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Effects of Monomer Impurities on the Emulsion Polymerization of Chloroprene and Properties of Polychloroprene. II. Effect of Monovinylacetylene

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Synopsis

The free-radical emulsion polymerization of chloroprene containing monovinylacetylene in concentrations from 0% to 10% has been studied. It was found that in the presence of monovinylacetylene, a polymer with a great gel content, increased values of plasticity, and deteriorated physical and mechanical properties is formed. Monovinylacetylene has been proved to copolymerize with chloroprene under the conditions used. Acetylenic groups remain unchanged in the copolymer; they cause the crosslinking of polychloroprene macromolecules and corresponding changes in polymer properties. Copolymerization reactions of monovinylacetylene with chloroprene together with the crosslinking effect of monovinylacetylene cause a substantial lowering of the crystallization rate of polychloroprene.

INTRODUCTION

The purity of the monomer used is one of the main factors predetermining the properties of polymer. Technical chloroprene which is used for the manufacture of polychloroprene rubber contains usually small amounts of intermediate and by-products; the most common of them are 1-chloro-1,3-butadiene (isomer of chloroprene), methyl vinyl ketone, monovinylacetylene, divinylacetylene, 1,3-dichloro-2-butene, or peroxides and dimers of chloroprene.

The influence of methyl vinyl ketone on the emulsion polymerization of chloroprene was described in the previous part of this series.[1] It was shown that methyl vinyl ketone has an adverse effect on polychloroprene properties and polymerization kinetics, and the mechanism of this effect was fully explained.

The purpose of further studies has been to determine the effect of monovinylacetylene on the properties of polychloroprene and the rate of the emulsion polymerization of chloroprene with mercaptans as molecular weight regulators.

There have been published only very sporadic data about the effect of monovinylacetylene on the polymerization of chloroprene; in addition, some results contradict one another. For the emulsion polymerization of chloroprene using sulfur and tetraalkylthiuram disulfide as an indirect method of molecular weight regulation,[2,3] Klebanskyi et al.[4] found that monovinylacetylene in concentrations up to 0.2% in chloroprene has no effect on polymer plasticity. Shikama[5] mentioned the lowering of tensile strength of polychloroprene prepared from monomer contaminated with monovinylacetylene.

The investigation of the effect of monovinylacetylene on polymerizations of other dienes showed that, e.g., the solubility of polybutadiene prepared in the presence of monovinylacetylene was lowered[6,7] and that the tensile strength of polybutadiene vulcanizates was decreased. Other authors[9,10] found that monovinylacetylene increased the viscosity of butadiene–styrene copolymers and was an effective crosslinking agent. The crosslinking effect of monovinylacetylene was also observed in the copolymerization of isoprene and styrene.[11]

In general, acetylenic monomers tend to retard free-radical polymerizations of vinyl monomers.[12] Monovinylacetylene acts as a powerful retarder in the copolymerization of isoprene and styrene,[11] while in the copolymerization of butadiene and styrene its retarding effect is rather slight.[7,9]

Monovinylacetylene itself is an easily polymerizable substance.[13–15] The properties of polyvinylacetylene depend on the polymerization conditions. The data published on the polymer structure differ substantially from one another. According to Dykstra[13] the polymers of vinylacetylene are composed of poly(cyclobutene–cyclobutane) units with acetylenic end-groups. Other authors[12,14] found that the polymerization of monovinylacetylene takes place predominantly on the vinylic double bond and the triple bonds remain in the polymer as side ethinyl groups on the hydrocarbon chain. In addition, polyvinylacetylene may also contain some portion of allene structure, as was proved by infrared spectroscopic analysis.[12] The polymers of monovinylacetylene very easily undergo a rapid oxidative crosslinking.[12] Freshly prepared polymers are soluble; but after a very short period of aging the characteristic carbonyl bonds appear in infrared spectra and the polymer becomes insoluble. Thus, a small amount of monovinylacetylene could be expected to act as a crosslinking agent in the polymerization of chloroprene.

Monovinylacetylene rather easily copolymerizes with other monomers.[12,16] Even the triple bond can (though rather unwillingly) enter the free-radical copolymerization reaction, as was shown in the case of phenylacetylene.[17]

From the published Q,e data[18] for chloroprene (M_1) and monovinylacetylene (M_2), we have calculated the corresponding reactivity ratios for the copolymerization of the two monomers: $r_1 = 10.6$, $r_2 = 0.08$. These calculated reactivity ratios are comparable with the reactivity ratios for the copolymerization of chloroprene with styrene or acrylonitrile. Accordingly, monovinylacetylene will behave as the less reactive monomer in the copolymerization with chloroprene.

EXPERIMENTAL

Polymerization of Chloroprene

The technique of the emulsion polymerization of chloroprene at 40°C with persulfate as an initiator and primary or tertiary dodecylmercaptan was described in detail in the first paper of this series.[1] Polymerizations were short-stopped at a conversion of 69 ± 2%.

Materials

Chloroprene. The preparation and purification of chloroprene for polymerization were described in the previous work.[1] The chloroprene used for experiments contained less than 0.2% by weight of 1-chloro-1,3-butadiene (gas chromatographic method) and less than 10 ppm peroxidic compounds (polarographic method).

Monovinylacetylene (MVA). The technical-grade monovinylacetylene containing vinylchloride, acetaldehyde, and acetylene was purified in the following way: gaseous monovinylacetylene from the bomb passed through a 5% solution of hydroxylamine hydrochloride and then through 10% solution of sodium hydroxide. Monovinylacetylene was condensed by means of the cooling mixture methanol–solid carbon dioxide. The liquefied monovinylacetylene was protected by dried nitrogen against air moisture, as it forms readily the crystalline dihydrate.[13] Then the acetylene was removed by distilling off from monovinylacetylene. Gas chromatographic analysis showed only traces of vinylchloride and acetylene.

Other Materials. The purity of other substances used for polymerizations was defined in the previous paper.[1]

Dosage of Monovinylacetylene

As monovinylacetylene is a gaseous substance under normal conditions (bp +5.5°C), it was necessary to add it into the polymerization charge by a special technique. The freshly purified liquid monovinylacetylene was added into the stainless steel bottles in exactly weighted portions sealed in little thin-walled glass ampules. These ampules were then broken by cylindrical stainless steel pieces inside the bottles at the start of the polymerization (by rotating the bottles). When greater amounts of monovinylacetylene were to be added, monovinylacetylene was fed into the closed polymerization bottles by a special dosing ampule fitted with a hypodermic needle and valve. Monovinylacetylene was transferred to the bottle through the self-sealing gaskets of the cap by warming the dosing ampule. The ampule was weighed before and after injection into the polymerization charge.

All concentrations of monovinylacetylene are given in percentage by weight based on chloroprene in the polymerization charge.

Testing Methods

Infrared spectra of chloroprene polymers were recorded with the Zeiss UR-10 infrared spectrophotometer equipped with a lithium fluoride prism. Polychloroprenes were analyzed in the form of 1.5% solutions in carbon disulfide. For the determination of the monovinylacetylene in the polychloroprene, the intensity of the band at 3300 cm^{-1}, corresponding to the $—C{\equiv}CH$ group, was compared with the spectra of polymers prepared in the absence of monovinylacetylene. The published molar extinction coefficient of this group[19] was used for calculations ($E = 100$).

The rate of crystallization of polychloroprene was measured by the dilatometric method[24,25] and characterized as the crystallization half-time ($\tau/2$). Dilatometers were charged with 10 g finely cut polymer, then filled with purified mercury under reduced atmosphere (less than 10^{-2} mm Hg) and transferred into amorphous state by tempering at 70°C for 30 min. By measuring time-dependent volume changes of polymer sample at 0°C, a crystallization isotherm was obtained; the time corresponding to $^1/_2$ of the total volume contraction is the crystallization half-time.

The methods of the determination of intrinsic viscosity, solubility, Defo plasticity, and Mooney viscosity of polymer and the physical properties of polychloroprene vulcanizates were described in the first part of this series.[1]

RESULTS AND DISCUSSION

Effect of Monovinylacetylene on Rate of Polymerization of Chloroprene

No differences in the rate of the emulsion polymerization of chloroprene were found in the presence of low concentrations of monovinylacetylene (up to about 2% MVA in chloroprene). The polymerization rates for relatively high concentrations of monovinylacetylene in chloroprene are shown in Figure 1. As it can be seen, a dropping off of the polymerization rate occurred after about 35% conversion. This effect might be due to the increase of relative concentration of monovinylacetylene in the polymerization charge during the course of the polymerization (since MVA is a less reactive monomer than chloroprene). However, the retarding effect of MVA in the later part of the polymerization curve is not significant; considering the small concentrations of monovinylacetylene usually present in technical chloroprene, its influence on the polymerization rate has no practical importance.

Effect of Monovinylacetylene on Structure of Polychloroprene

It was found in many experiments that monovinylacetylene causes substantial structural changes of resulting polymers, which appear especially in crosslinking. The dependency of the amount of insoluble gel in polychloroprene on monovinylacetylene concentration is shown in Figure 2 for

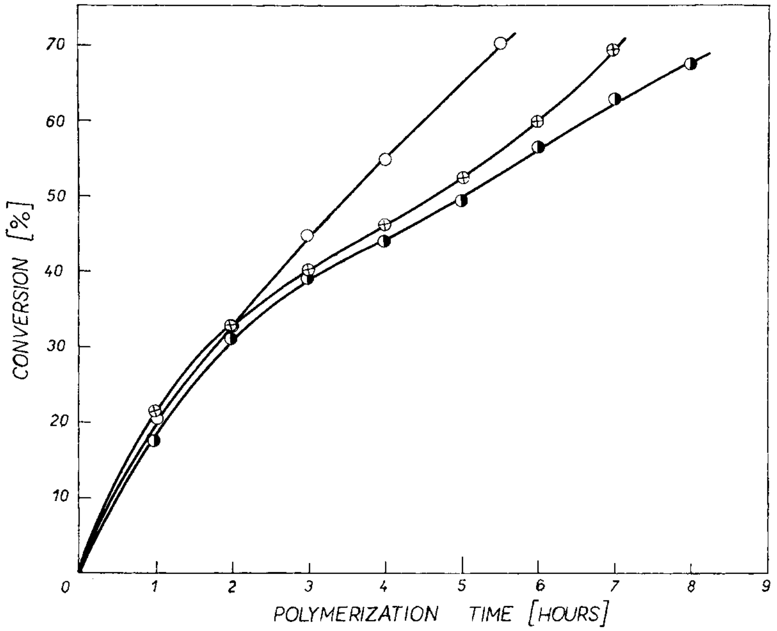

Fig. 1. Rates of emulsion polymerizations of chloroprene containing various amounts of monovinylacetylene (*n*-dodecylmercaptan as molecular weight regulator): (O) 0%; (⊗) 5.0%; (◑) 10.0%.

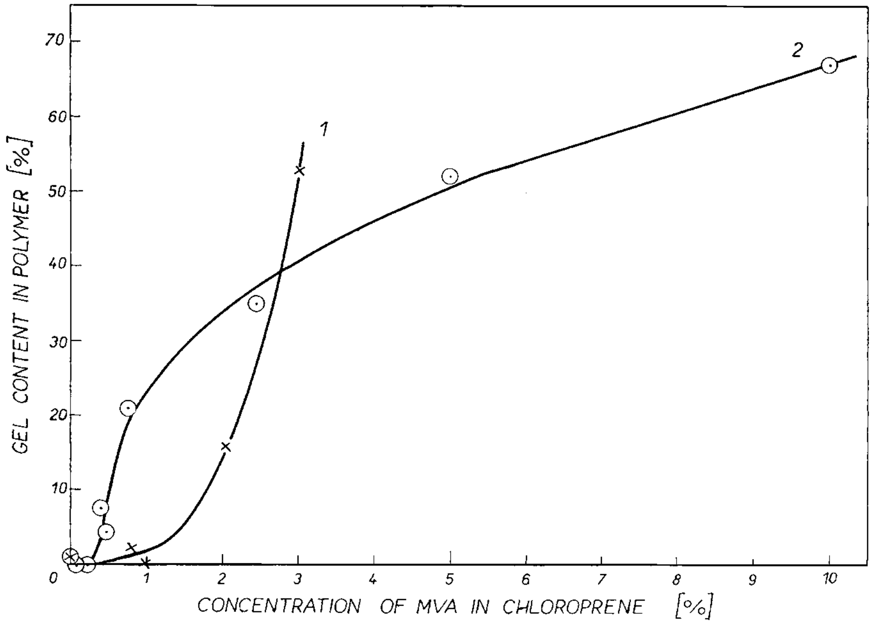

Fig. 2. Effect of monovinylacetylene on gel content in polychloroprene: tertiary (1) and primary (2) dodecylmercaptans as molecular weight regulators.

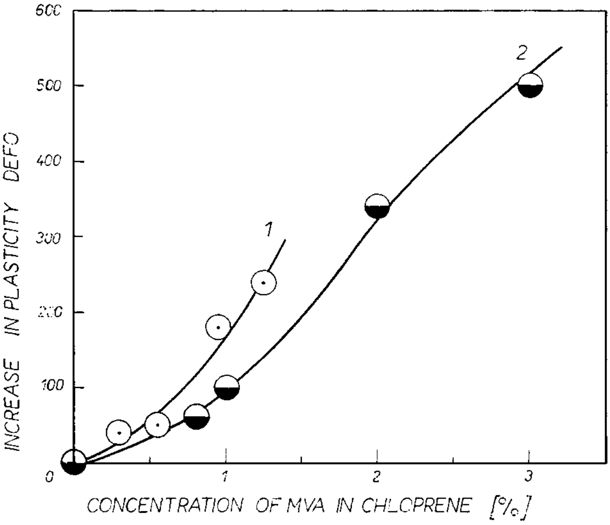

Fig. 3. Increase of polymer plasticity in dependence on concentration of monovinylacetylene in chloroprene: primary (1) and tertiary (2) dodecylmercaptan as molecular weight regulators.

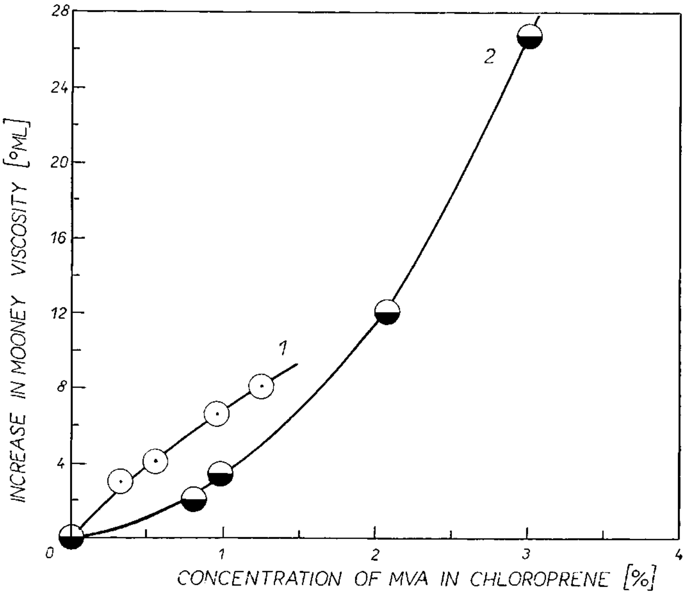

Fig. 4. Change in Mooney viscosity of polymer with concentration of monovinylacetylene in chloroprene: primary (1) and tertiary (2) dodecylmercaptan as molecular weight regulators.

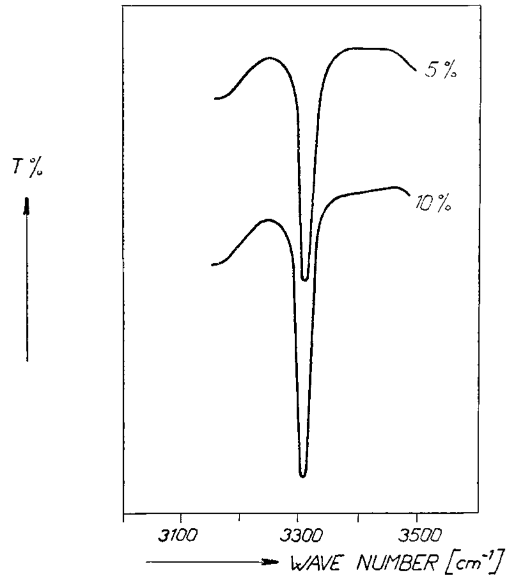

Fig. 5. Sections of infrared spectra of polychloroprene samples polymerized in the presence of 5% and 10% MVA in chloroprene.

both primary and tertiary dodecylmercaptan as molecular weight regulators.

Because of the gel content in polychloroprene, the intrinsic viscosity relationship cannot be used for indication of changes in the molecular weight of polymer. However, these changes can be well followed by measuring the plasticity and Mooney viscosity of polymer in dependence on monovinylacetylene concentration in chloroprene. The data obtained are plotted in Figures 3 and 4.

Somewhat different results found for primary and tertiary dodecylmercaptan can be accounted for by the different regulation efficiency[1,20,21] of both the molecular weight regulators. The tertiary dodecylmercaptan is a less effective regulator than the primary one; a greater amount of it is necessary to be charged into the system, and it is consumed more slowly in the course of polymerization. Thus, while the consumption of primary dodecylmercaptan takes place at the same rate as chloroprene polymerizes, the relative amount of tertiary dodecylmercaptan in the system substantially increases to the end of the polymerization and by transfer reactions it can suppress crosslinking reactions to some extent.

The results indicate that apparently monovinylacetylene enters the polymerization reaction and that the vinylacetylene units in polychloroprene chains are the points of crosslinking.

The occurrence of the copolymerization reaction of monovinylacetylene with chloroprene has been proved in two ways. The first one was the infrared analysis of polychloroprene samples polymerized in the presence

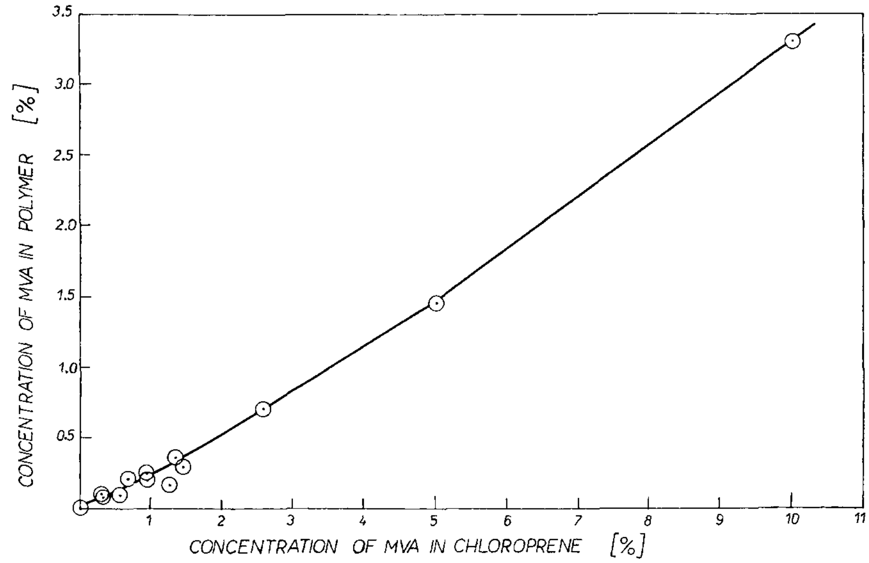

Fig. 6. Dependence of amount of monovinylacetylene units in polychloroprene on monovinylacetylene concentration in chloroprene.

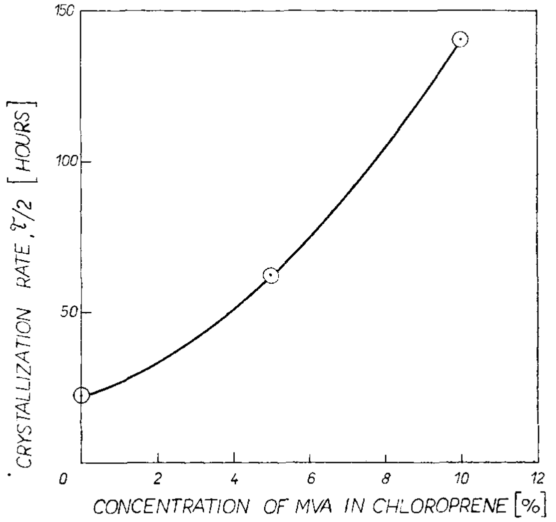

Fig. 7. Effect of monovinylacetylene on crystallization rate of polychloroprene.

of various amounts of monovinylacetylene in the polymerization charge (Fig. 5). The analyses showed the increasing content of —C≡CH groups in polymers with increasing concentration of monovinylacetylene (Fig. 6). However, the actual amount of monovinylacetylene built into the polymer should be somewhat greater, because a part of —C≡CH is involved in crosslinking reactions.

The accuracy of results obtained as regards the absolute value of the concentration of monovinylacetylene units in polymer depends also on the accuracy of the extinction coefficient[19] used for the calculations. Anyway, the infrared method of estimation of —C≡CH groups in polychloroprene has been found to be precise enough (under the condition of the same conversion in polymerization) to ascertain subsequently the presence or absence of monovinylacetylene in the starting monomer and to determine approximately the initial amount of monovinylacetylene in chloroprene in concentrations as low as about 0.3%.

The results of infrared analyses have also demonstrated that monovinylacetylene enters the polymerization reaction as a vinyl-type monomer, i.e., the ethinyl groups remain in the resulting copolymer as side groups on polymer chain.

Another evidence of the copolymerization of monovinylacetylene with chloroprene is the lowering of the crystallization tendency of polychloroprene. It is well known that the introduction of any irregularity into polymer chains results in a decrease of the crystallization rate of polymer. Crosslinking of polymer has a similar effect on crystallization[22,23]; the crosslinks between polymer chains prevent the regular crystalline arrangement of macromolecules.

Figure 7 shows the crystallization half-times of polychloroprene samples in dependence on monovinylacetylene concentration in the starting monomer. The results indicate a very substantial lowering of the rate of crystallization caused by monovinylacetylene.

Effect of Monovinylacetylene on Properties of Polychloroprene

The effect of monovinylacetylene on the physical and mechanical properties of polychloroprene can be well demonstrated on the samples with a relatively high content of monovinylacetylene. At concentrations below 1% monovinylacetylene in chloroprene, the corresponding changes in polymer properties are often within the limits of experimental error of the testing methods. The most interesting results are presented in Table I. The samples tested were unloaded vulcanizates.

The experimental results showed a considerable decrease in tensile strength and elongation at break of polychloroprene vulcanizates with increasing content of monovinylacetylene, while the values of modulus increased. In addition, a worse processability of polymers with monovinylacetylene was found on milling as well as an increased tendency to scorch.

Some differences in color were observed after several months of shelf-aging (in darkness, 20°–30°C) of polychloroprene samples with various amounts of monovinylacetylene. Polymers with considerable amounts of monovinylacetylene were getting dark more rapidly than polymers with a low content of monovinylacetylene or reference samples prepared from pure chloroprene.

The lowering of modulus, the tendency to scorching, and the more difficult processability of polymers are apparently due to the formation of crosslinked polymer in the presence of monovinylacetylene.

TABLE I
Properties of Polychloroprene Vulcanizates Polymerized in Presence of Monovinylacetylene

	Vulcanization time, min	Numerical values of properties		
		0% MVA[a]	5.0% MVA	10.0% MVA
Tensile strength, kg/cm^2	5	210	145	112
	10	220	140	90
	15	181	100	93
Elongation at break, %	5	1000	800	700
	10	920	720	470
	15	800	520	440
300% Modulus, kg/cm^2	5	13	18	28
	10	14	30	50
	15	14	40	51
500% Modulus, kg/cm^2	5	28	48	60
	10	30	67	—
	15	30	75	—
Permanent set[2] %	5	18	20	16
	10	14	16	6
	15	12	6	4

[a] Concentration of monovinylacetylene in monomer.

The decrease in tensile strength of polychloroprene vulcanizates with increasing concentration of monovinylacetylene in polymerization charge is in good correlation with the relationship between the crystallization rate of polymers and monovinylacetylene concentration in chloroprene (Fig. 6), as it is known that tensile strength generally decreases with increasing crystallization half-time.

CONCLUSIONS

The presence of monovinylacetylene in the emulsion polymerization of chloroprene causes some changes of polymer properties. The most significant of them are: formation of insoluble crosslinked polymer, increase of molecular weight, deterioration of physical and mechanical characteristics of vulcanizates, and lowering of crystallization rate of polychloroprene. When molecular weight of polymer is regulated by *n*-dodecylmercaptan, these changes can be observed at monovinylacetylene concentrations as low as about 0.5% in chloroprene.

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