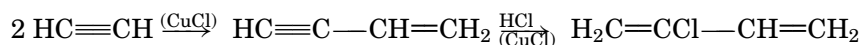


## CHLOROPRENE

Chloroprene (2-chloro-1,3-butadiene), [126-99-8] was first obtained as a by-product from the synthesis of divinylacetylene (1). When a rubbery polymer was found to form spontaneously, investigations were begun that promptly defined the two methods of synthesis that have since been the basis of commercial production (2), and the first successful synthetic elastomer, Neoprene, or DuPrene as it was first called, was introduced in 1932. Production of chloroprene today is completely dependent on the production of the polymer. The only other use accounting for significant volume is the synthesis of 2,3-dichloro-1,3-butadiene, which is used as a monomer in selected copolymerizations with chloroprene.

The original commercial production was from acetylene through monovinyl-acetylene [689-97-4],  $C_4H_4$ .



Since the 1960s, because of an increasing price for acetylene and decreasing price for butadiene, 1,3-butadiene [106-99-0],  $C_4H_6$ , has displaced acetylene as the feedstock.

### 1. Physical Properties

Selected physical properties of chloroprene are listed in Table 1. When pure, the monomer is a colorless, mobile liquid with slight odor, but the presence of small traces of dimer usually give a much stronger, distinctive odor similar to terpenes and inhibited monomer may be colored from the stabilizers used. Ir and Raman spectroscopy of chloroprene (4) have been used to estimate vibrational characteristics and rotational isomerization.

### 2. Chemical Properties

The chemical properties of chloroprene are generally similar to those of butadiene. Chloroprene has very low reactivity with nucleophilic reagents; the chlorine atom is very difficult to replace. Toward electrophilic reagents, eg, chlorine or maleic anhydride, it is somewhat less reactive than butadiene (5, 6) though it does oxidize with air. It is markedly more reactive in free-radical additions and polymerization.  $Q$  and  $e$  values of 7.3 and  $-0.02$  have been given compared to 2.4 and  $-1.05$  for butadiene (7, 8), indicating higher reactivity in copolymerizations without strong alternating tendency.

#### 2.1. Dimerization

Presumably because it is more active as a dienophile, chloroprene reacts with itself to form dimers, isomeric chlorovinylchlorocyclohexenes, at a considerably faster rate than that at which butadiene is converted to vinylcyclohexene. At the same time, 1,2-divinyl, 1,2-dichlorocyclobutanes are also formed, amounting initially to

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**Table 1. Physical Properties of Chloroprene<sup>a</sup>**

Property	Value
molecular formula	C <sub>4</sub> H <sub>5</sub> Cl
mol wt	88.54
melting point, °C	-130 ± 2
boiling point at 101 kPa <sup>b</sup> , °C	59.4
critical temperature, °C	261.7
vapor pressure ( <i>T</i> in K, <i>p</i> in kPa <sup>b</sup> )	$\log_{10} p = 6.652 - 1545/T$
viscosity at 25°C, mPa·s( = cP)	0.394
density at 20°C, g/mL	0.9585
average coefficient of volumetric expansion (20–61°C), K <sup>-1</sup>	0.001235
refractive index, <i>n</i> <sub>D</sub> <sup>20</sup>	1.4583
flash point (ASTM, open cup), °C	-20
latent heat of vaporization, kJ/g <sup>c</sup>	
0°C	0.3328
60°C	0.3027
specific heat, kJ/(kg·K) <sup>c</sup>	
liquid at 20°C	1.314
gas at 100°C	1.0383
thermal conductivity (where <i>t</i> is °C)	
mW/(m·K),	$2.410 \times 10^{-5} + 0.160 \times 10^{-5} t$
dielectric constant at 27°C	4.9

<sup>a</sup> Ref. 3.

<sup>b</sup> To convert kPa to mm Hg, multiply by 7.5.

<sup>c</sup> To convert J to cal, divide by 4.184.

about 60% of the dimer mixture. After a period of time, depending on the temperature, the composition of the crude dimers shifts, reflecting the slow decomposition of the *cis*-substituted cyclobutane isomer to form the *trans*-substituted isomer, a vinylchlorocyclohexene, and 1,6-dichlorocyclooctadiene, and probably to regenerate some monomer. At higher temperature (>100°C) the *trans* isomer undergoes a similar decomposition. Except for these decomposition processes, the ratio of products is relatively independent of temperature. The proportion of vinylcyclohexenes is significantly increased at high pressure, however. The effect has been attributed to a more compact four-center transition state for the formal Diels-Alder products vs a less compact two-center one for the cyclobutanes (9, 10). The rate of dimerization is about 1%/h at the normal boiling point and about 0.35%/d at room temperature, so that low temperature storage is required to maintain purity of the monomer for polymerization and some dimer will be formed during polymerization by any of the normal processes.

### 2.2. Polymerization

Chloroprene is normally polymerized with free-radical catalysts in aqueous emulsion, limiting the conversion of monomer to avoid formation of cross-linked insoluble polymer. At a typical temperature of 40°C, the polymer is largely head-to-tail in orientation and *trans* in configuration, but modest amounts of head-to-head, *cis*, 1,2, and 3,4 addition units can also be detected. A much more regular and highly crystalline polymer can be made at low temperature (11). Chloroprene can also be polymerized with cationic polymerization catalysts, giving a polymer with significantly more 1,2 and 3,4 structures, frequently with partial or extensive elimination of HCl and cross-linking during the process. Anionic catalysts are generally ineffective. A largely *cis* polymer of chloroprene has been prepared by an indirect route (12).

### 2.3. Isomers and Analogues

Structural isomers and analogues are significant because they occur as impurities of the manufacturing process and are also common comonomers.

#### 2.3.1. 4-Chloro-1,2-butadiene

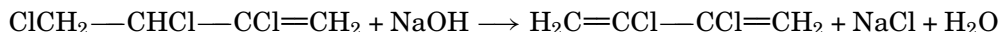
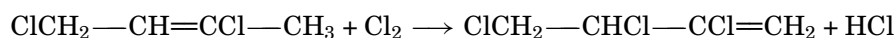
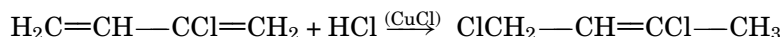
[25790-55-0] is mainly of historical interest (2). It is formed from vinylacetylene and HCl in the absence of an isomerization catalyst. In the usual process for chloroprene using cuprous chloride, a portion of this isomer may be formed initially and then isomerize, but most of the chloroprene is apparently formed directly by the addition.

#### 2.3.2. 1-Chloro-1,3-butadiene

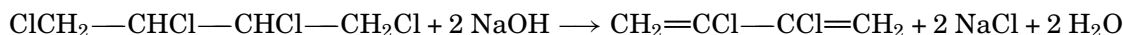
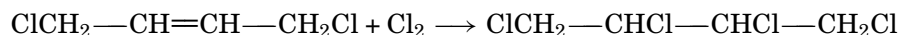
[627-22-5] is present as an impurity by any of the synthetic methods customarily used. It is formed as a by-product in the hydrochlorination of vinylacetylene or in the dehydrochlorination of 3,4-dichloro-1-butene. It can also be introduced as an impurity from the chlorination of butadiene or formed by dehydrochlorination of 1,4-dichlorobutenes. Cis and trans isomers are both present in varying proportion. Both copolymerize with chloroprene but at a lower rate, so that monomer recovered from partial polymerization is less pure than the original mixture.

#### 2.3.3. 2,3-Dichloro-1,3-butadiene

[1653-19-6] is a favored comonomer to decrease the regularity and crystallization of chloroprene polymers. It is one of the few monomers that will copolymerize with chloroprene at a satisfactory rate without severe inhibition. It is prepared from by-products or related intermediates. It is also prepared in several steps from chloroprene beginning with hydrochlorination<sup>2</sup>. Subsequent chlorination<sup>3</sup> to 2,3,4-trichloro-1-butene, followed by dehydrochlorination<sup>4</sup> leads to the desired monomer in good yield if polymerization is prevented.



Similarly, preparation of dichlorobutenes from butadiene and Cl<sub>2</sub> is accompanied by formation of tetrachlorobutanes<sup>5</sup>, which can be dehydrochlorinated<sup>6</sup> to form the desired product.

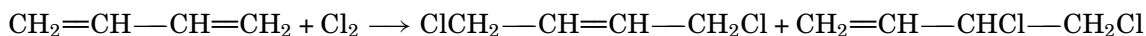


It is preferable to prepare the 1,2,3,4-tetrachlorobutane [3405-32-1] from *trans*-1,4-dichloro-2-butene [110-57-6], which gives mainly the meso tetrachloride [28507-96-2], which in turn gives a better yield and higher isomeric purity of the resulting monomer (13).

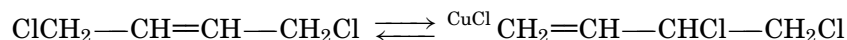
## 4 CHLOROPRENE

### 3. Manufacture

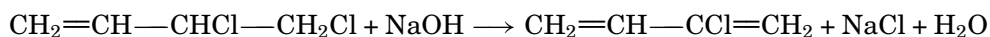
The vinylacetylene [689-97-4] route to chloroprene has been described elsewhere (14). It is no longer practical because of costs except where inexpensive by-product acetylene and existing equipment are available (see Acetylene-derived chemicals). In the production of chloroprene from butadiene [106-99-0], there are three essential steps, chlorination, isomerization, and caustic dehydrochlorination of the 3,3-dichloro-1-butene, as shown by the following equations:



*Isomerization*



*Dehydrochlorination*



#### 3.1. Chlorination of Butadiene

Butadiene and chlorine combine under almost any conditions; reaction occurs by a variety of mechanisms. In gas-phase chlorination<sup>7</sup>, the process is a free-radical chain reaction and leads to a near-equilibrium mixture of 1,4-dichloro-*cis* and *trans*-2-butene [110-57-6] isomers. The reaction is highly exothermic and relatively unselective. Good yields have been claimed (15–19) as long as a reasonable excess of butadiene is used, reactants are well mixed before appreciable reaction takes place, and temperature is maintained high enough to avoid condensation of liquid products but not so high that extensive dimerization of butadiene and carbonization occurs. Generally, one mole of chlorine is mixed with 4 to 15 moles of preheated butadiene or butadiene and diluent. The gases are allowed to react in a tubular (plug flow) reactor with or without surface cooling or in a partially back-mixed reactor followed by a plug-flow zone. Most of the reaction occurs at 200–350°C at 100–200 kPa (1–2 atm). Yields of 85 to 92% based on butadiene are expected. By-products include HCl, 1-chloro-1,3-butadiene [627-22-5], trichlorobutenes and tetrachlorobutanes, butadiene dimer, and higher boiling products, several of which involve two moles of butadiene to one of chlorine. The products are obtained by cooling the gas stream and distilling the condensate, recycling uncondensed excess butadiene for further reaction.

Liquid-phase chlorination<sup>7</sup> of butadiene in hydroxylic or other polar solvents can be quite complicated in kinetics and lead to extensive formation of by-products that involve the solvent. In nonpolar solvents the reaction can be either free radical or polar in nature (20). The free-radical process results in excessive losses to tetrachlorobutanes if near-stoichiometric ratios of reactants are used or polymer if excess of butadiene is used. The “ionic” reaction, if a small amount of air is used to inhibit free radicals, can be quite slow in a highly purified system but is accelerated by small traces of practically any polar impurity. Pyridine, dipolar aprotic solvents, and oil-soluble ammonium chlorides have been used to improve the reaction (21). As a commercial process, the use of a solvent requires that the products must be separated from solvent as well as from each other and the excess butadiene which is used, but high yields of the desired products can be obtained without formation of polymer at higher butadiene to chlorine ratio.

#### 3.2. Refining and Isomerization

Whatever chlorination process is used, the crude product is separated by distillation. In successive steps, residual butadiene is stripped for recycle, impurities boiling between butadiene (–5°C) and 3,

4-dichloro-1-butene [760-23-6] (123°C) are separated and discarded, the 3,4 isomer is produced, and 1,4 isomers (140–150°C) are separated from higher boiling by-products. Distillation is typically carried out continuously at reduced pressure in corrosion-resistant columns. Ferrous materials are avoided because of catalytic effects of dissolved metal as well as unacceptable corrosion rates. Nickel is satisfactory as long as the process streams are kept extremely dry.

Commercial production of dichlorobutenes was originally established to produce hexamethylene diamine by cyanating the 1,4-dichlorides and hydrogenating the product. Unless the 1,4 dichlorides are desired for this or other purposes, these must be isomerized to obtain a satisfactory yield<sup>8</sup> of the desired isomer. When the isomers are heated with cuprous chloride and any of a variety of solubilizing agents (22), rapid exchange occurs and a vapor richer in the more volatile 3,4-dichloride can be removed. The crude condensed isomerization product can be mixed with the original chlorination product for refining or distilled separately, recycling residual 1,4-dichlorides to the isomerization process. The isomerization process is very nearly quantitative except for a small loss to 1-chloro-1,3-butadiene [627-22-5]. The equilibrium concentrations are approximately 21% 3,4; 7% *cis*-1,4; and 72% *trans*-1,4 isomers in the liquid phase, 52%, 6%, and 42% in the vapor phase.

### 3.3. Dehydrochlorination

In the dehydrochlorination process<sup>9</sup> as first described (23), 3,4-dichloro-1-butene [760-23-6] is added at a slow, continuous rate to a well-stirred reactor along with a sodium hydroxide solution at about 10 wt % concentration, typically at about 85°C, distilling off a chloroprene stream containing water and a small amount of unreacted dichlorobutene. At lower sodium hydroxide concentration, an undesirably large volume of waste salt solution is generated. At higher concentration, reaction is actually slower, presumably because of the limited solubility of organics in the reaction medium. The maximum rate of reaction and effective conversion are related to the steam distillation temperature of the water-insoluble organic mixture as well as the conversion of NaOH to NaCl. Variations of this basic process that have been described include the use of intense agitation or surfactants, addition of various catalytic species, and decantation or stripping of products in a separate step so that reaction can be carried out more selectively at lower temperature (24–26). Reaction has also been described using butanol or other solvents to provide a homogeneous, low polarity medium for reaction (27). In each case, careful attention to inhibition of polymerization is required (28), and materials resistant to wet dichlorobutene corrosion must be used (29).

Except for the solvent process above, the crude product obtained is a mixture of chloroprene, residual dichlorobutene, dimers, and minor by-products. Depending on the variant employed, this stream can be distilled either before or after decantation of water to separate chloroprene from the higher boiling impurities. When the concentration of 1-chloro-1,3-butadiene [627-22-5] is in excess of that allowed for polymerization, more efficient distillation is required since the isomers differ by only about seven degrees in boiling point. The latter step may be combined with repurifying monomer recovered from polymerization. Reduced pressure is used for final purification of the monomer. All streams except final polymerization-grade monomer are inhibited to prevent polymerization.

#### 3.3.1. Waste Disposal

The waste brine from the dehydrochlorination process, after removal of separate-phase organics, is a relatively pure solution of sodium chloride and hydroxide in water. It can be electrochemically regenerated, recovering half of the chlorine initially used, or neutralized and purified further and discharged to naturally occurring seawater or underground brines. The organic wastes from the various purification steps are high in chlorine content and in some cases quite toxic. These are generally incinerated, scrubbing the flue gases to recover HCl.

**Table 2. World Production<sup>a</sup> of Dry Polychloroprene**

Year	Annual consumption, 10 <sup>3</sup> t
1940	2.6
1950	51
1960	135
1970	254
1980	314
1989	321

<sup>a</sup> Excluding Russia, China, and Eastern Bloc countries.

#### 4. Storage, Handling, and Shipment

Uninhibited chloroprene suitable for polymerization must be stored at low temperature ( $<10^{\circ}\text{C}$ ) under nitrogen if quality is to be maintained. Otherwise, dimers or oxidation products are formed and polymerization activity is unpredictable. Insoluble, autocatalytic “popcorn” polymer can also be formed at ambient or higher temperature without adequate inhibition. For longer term storage, inhibition is required. Phenothiazine [92-84-2], *tert*-butylcatechol [2743-78-1], picric acid [88-89-1], and the ammonium salt of *N*-nitroso-*N*-phenylhydroxylamine [135-20-6] have been recommended.

Because chloroprene is a flammable, polymerizable liquid with significant toxicity, it must be handled with care even in the laboratory. In commercial quantities, precaution must be taken against temperature rise from dimerization and polymerization and possible accumulation of explosive vapor concentrations. Storage vessels for inhibited monomer require adequate cooling capacity and vessel pressure relief facilities, with care that the latter are free of polymer deposits. When transportation of monomer is required, it is loaded cold ( $<-10^{\circ}\text{C}$ ) into sealed, insulated vessels with careful monitoring of loading and arrival temperature and duration of transit.

#### 5. Economic Aspects

Chloroprene production can be approximately equated to the amount of polymer produced. Table 2 lists estimated volumes of dry polychloroprene consumed annually for the world excluding China, Russia, and Eastern Bloc countries. This should be increased about 10% to include polymer sold as latex, yield losses, and other uses. Somewhat lower figures given elsewhere (30) are apparently for free-world consumption, not including exports to Eastern Bloc countries. About half of this volume is consumed in the United States. Production in the United States is by Du Pont and Mobay. Production elsewhere is by Distugil (France), Bayer AG, and Knapsack-Griesheim AG (Germany), Denki Kagaku, Showa Denko, and Toyo Soda (Japan), as well as Du Pont (Northern Ireland). Production capacity also exists in the former Soviet republics and China, but utilization is unknown at this time.

Compared to natural rubber or general-purpose SBR synthetic rubber, polychloroprene [9010-98-4] has typically been 25 to 75% higher in cost, slightly more when compounded formulations are calculated on a volume basis. Because of this and unsatisfactory properties at low temperature except in specialized formulations, it has been used mainly where material cost is not controlling or where its superior properties with regard to thermal stability, aging, flexing, and oil resistance, and resistance to abrasion are needed (see Elastomers, synthetic-polychloroprene). Principal areas of use are in molded goods, insulation of electrical wiring, belts, and hoses. In recent years, much of the growth in these markets, particularly wire coatings, has been filled with thermoplastic compositions of other polymers if the dimensional characteristics of a thermoset are not needed. Polychloroprene foams have also found uses where an intermediate level of fire protection is required.

It is consumed if a sufficiently vigorous fire occurs, but in contrast to general-purpose compositions, it chars and extinguishes instead of melting and initiating a fire with some of the common sources of ignition.

## 6. Specifications and Quality Control

Polymerization-grade chloroprene is typically at least 99.5% pure, excluding inert solvents that may be present. It must be substantially free of peroxides, polymer [9010-98-4], and inhibitors. A low, controlled concentration of inhibitor is sometimes specified. It must also be free of impurities that are acidic or that will generate additional acidity during emulsion polymerization. Typical impurities are 1-chlorobutadiene [627-22-5] and traces of chlorobutenes (from dehydrochlorination of dichlorobutanes produced from butenes in butadiene [106-99-0]), 3,4-dichlorobutene [760-23-6], and dimers of both chloroprene and butadiene. Gas chromatography is used for analysis of volatile impurities. Dissolved polymer can be detected by turbidity after precipitation with alcohol or determined gravimetrically. Inhibitors and dimers can interfere with quantitative determination of polymer either by precipitation or evaporation if significant amounts are present.

## 7. Safety and Health Factors

Uncontrolled polymerization and fire are the most important acute hazards in handling chloroprene. Flammable limits in air are 1.9 to 10%. It is detectable by odor at about 1 ppm in air, or lower if appreciable dimer impurities are present. A dose of several grams can produce anesthesia, but a single, brief exposure is not otherwise expected to result in lasting health effects. Long-term exposure must be more strictly controlled. Although chloroprene is mutagenic to bacteria, animal testing indicates that it does not have carcinogenic, embryotoxic, or reproductive effects. It is, however, physiologically active. Inhalation, ingestion, or absorption through the skin can result in reduced blood pressure, loss of appetite, headache, indigestion, or abnormal urine characteristics. Dermatitis, conjunctivitis, and hepatic or renal damage can also occur (31). The maximum exposure limit is 10 ppm in air. 1,3-butadiene [106-99-0] and 1,4-dichlorobutenes [110-57-6] used in manufacture must be treated as suspect human carcinogens. The 1,4-dichlorobutenes are also acutely toxic and irritating, particularly to mucous membranes.

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## Related Articles

Chlorocarbons and Chlorohydrocarbons, Survey; Elastomers, synthetic; polychloroprene