chains would have the formula XIII.



This formula readily accounts for the fact that oxidation of the  $\mu$ -polychloroprene yields succinic acid (XIV). It also explains why the chlorine

<sup>11</sup> Harries, *Ber.*, **37**, 2708 (1904); **38**, 3985 (1905); Pummerer, Ebermayer and Gerlach, *ibid.*, **64**, 809 (1931).

<sup>12</sup> Harries, "Untersuchungen," Julius Springer, 1919, p. 222.



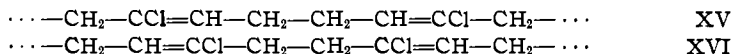
atom is very resistant to the action of alkalis: as in vinyl chloride, the chlorine is attached to a carbon atom bearing a double bond. This situation is changed however by autoxidation. This must lead to some such grouping as  $\begin{array}{c} \text{—CCl—CH—} \\ \diagdown \quad / \\ \text{O} \end{array}$ , in which the chlorine atom would be exceedingly mobile.

Some evidence for this formula is also found in the physical properties of the  $\mu$ -polychloroprene. The molecular refractivity calculated for this formula (22.95) agrees exactly with the experimental value (22.95). The x-ray diffraction pattern indicates an identity period of 4.8 Å., which corresponds quite well with that calculated for one chloroprene unit.

It appears to be generally true that the presence of a chlorine atom at a double bond decreases the tendency of the double bond to react with ozone, and in this connection it is significant that  $\mu$ -polychloroprene is much more resistant than natural rubber to the deteriorating action of ozone.

In the formulas IX and XIII the isoprene and chloroprene units have been represented as being united regularly in 1,4-1,4- . . . order. The units however are not symmetrical and in joining of two units one or both of them might be inverted. This would lead to the arrangements 1,4-4,1- . . . and 4,1-1,4- . . . . It has been demonstrated that such inversions<sup>13</sup> do occur in the polymerization of isoprene in the presence of sodium and alcohol. On the other hand isoprene rubber formed by thermal polymerization, since its behavior toward ozone is normal,<sup>14</sup> must be free from any considerable proportion of such inversions in its molecules.

The oxidation of  $\mu$ -polychloroprene to succinic acid gives no indication as to whether the arrangement of the units is normal as represented in XIII or inverted as in XV and XVI, since the latter would also yield succinic acid.



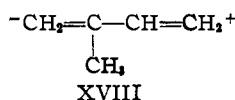
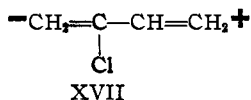
On the other hand the fact that  $\mu$ -polychloroprene like natural rubber yields a sharp x-ray diffraction pattern whereas this property is absent from other synthetic rubbers perhaps indicates that the polychloroprene is freer from irregularities in the structure of its molecules than other synthetic rubbers.

The spontaneous polymerization of isoprene requires several years for its completion; with chloroprene the transformation is complete in a few days. The great difference in speed may be ascribed, in part at least, to the activating influence of the chlorine atom. The methyl group is too

<sup>13</sup> Midgley and Henne, *THIS JOURNAL*, **52**, 2077 (1930).

<sup>14</sup> Cf. Pummerer and Koch, in Memmler's "Handbuch der Kautschukwissenschaft," S. Hirzel, Leipzig, 1930, p. 270.

feebly polar to exert any such effect. A similar difference exists between vinyl chloride and propylene in their tendency to polymerize. The chlorine atom here functions not only to powerfully activate the double bond, it also exerts a greater effect than methyl on the direction of addition reactions at the double bond: it more effectively controls the polarity of the molecule. A similar directive effect in chloroprene is demonstrated by its behavior toward hydrogen chloride. Thus the relation between chloroprene and isoprene may be symbolized by the formulas XVII and XVIII.



It seems highly probable therefore on theoretical grounds not only that the polymerization of chloroprene will proceed much more rapidly than the polymerization of isoprene, but that there will be much less chance of inversions of the units in the polychloroprene chains.

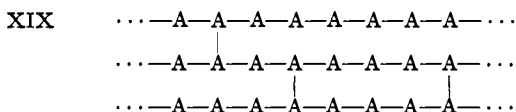
Formula XIII adequately represents the chemical behavior of  $\mu$ -polychloroprene, but it is not sufficiently complete to account for the remarkable physical behavior of this material. The difficulties in this connection are precisely the same as those presented by natural rubber. The linear polymeric structure partially represented in formula IX furnishes a sufficient basis for describing the chemical behavior of rubber. It is known further that the molecular weight of rubber is exceedingly high—perhaps in the neighborhood of 70,000;<sup>15</sup> but no entirely adequate explanation of the elastic properties of rubber in terms of this structure has been offered. It seems scarcely necessary to review the numerous speculations that have been devoted to this subject.<sup>16</sup> We merely point out that the units in a substituted polyprene chain (*e. g.*, rubber or polychloroprene) present the possibility of geometrical isomerism and that they may be arranged in *cis-cis-cis- . . .* order or *trans-trans-trans- . . .* order; or both arrangements may be present in a single chain. The molecules may be coiled into spirals rather than rigidly extended. On these questions we have no data concerning polychloroprene (see however the above paragraph entitled x-Ray Diffraction Pattern). Moreover, we have no direct information concerning the molecular weight of polychloroprene. It seems certain, however, that the chains must be very long.

We observe finally that  $\mu$ -polychloroprene resembles vulcanized rather than unvulcanized rubber. It is not plastic; it does not become plastic when heated; and it does not dissolve but merely swells in rubber solvents

<sup>15</sup> Staudinger and Bondy, *Ann.*, **488**, 127 (1931).

<sup>16</sup> Some of the most suggestive are Staudinger, *Kautschuk*, **5**, 911, 1261 (1929); Meyer and Mark, "Der Aufbau der hochpolymeren organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930; Fikentscher and Mark, *Kautschuk*, **6**, 2 (1930).

such as benzene and chloroform. This behavior is much more consistent with a three-dimensional polymeric structure than with a simple linear structure. We assume therefore that in  $\mu$ -polychloroprene chains of the type already described are chemically linked together at occasional points. The resulting structure as we conceive it may be symbolized by formula XIX in which A stands for the structural unit. The cross-linking may occur through the mediacy of oxygen atoms, but it seems more likely that the double bonds of parallel chains mutually saturate one another directly. Since the chains are exceedingly long they need to be linked together only at occasional points to produce a non-plastic structure.



**$\beta$ -Polychloroprene.**—When chloroprene is polymerized at elevated temperature, *e. g.*, at 60° especially in the absence of air, the product is somewhat less dense and softer than that formed at ordinary temperature, and it has a pronounced terpene-like odor. This odor is due to the presence of volatile chloroprene polymers ( $\beta$ -polymer). This product can be prepared in quantity by storing or heating chloroprene in the presence of substances such as pyrogallol or trinitrobenzene that inhibit the transformation of chloroprene into the  $\mu$ -polymer. By distillation the  $\beta$ -polymer can be separated into two fractions, one boiling at 92 to 97° at 27 mm. and the other boiling chiefly at 114 to 118° at 27 mm. The odor of the fractions is very similar—fragrant and terpene-like. The constitution of these products has not been determined, but there is little doubt that they are cyclic dimers of chloroprene. It is already known that analogous products are formed from isoprene,<sup>17</sup> butadiene<sup>18</sup> and dimethylbutadiene.<sup>19</sup> The  $\beta$ -polychloroprenes are stable substances, which show no tendency to polymerize further. They have therefore no direct bearing on the formation of the rubber-like polymers, and they are relatively unimportant, especially since they appear in significant amounts only under rather exceptional conditions.

**Influences Affecting the Polymerization of Chloroprene.**—A few typical data are assembled in Table I.

(a) **Catalysts.**—Oxygen is an exceedingly powerful catalyst for the transformation of chloroprene into the  $\mu$ -polymer. Samples of chloroprene distilled in high vacuum and sealed off in glass tubes without exposure to the air show an appreciable increase in viscosity only after a period of one or two months, and the transformation to  $\mu$ -polymer is still

<sup>17</sup> Pummerer and Koch, *loc. cit.*, p. 284.

<sup>18</sup> Hofmann and Tank, *Z. angew. Chem.*, **25**, 1465 (1912).

<sup>19</sup> Van Romburgh and Van Romburgh, *Proc. Roy. Acad. Amsterdam*, **34**, 224 (1931)

TABLE I  
ESTIMATED TIME REQUIRED FOR 90% OF A SAMPLE OF CHLOROPRENE TO POLYMERIZE  
UNDER VARIOUS CONDITIONS (ABSENCE OF DIRECT LIGHT)

No.	Temp., °C.		Conditions		Time, days	Character of product
	Air		Pressure, atm.	Other added substances		
1	25	Present	1	None	8	Colorless, strong, tough
2	25	Absent	1	None	400	Soft, low density, strong odor of dimer
3	62	Present	1	None	2	Strong, tough, slight odor of dimer
4	62	Absent	1	None	10	Strong, tough, odor of dimer
5	100	Absent	1	None	< 1	Semi-fluid, black, much dimer
6	25	Present	4500	None	< 2	Transparent, rather hard, very tough
7	25	Present	6000	None	0.7	Transparent, rather hard, very tough
8	60	Absent	6100	None	2	Rather soft, odor of dimer
9	62	Absent	1	1.5% Benzoyl peroxide	1	Product variable
10	62	Present	1	0.5% Benzoyl peroxide	1	Strong, tough, colorless
11	25	Absent	1	0.1% Catechol		Still fluid after 65 days
12	25	Present	1	1.6% Thiodiphenylamine		Still fluid after 13 months; strong odor of dimer

incomplete after twelve months. From some recent studies of the behavior of isoprene<sup>20</sup> it appears that the active catalyst in such transformations is a volatile peroxide. Since it is practically impossible to prepare a sample of chloroprene without exposing it to air at some time during the course of its preparation, it seems probable that even the products distilled in high vacuum are not altogether free from catalyst.

The amount of oxygen necessary to produce an optimum catalytic effect is quite small. At ordinary temperatures the presence of a volume of air equal to about 10% of the volume of the chloroprene sample causes the transformation to  $\mu$ -polymer to be completed in about eight to ten days. If the volume of air is much smaller than this the time required for the transformation is somewhat greater, but much larger ratios of air or oxygen do not greatly increase the velocity. Large quantities of oxygen do however affect the character of the final product. In general they lead to a product which, instead of being colorless or only slightly yellow, is dark brown and considerably harder and stiffer than the usual products.

Peroxides such as benzoyl peroxide also function as catalysts. Their use, however, presents no practical advantages, and is in fact somewhat hazardous. In samples containing benzoyl peroxide there is frequently a considerable induction period, and then reaction suddenly starts at some point in the sample and spreads very rapidly through the mass. The heat of reaction may be sufficient to char the sample.

The rate of formation of  $\beta$ -polychloroprene is not appreciably accelerated by oxygen or peroxides.

<sup>20</sup> Conant and Peterson, private communication.

(b) **Temperature, Pressure and Light.**—Catalytic and anticatalytic effects in the polymerization of chloroprene are very powerful and difficult to regulate exactly; for this reason it is impossible to obtain precise quantitative correlations concerning the effect of temperature, pressure and light on the reaction velocity. It appears, however, that in the presence of air the transformation of chloroprene into the  $\mu$ -polymer occurs about four times as fast at 62° as at 25°. Thus the temperature coefficient of the catalyzed reaction is abnormally low. The relative rate of the formation of  $\beta$ -polymer, which is negligible at ordinary temperature, is more strongly affected by rise in temperature. Polymers produced at temperatures above 50° contain appreciable proportions of  $\beta$ -polymer. These proportions are still further increased if the reaction is carried out in the absence of air since this greatly reduces the speed with which  $\mu$ -polymer is formed without affecting the formation of  $\beta$ -polymer. In the absence of air the effect of increased temperature on the rate of transformation of chloroprene into  $\mu$ -polymer appears to be much greater than in the presence of air.

When chloroprene is polymerized at temperatures above 80° (in the absence of solvents) considerable decomposition occurs with liberation of appreciable amounts of hydrogen chloride, and the product is dark in color and tarry in consistency.

At a pressure of 6000 atmospheres the polymerization of chloroprene occurs about ten times as rapidly as at ordinary pressure.

Light has a considerable accelerating effect on the transformation of chloroprene into the  $\mu$ -polymer. The rate of formation of  $\beta$ -polymer is not affected. The active wave lengths lie in the blue, violet, and near ultraviolet.

(c) **Inhibitors.**—Substances that generally function as antioxidants act as powerful inhibitors for the transformation of chloroprene into the  $\mu$ -polymer. Under ordinary conditions a sample of chloroprene will set in four days to a stiff jelly containing about 40% polymer but the presence of 0.1% of catechol will permit the sample to remain fluid for several months. This fact confirms indications already mentioned that the spontaneous transformation of chloroprene into  $\mu$ -polymer is normally dependent upon the presence of traces of autoxidation products of the chloroprene. The formation of  $\beta$ -polymer is not thus dependent upon oxidation. Samples of chloroprene containing inhibitors, after several months at the ordinary temperature, are found to contain several per cent. of  $\beta$ -polymer, and frequently they are quite free of  $\mu$ -polymer. A sample of chloroprene containing 0.2% of pyrogallol yielded 49% of crude  $\beta$ -polymer after being heated for forty days at 62°.

The following types of compounds generally function as inhibitors: phenols, quinones, amines, mercaptans, thiophenols, aromatic nitro com-

pounds, halogens. Some compounds in each of these classes function as powerful inhibitors, others have a feebler effect. It is somewhat surprising to find aromatic nitro compounds in this list. Trinitrobenzene is among the most powerful of the inhibitors.

In the presence of relatively feeble inhibitors or small amounts of the more powerful inhibitors the polymerization of chloroprene can be effected at a somewhat diminished rate. The non-volatile polymer formed under these conditions, however, differs very considerably in its properties from that formed in the absence of inhibitors.

(d) **Solvents.**—The polymerization of chloroprene can be effected in the presence of solvents. If the solvent is one such as benzene, toluene, ethylene chloride, or carbon disulfide that powerfully swells  $\mu$ -polychloroprene, the resulting polymer remains dissolved. The polymerization of solutions containing as much as 50% by volume of chloroprene leads to the formation of stiff jellies. Even as little as 10% of chloroprene leads to highly viscous solutions. The solutions are generally colorless and transparent. The polymers contained in these solutions are somewhat different in their properties from the  $\mu$ -polychloroprenes produced under ordinary conditions. They are softer, and unless the solution is very old they can usually be redissolved in benzene.

The presence of the solvent considerably diminishes the rate of the polymerization, and dilute solutions polymerize more slowly than concentrated ones. Solvents also frequently exert a specific effect. Chloroprene dissolved in benzene polymerizes very much more rapidly than chloroprene dissolved in ether or pyridine.

Chloroprene may also be polymerized in the presence of non-volatile solvents, inert fillers and foreign materials of various kinds.

**Granular Polymer ( $\omega$ -Polymer).**—The polymerization of chloroprene occasionally leads to a coherent mass of glistening, hard, rubbery granules or globules ( $\omega$ -polymer). This material is non-plastic and it shows scarcely any tendency to imbibe solvents. The conditions favoring its formation are not very clearly understood, since it occasionally appears under the most diverse conditions. It seems certain, however, that its formation is autocatalytic. When a speck of this polymer appears in a sample of chloroprene during the early stages of its polymerization the granular growth continues to spread through the whole sample. Because of its cell-like structure it occupies more volume than the same amount of  $\mu$ -polymer, and if the growth begins to spread laterally through a sample it may burst the walls of a heavy Pyrex container even when the total volume of the container is much greater than the volume of the product. The presence of metallic sodium especially favors the formation of the granular polymer. It frequently appears under other conditions that result in very slow polymerization.

According to experiments made by Dr. H. W. Starkweather the formation of the  $\omega$ -polymer is initiated (or accelerated) by light of 3130 Å. wave length. The following observation is especially interesting.

Chloroprene containing pyrogallol to inhibit polymerization was placed in the bottom of a long Pyrex tube. The chloroprene was cooled to  $-80^{\circ}$ , and the tube was evacuated and sealed off. The lower half of the tube was covered with black friction tape to exclude light and the upper part was exposed to light from a mercury arc. During the exposure the lower part of the tube was kept in a bath at  $10^{\circ}$ ; the upper half was at  $60-65^{\circ}$ . After twelve hours there was a white deposit at the top of the tube. This deposit gradually increased during two and one-half days. Exposure to the light was then discontinued. The solid deposit, however, continued to form at the top of the tube as a white, crinkly mass, until the liquid in the bottom of the tube was completely exhausted.

It is interesting to observe that products similar to this granular polymer have been obtained from other dienes. Kondakow<sup>21</sup> observed that dimethylbutadiene in a closed flask in diffused daylight is gradually transformed into a white, insoluble mass, and Harries<sup>22</sup> obtained a similar product by the action of ultraviolet light on isoprene.

The great resistance of the  $\omega$ -polychloroprene as compared with the  $\mu$ -polymer to the swelling action of solvents indicates a considerably higher degree of cross-linking of the chains in the  $\omega$ -compound. If such a cross-linking should occur in a sufficiently regular fashion, it would lead to a three-dimensional primary valence lattice, a type of structure which is illustrated by the diamond, but is not known among synthetic organic compounds. The conditions under which the  $\omega$ -polymer is formed are such as might be especially favorable to the development of a regular three-dimensional structure. The formation of  $\omega$ -polymer is catalyzed by an  $\omega$ -polymer surface; the process is one of heterogeneous autocatalysis. It seems most probable that the function of the  $\omega$ -polymer surface in this connection is not (or at least not wholly) to activate adsorbed molecules of the monomer, but rather to orient the adsorbed molecules into a configuration favorable for mutual union. The incidence of activating energy could then bring about the combination of a very large number of molecules in a single act.

As a matter of fact the granular polymer at first sight gives the impression of being definitely macrocrystalline, but on closer observation the crystals turn out to be globules. x-Ray examination gives only an amorphous pattern.

It is interesting to note that the granular polymer never appears in samples of  $\alpha$ -polychloroprene (described later) that contain phenyl- $\beta$ -naphthylamine.

<sup>21</sup> Kondakow, *J. prakt. Chem.*, [2] **64**, 109 (1901).

<sup>22</sup> Pummerer and Koch, *loc. cit.*, p. 268.

**Progressive Changes during the Spontaneous Polymerization of Chloroprene.**—The following table illustrates in more detail the changes in properties and composition that occur when a sample of chloroprene is allowed to stand under ordinary conditions in the presence of a little air.

TABLE II  
CHANGES DURING THE POLYMERIZATION OF CHLOROPRENE

Time, days	Polymer, %	Density	Viscosity in centipoises
0	0	0.952	0.4
1	4	..	6.0
2	14	0.98	550.0
4	45	1.06	Stiff jelly
10	99+	1.23	Non-plastic

The polymer formed during the early stages of the reaction can be isolated by precipitation with alcohol, or by distilling off the unchanged chloroprene *in vacuo*. This material is very different in its properties from the final product, the  $\mu$ -polychloroprene already described. It is soft, plastic, and completely soluble in benzene. We call this plastic polymer  $\alpha$ -polychloroprene. When allowed to stand at the ordinary temperature it slowly reacts with itself and in the course of a day or two is transformed into a product apparently identical with the  $\mu$ -polymer.

**Mechanism of the Formation of  $\alpha$ - and  $\mu$ -Polymers.**—The isolation of the  $\alpha$ -polymer demonstrates that the transformation of chloroprene into the  $\mu$ -polymer is a step-wise reaction. Some of the facts concerning the two polymers and their relation to each other are best correlated by a brief discussion of mechanism.

The transformation of chloroprene into the  $\alpha$ -polymer is evidently a chain reaction. It is enormously susceptible to catalytic and anticatalytic effects; it is accelerated by light; and although a large number of molecules is combined to form a single larger molecule, the apparent order of the reaction is low. The reaction probably first involves the coupling of an activated molecule of chloroprene with another chloroprene molecule. The activating energy persists in the polymeric chain until it has been built up to a considerable length. The molecules of  $\alpha$ -polymer thus formed doubtless have the linear structure already suggested in formula XIII. The formation of a molecule of  $\alpha$ -polymer involves a series of separate acts, but these follow one another in very rapid succession. Under ordinary conditions the  $\alpha$ -polymer present when 4% of a sample of chloroprene has polymerized is indistinguishable from the polymer present when 20% of the chloroprene has polymerized.

The transformation of the  $\alpha$ -polymer into the  $\mu$ -polymer consists in the cross-linking of the long chains into a three-dimensional structure of the type represented in formula XIX. In a sample of chloroprene undergoing spontaneous polymerization this process becomes noticeable when



the concentration of polymer has reached about 25%. It is marked by an abrupt change in properties. The viscosity increases very rapidly and the sample soon sets to a stiff jelly. If the polymer is isolated just before this point is reached, it is found to be soft and plastic. Polymer isolated just after this abrupt change is still soft, but the manner in which it resists permanent deformation indicates the presence of a considerable proportion of the  $\mu$ -polymer.

The reactions, (1) chloroprene  $\longrightarrow$   $\alpha$ -polymer, and (2)  $\alpha$ -polymer  $\longrightarrow$   $\mu$ -polymer, are not merely two stages of a single process, but are different reactions. The polymerization of chloroprene is rather strongly inhibited by primary aromatic amines, such as aniline, the naphthylamines, and benzidine; but these same compounds when mixed with isolated  $\alpha$ -polymer accelerate its conversion into  $\mu$ -polymer. The temperature coefficients of the two reactions are different. For reaction (2) the ratio of the velocity constants for a temperature increase of  $10^\circ$  is about two; for reaction (1) the ratio is considerably less than two.

**Other Polymers; Balata-like Polymer.**—The  $\alpha$ -,  $\mu$ - and  $\omega$ -types are not chemical individuals but rather qualitatively different species of polymeric mixtures. The properties of each type may vary over a considerable range and in practice no doubt one generally has to do not with a pure species but with a mixture in which one of the species may preponderate. A consideration of the formulas assigned to the  $\alpha$ - and  $\mu$ -polymers will suggest some of the complications that might arise. The molecules of the  $\alpha$ -polymer are no doubt chains of very great length, but in the polymerization of chloroprene under certain conditions, *e. g.*, at elevated temperature, the process of cross-linking may set in before the chains have attained the usual length of  $\alpha$ -polymer chains. One will then have a product very different in its properties from that produced by the vulcanization of  $\alpha$ -polymer. Stereochemical factors (*e. g.*, *cis-trans* isomerism) may also produce great variations in the character of the products.

The  $\alpha$ -,  $\beta$ -,  $\mu$ - and  $\omega$ -polymers by no means exhaust the different types of polychloroprenes. Anything that influences the velocity of the polymerization has some effect on the properties of the product, and the modifications produced by inhibitors and catalysts are especially marked. The phenomena in this connection are very complex. It would be useless to attempt to recognize as distinct species all the distinguishably different polymeric products derived from chloroprene.

There is, however, one type of product that appears to be qualitatively different from the  $\alpha$ -,  $\beta$ -,  $\mu$ - and  $\omega$ -polymers. This material rather closely resembles balata in its properties. It is obtained more or less contaminated with the other types of polymers under various conditions, but especially by the polymerization of chloroprene in the presence of inhibitors such as iodine or the tetraalkyl thiuramdisulfides.

A typical specimen of this balata-like material when cold is a hard, amorphous, non-brittle mass. When warmed to 60° it becomes soft and plastic. At higher temperatures it is quite sticky. When heated under vulcanizing conditions the plasticity is partly lost, but the transformation to the elastic condition is very incomplete. We make no attempt to suggest a structure for this material.

**Conditions for the Isolation of  $\alpha$ -Polymer.**—Owing to the effect of changing concentrations, the rate of formation of  $\alpha$ -polymer progressively decreases during the polymerization of chloroprene, and the rate of the conversion of  $\alpha$ -polymer into  $\mu$ -polymer progressively increases. For this reason if pure  $\alpha$ -polymer is to be obtained, the reaction must be interrupted before all of the chloroprene has polymerized.

Under the most favorable conditions the concentration of the  $\alpha$ -polymer in the polymerizing mixture can be built up to 30 or 40% before any appreciable transformation to  $\mu$ -polymer occurs. The reaction is best conducted in glass vessels under strong illumination from a Mazda lamp or a mercury arc in glass. The most effective wave lengths lie in the long ultraviolet, but the use of a quartz container with mercury arc radiation is not advisable on account of the danger of forming granular polymer. The temperature should be kept in the neighborhood of 35°. Under these conditions about 30% of the chloroprene is polymerized in sixteen to twenty-four hours. The product is a thick, colorless, transparent sirup. If this sirup is poured into a large volume of alcohol, the  $\alpha$ -polymer separates as a colorless mass and the unchanged chloroprene remains dissolved in the alcohol. The  $\alpha$ -polymer can also be separated by allowing the unchanged chloroprene to distil out of the mixture under diminished pressure. The mixture is preferably stirred during the distillation.

**Properties of the  $\alpha$ -Polymer.**—In density and refractive index the  $\alpha$ -polymer lies very close to the  $\mu$ -polymer. The  $\alpha$ -polymer resembles milled smoked sheets in its physical properties and mechanical behavior. It is plastic and it dissolves completely in benzene to form highly viscous solutions. It can be calendered into thin sheets or extruded with the usual rubber machinery.

At 30° the  $\alpha$ -polymer loses its plastic properties and becomes completely changed to the elastic form ( $\mu$ -polymer) in about forty-eight hours. At 130° the transformation is complete in about five minutes. This process corresponds to the vulcanization of natural rubber, but sulfur is not needed and when present it takes no part in the process. The speed of this transformation can be greatly modified by the addition of various substances, some of them materials that are used in the vulcanization of natural rubber.

Zinc oxide brings about the vulcanization of  $\alpha$ -polymer in eight to ten hours at 30°. Zinc chloride, zinc butyrate and ferric chloride are even

more active catalysts. The most effective organic catalysts are primary aromatic amines such as aniline, the naphthylamines and benzidine. Diphenyl guanidine, which is a relatively active vulcanization accelerator for natural rubber, is a mild accelerator for  $\alpha$ -polymer. On the other hand mercaptobenzothiazole and tetraalkylthiuram sulfides, which are active natural rubber accelerators, have no accelerating action on the  $\alpha$ -polymer. Basic inorganic materials such as lime and magnesium oxide, which may accelerate natural rubber through their action with sulfur, have a slight retarding influence on the vulcanization of  $\alpha$ -polymer. Strong acids and acidic materials that retard the vulcanization of natural rubber have no influence on the curing of plastic polymer.

Secondary aromatic amines such as phenyl- $\beta$ -naphthylamine powerfully inhibit the vulcanization of  $\alpha$ -polymer at ordinary temperature. This fact is of considerable practical importance since it brings about the possibility of storing the plastic polymer over long periods of time. The phenyl- $\beta$ -naphthylamine also acts as an antioxidant and confers age-resisting properties on the final product. The inhibiting effect of the phenyl- $\beta$ -naphthylamine on the curing of the  $\alpha$ -polymer largely disappears above 100°.

**Behavior of  $\alpha$ -Polymer in Compounding and Properties of the Cured Rubber.**—The compounding ingredients that can be used with  $\alpha$ -polymer are similar to those used with natural rubber, but there are a number of important additions. Materials such as ground leather and cork which strongly retard the vulcanization of natural rubber act as inert ingredients in  $\alpha$ -polymer. Carbon black and zinc oxide act as reinforcing agents as they do in natural rubber and impart good abrasion resistance. In contrast to their action in rubber, whiting and clay are perfectly wet by  $\alpha$ -polymer, and they produce compounds having good tear resistance. Cotton and other vegetable fibers are also much more perfectly wet by  $\alpha$ -polymer than by rubber. Most plasticizing and softening materials such as mineral oil, stearic acid and pine tar are insoluble in  $\alpha$ -polymer and have little true softening action. Milling also produces little softening other than a temporary thermal effect. Mineral rubber and similar asphaltic materials act as diluents with little effect on the physical properties of the vulcanized material.

Natural rubber can be successfully milled into  $\alpha$ -polymer, although there is little affinity between the two. Sheets of the two rubbers before vulcanization may be firmly pressed together and easily separated. A reasonably firm union can be obtained between natural and chloroprene rubber when they are vulcanized together under sufficient pressure. Benzene solutions of rubber and  $\alpha$ -polymer are not compatible; when thoroughly mixed they quickly separate into two layers.

Table III gives the composition of compounded stocks prepared from

$\alpha$ -polychloroprene and from smoked sheets. These were used for a series of parallel tests to compare the behavior of the two rubbers. All the processing and testing were carried out with the usual rubber laboratory equipment.

TABLE III

COMPOSITION OF COMPOUNDED STOCKS FROM  $\alpha$ -POLYCHLOROPRENE AND FROM SMOKED SHEETS

Materials	Amount in grams	
	Compound from $\alpha$ -polychloroprene	Compound from smoked sheets
$\alpha$ -Polychloroprene	100	...
Smoked sheet rubber	...	100
Zinc oxide	10	10
Sulfur	...	3
Stearic acid	2	2
Diphenylguanidine	...	1
Benzidine (accelerator)	0.5	..
Phenyl- $\beta$ -naphthylamine	1	1

The effect of different times and temperatures of vulcanization on the physical properties of the two compounds is shown in Table IV. The chloroprene rubber reaches a maximum tensile strength after only five minutes at 140°; but the strength is not adversely affected if the curing time is extended to sixteen hours. In contrast to this, the natural rubber compound vulcanizes more slowly and softens rapidly under the action of prolonged vulcanization. The maximum tensile strength for the chloroprene compound is slightly lower than that for the natural rubber compound. In contrast to the smoked sheet compound the chloroprene compound shows no reversion and the load supported at 500% elongation continues to increase slowly throughout the curing range. When the

TABLE IV

EFFECT OF VULCANIZATION ON PHYSICAL PROPERTIES OF COMPOUNDED STOCKS

Vulcanization temp., °C.	Minutes vulcanization time	Load at 500% elongation, kg. per sq. cm.		Tensile strength at break, kg. per sq. cm.		% Elongation at break	
		Chloroprene rubber	Smoked sheet	Chloroprene rubber	Smoked sheet	Chloroprene rubber	Smoked sheet
110	20	16.0	..	166.9	...	920	...
110	40	28.1	..	177.5	...	860	...
120	20	28.2	..	169.3	...	860	...
120	40	30.2	..	171.2	...	820	...
140	5	29.9	..	170.5	...	825	...
140	10	33.4	..	170.5	...	780	...
140	15	38.6	12.2	172.2	12.6	770	860
140	20	38.6	16.0	170.5	15.2	760	830
140	30	42.2	21.0	172.2	175.0	750	820
140	60	42.2	35.1	167.0	210.0	750	760
140	90	43.9	46.2	167.0	192.0	720	680
140	120	45.7	42.0	181.0	205.0	740	720
140	480	54.4	14.0	165.2	87.0	700	800
140	960	63.3	11.9	151.1	82.1	640	820

polychloroprene compound is heated longer than sixteen hours at 140° a material resembling hard rubber is formed.

The chloroprene compound is very resistant to the action of ozone. The two compounds were stretched about fifteen per cent. and exposed to ozone-containing air. The natural rubber compound was ruptured in three minutes; the chloroprene compound was not detectably affected during an exposure of three hours.

Table V shows the results of artificial aging tests on the two compounds of Table III. The chloroprene compound was cured for fifteen minutes and the natural rubber compound for sixty minutes at 140°. The tests were carried out at 70° in oxygen at twenty atmospheres. Under these conditions twenty-four hours is generally considered to approximate one year of natural aging for rubber. These data indicate that the chloroprene rubber is considerably more resistant to oxidation than natural rubber. Natural aging tests have not been carried out for a length of time sufficient to confirm this conclusion, but samples of the chloroprene rubber compound that have been kept for one year show no deterioration.

TABLE V  
AGING PROPERTIES OF COMPOUNDS FROM SMOKED SHEETS AND FROM  
 $\alpha$ -POLYCHLOROPRENE

Days in oxygen bomb at 70°	Tensile strength, kg. per sq. cm.		% Elongation at break Chloroprene rubber	Elongation at break Smoked sheets
	Chloroprene rubber	Smoked sheets		
0	172.2	232.0	890	720
1	212.6	195.0	845	660
2	181.0	163.4	820	660
3	193.3	159.9	805	670
8	209.1	116.1	720	595
14	165.2	54.5	690	510

Chloroprene rubber is much more resistant than the natural product to the action of solvents and many chemicals. After seventy-two hours the chloroprene compound had increased 7% in weight by immersion in light machine oil and 25% by immersion in kerosene, and it had retained more than half of its original tensile strength in each case. The tensile strength of the natural rubber was destroyed under these conditions. In contrast to natural rubber, chloroprene rubber is not attacked by hydrogen chloride, hydrogen fluoride, sulfur chloride, ozone and many other chemicals. The high chlorine content of the chloroprene rubber also renders it very resistant to combustion. Measurements of diffusion of both hydrogen and helium through a polychloroprene membrane show it to be only 40% as permeable as natural rubber. The absence of water-soluble materials in chloroprene rubber makes it very resistant to penetration by water.

**Synthetic Latex.**—Chloroprene is readily emulsified by shaking or

stirring it with water containing an emulsifying agent such as sodium oleate. The resulting emulsion polymerizes very rapidly and completely. The polymer remains suspended or emulsified and constitutes an artificial latex. When the water is allowed to evaporate from a layer of this latex, a thin coherent, strong, elastic film remains. This film in its physical and mechanical properties very closely resembles the  $\mu$ -polychloroprene already described: it is strong, extensible, elastic, resilient, non-plastic and not thermoplastic, and it is swelled but not dissolved by benzene.

The following example illustrates the preparation of a synthetic latex. Four hundred grams of chloroprene is slowly added with vigorous stirring to 400 g. of water containing 8 g. of sodium oleate in a wide-mouthed bottle. A smooth emulsion results. After a time (usually about thirty minutes) the temperature of the mixture begins to rise and it may quickly reach the boiling point of the chloroprene unless cooling is applied. After standing for two to eight hours at room temperature the polymerization is complete. The mixture is then practically odorless.

More uniform products are obtained if the temperature is carefully controlled during the emulsification and polymerization. At a temperature of  $10^{\circ}$  the process is complete in about twenty-four hours—always in less than forty-eight hours. The reaction is always characterized by an induction period, which at  $10^{\circ}$  usually lasts forty to sixty minutes. It is evident that the speed of polymerization of chloroprene is much greater (apparently at least 20-fold) in emulsion than otherwise. The particular nature of the interface appears to be of great importance in determining the rate of polymerization. The rate is much more rapid with sodium oleate than with egg albumen although both of these emulsifying agents produce very small particles.

A small amount of free acid is developed during the polymerization of the emulsions, and this gradually brings about coagulation during storage. However, if a little ammonia (*e. g.*, 5 g. of  $\text{NH}_3$  per liter) is added to the latex after completion of the polymerization this tendency is avoided. Latex stabilized in this way can be stored indefinitely without change. In addition to the ammonia it is ordinarily desirable to add an antioxidant such as phenyl- $\beta$ -naphthylamine since this greatly prolongs the life of articles prepared with the latex.

The particle size of latex prepared according to the above example is very small and remarkably uniform. Figure 4 gives the results of some measurements made by Dr. J. B. Nichols with the ultracentrifuge. When sodium oleate is used as the emulsifying agent the mean radius of the particles is about  $0.063\mu$  and more than 60% of the particles lie between 0.05 and  $0.07\mu$ . It appears that the ultracentrifugal method has not been applied to natural latex, but according to Hauser<sup>23</sup> the latex from

<sup>23</sup> Hauser, "Latex," Theodor Steinkopff, Leipzig, 1927, p. 56.

mature *Hevea* trees contains particles ranging in diameter from 0.5 to  $3\mu$  as well as a considerable proportion of smaller particles. The particle size of the synthetic latex can be controlled to a certain extent by suitably modifying the nature and the amount of the emulsifying agent. The use of lithium oleate in the ratio of two grams to one hundred grams of chloroprene gives particles having a mean radius of about  $0.087\mu$ .

In the preparation of the synthetic latex the ratio of chloroprene to water can be varied over a wide range. As long as the concentration lies below 55% by weight of polychloroprene, the latices are very fluid. Above this concentration there is a sharp increase in viscosity, and a 60% latex is quite thick.

The synthetic latex is rapidly coagulated by acids, alcohol, acetone and many salts. The polychloroprene separates as a coherent mass, which is at first quite soft and plastic. However, as soon as the water is squeezed out, this plasticity is lost. The mass then has the properties already indicated for  $\mu$ -polychloroprene—it is analogous to a soft, vulcanized natural rubber.

**Applications of the Latex.**—The chloroprene latex can be directly applied to many uses after the manner of vulcanized

natural latex. In this connection it has some special advantages owing to its peculiar properties. Thus on account of its small particle size it penetrates porous articles such as leather and wood in a manner that can hardly be approached with natural latex.

Shaped articles are readily prepared by dipping forms of glass, metal or porcelain into the latex and coagulating the resulting film or allowing it to dry. By repeated dipping, articles of any desired thickness can be built up.

The latex can be mixed with dyes, fillers and modifying and protective agents of various kinds to adapt it to specific uses.

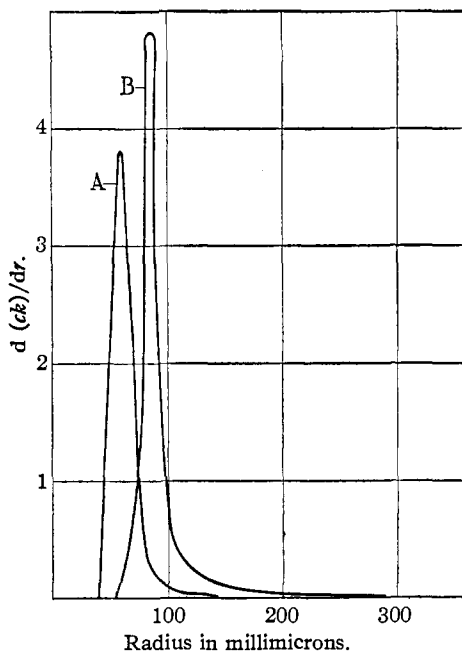


Fig. 4.—Weight distribution curve for chloroprene lattices. The units are such that the area under the curves for any radius interval equals the fraction of the total weight of particles whose radii lie in that interval. Curve A, latex made with sodium oleate. Curve B, latex made with lithium oleate.

**Polymerization of Chloroprene in Porous Materials.**—Attempts to impregnate such porous materials as leather, wood and tile with natural rubber are unsuccessful, whether the rubber is used in the form of latex or dissolved in a solvent such as benzene; but a very intimate impregnation of these materials with chloroprene rubber can be accomplished by soaking them in chloroprene and then allowing the rubber to be formed in place. Chamois or kid leather saturated with its own weight of chloroprene and sealed to prevent evaporation until polymerization is complete becomes translucent and assumes a rubber-like flexibility without extensibility. Impregnated spruce becomes water resistant but its appearance is unchanged. This process may be used with any porous or bibulous material that does not contain inhibitors for the spontaneous polymerization of chloroprene.

**Conclusion.**—If space permitted it would be possible to review the literature on synthetic rubber from diene hydrocarbons and to show that almost every recorded peculiarity and complication in this field finds some analogy in the behavior of chloroprene. Chloroprene is therefore capable of serving adequately as a representative diene in studying as a scientific problem the synthesis of rubber-like materials, and for this purpose it has the great advantage of its very high speed of polymerization as compared with dienes previously available.

On the economic side the greatly diminished costs of producing natural rubber have obviated the need for an artificial material having the same properties. There remains, however, the need for a synthetic rubber that is free from some of the inherent defects of the natural product. The differences between polychloroprene and natural rubber are sufficient to suggest considerable potentialities for the new synthetic product.

### Summary

Chloro-2-butadiene-1,3 (chloroprene) is described and its structure established through reactions leading to its conversion into butane- $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -tetracarboxylic acid, and into  $\beta$ -chloroanthraquinone.

Within ten days under ordinary conditions in a closed vessel containing a little air, chloroprene spontaneously changes into a transparent, resilient, strong, non-plastic, elastic mass resembling vulcanized rubber. This product is called  $\mu$ -polychloroprene. By interrupting the polymerization before it has proceeded to completion one obtains a soft, plastic product ( $\alpha$ -polymer) that resembles unvulcanized rubber. Under the action of heat the  $\alpha$ -polymer rapidly changes to the  $\mu$ -polymer. Other polymers of chloroprene described are volatile ( $\beta$ -) polymer, granular ( $\omega$ -) polymer, and balata-like polymer. The structures of the polymers are discussed as well as the effect of conditions on the formation of each type.

Unlike any previously described synthetic rubbers,  $\mu$ -polychloroprene



resembles natural rubber in the fact that when it is stretched its x-ray diffraction pattern shows a point diagram.

The transformation of chloroprene into  $\mu$ -polychloroprene occurs very rapidly in aqueous emulsion. The resulting product constitutes a synthetic (vulcanized) latex. It has a much smaller particle size than natural latex and it penetrates porous materials more readily.

Chloroprene can also be polymerized in the pores of porous or bibulous materials. The materials thus become intimately impregnated with synthetic rubber.

Compared with natural rubber the new synthetic rubber is more dense, more resistant to absorption or penetration by water, less strongly swelled by petroleum hydrocarbons and less permeable to many gases. It is much more resistant to attack by oxygen, ozone, hydrogen chloride, hydrogen fluoride and many other chemicals.

WILMINGTON, DELAWARE

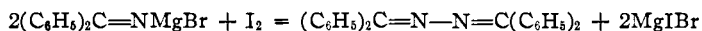
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## COMMUNICATIONS TO THE EDITOR

### A NEW METHOD FOR THE PREPARATION OF KETO-CHLORIMINES

*Sir:*

Recently, Morton and Stevens [THIS JOURNAL, 53, 2769 (1931)] have prepared diphenylketazine, in good yield, by heating with iodine the magnesium compound obtained from phenylmagnesium bromide and benzonitrile. The reaction is represented by the equation



When bromine was used instead of iodine, a small yield of the ketazine was obtained.

Since the corresponding reaction with chlorine has been carried out in this Laboratory [G. J. Haus, Master's Thesis, Duke University, May, 1931], it seemed desirable to make a preliminary report of our work at this time.

In the hope of developing a new method for the preparation of chlorimines [see Peterson, *Am. Chem. J.*, 46, 325 (1911)] the above magnesium compound was treated in the cold with an equivalent quantity of chlorine. A product was obtained which contained about 60% benzophenone-chlorimine as calculated from its active chlorine content. Although attempts to isolate the pure chlorimine have thus far failed, we have obtained further evidence that the crude product consists partly of benzophenone-chlorimine. Thus the fact that the chlorine content changed only a small amount even after standing in an open vessel at room temperatures for several weeks indicates the presence of a rather stable chlorine compound. Furthermore, when the crude product in anhydrous ether or benzene is