

Effects of Monomer Impurities on the Emulsion Polymerization of Chloroprene and Properties of Polychloroprene. IV. Effect of 1-Chloro-1,3-butadiene

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Synopsis

The influence of small amounts of 1-chloro-1,3-butadiene on the kinetics of the emulsion polymerization of 2-chloro-1,3-butadiene and on properties of the resulting polychloroprene has been studied. Some changes in the properties of the chloroprene polymers were observed at 1-chloro-1,3-butadiene concentrations in monomer as relatively high as about 5%. Polymer prepared in the presence of 5% 1-chloro-1,3-butadiene had decreased tensile strength, and also its crystallization tendency was somewhat lowered. At 1-chloro-1,3-butadiene concentrations near 1% or higher, the polychloroprene obtained had worsened thermo-oxidation stability which resulted in crosslinking during aging. The kinetics of emulsion polymerization of chloroprene are not influenced by 1-chloro-1,3-butadiene up to 5%.

INTRODUCTION

The importance of high purity of monomers used for polymerization processes and for obtaining polymers of required characteristics was discussed in the previous parts of this series.^{1,2,3} In this respect, chloroprene is a very sensitive monomer to the presence of some organic impurities, especially methylvinyl ketone,¹ monovinylacetylene,² and divinylacetylene.³ Relatively low concentrations of any of these compounds are sufficient to influence the properties of polychloroprene.

Using the method of preparative gas chromatography, it was only recently possible to identify^{4,5} another compound usually present in technical-grade chloroprene; this compound is 1-chloro-1,3-butadiene ("chloroprene isomer"). In this work, we have focused our attention on the determination of the influence of this compound on the kinetics of the emulsion polymerization of chloroprene and especially on the properties of the resulting polychloroprene.

1-Chloro-1,3-butadiene itself polymerizes relatively easily,⁶ though the polymerization rate is 100 times slower than in the case of 2-chloro-1,3-butadiene (chloroprene).⁷ This fact conforms with the general observation that substitution of butadiene in the alpha position results in decreased

polymerization activity of the derivative in comparison with corresponding beta-substituted butadiene.^{8,9}

The homopolymerization of 1-chloro-1,3-butadiene was investigated by Klebanskyi and co-workers.¹⁰ The different reactivity of butadiene derivatives substituted with chlorine in positions 1 or 2 was attributed by Klebanskyi to the sterical hindrance formed by the chlorine atom placed on the outer carbon atom. Different properties of the polymers of these two compounds are caused by polymerizing 2-chloro-1,3-butadiene mainly in the 1,4-configuration,¹¹ while, according to Klebanskyi,¹⁰ the addition of 1-chloro-1,3-butadiene takes place predominantly in the 3,4-configuration.

The properties of 1-chloro-1,3-butadiene polymers were found to be substantially worse from the point of view of their practical application than those of polychloroprene.¹⁰ These polymers have elastic behavior, but their tensile strength is considerably low.⁸

As regards the influence of 1-chloro-1,3-butadiene on the chloroprene polymerization, a number of disclosures in some patents recently published¹²⁻¹⁵ state that this influence is considered as "adverse" and that the complete removal of 1-chloro-1,3-butadiene from chloroprene results in substantial improvement in properties of the elastomer prepared. However, none of these sources gives more specified information about the individual properties of polychloroprene that are influenced by the presence of 1-chloro-1,3-butadiene.

Separating very small amounts of 1-chloro-1,3-butadiene from chloroprene is rather difficult because of their similarity in boiling points (chloroprene, 59.4°C; the published data on the bp of 1-chloro-1,3-butadiene^{10,16-19} differ from one another in the range of 65°-68°C).

It has been proved^{10,18,20,21} that 1-chloro-1,3-butadiene can exist both in the *cis* and *trans* configurations, which have different physical properties and chemical reactivity. Either of these forms may be isolated, and it is also possible to isomerize the *cis* form to the *trans* isomer.¹⁸

From the polymerization activities, it may be presumed that in the case of chloroprene containing some quantities of 1-chloro-1,3-butadiene, the copolymerization of both these monomers can take place under emulsion polymerization conditions. The preparation of such copolymers, i.e., 1-chlorine- and 2-chlorine-substituted butadiene, has been described.²⁴

EXPERIMENTAL

Polymerization of Chloroprene

The technique of the emulsion polymerization of chloroprene at 40°C with $K_2S_2O_8$ as initiator and primary dodecyl mercaptan as regulator was described in the first paper of this series.¹ Polymerizations were short-stopped at a conversion of $67 \pm 1\%$.

Materials

Chloroprene. Chloroprene used for polymerizations was rectified in nitrogen atmosphere under reduced pressure to such a degree that no im-

purity in the monomer could be identified by gas-chromatographic analysis. The content of peroxidic compounds as determined by the polarographic method was a maximum of 10 ppm active oxygen in chloroprene.

1-Chloro-1,3-butadiene (1-CB). 1-Chloro-1,3-butadiene was prepared in two ways:

(a) By chlorination of butadiene in the vapor phase²² at 70 °C, a mixture of chlorinated C₄-hydrocarbons was obtained. From the reaction mixture, the crude 1,4-dichloro-2-butene (fraction with bp 140°–150°C under normal conditions) was isolated by rectification. Pure 1-CB was obtained by dehydrochlorination of 1,4-dichloro-2-butene with powdered potassium hydroxide according to Starkweather and Collins,²³ using distillation and subsequent preparative gas-chromatography. Because this method was rather tedious and its yields were low, the greater portion of 1-CB was prepared by the second method.

(b) Using effective rectification (jacketed column 120 cm in length, 3 cm in diameter, packed with 3-mm Cu coils, reflux ratio from 1/10 to 1/15), a portion enriched with 1-CB was prepared from technical-grade chloroprene containing 5–6% 1-CB. Pure 1-CB was prepared from this enriched portion by means of preparative gas chromatography. 1-CB was immediately stabilized with 1% phenothiazine, sealed in an inert atmosphere into small glass ampoules, and stored at –25°C. The inhibitor was removed before the polymerization by distillation.

Other Materials. The purity of the other materials used in the polymerizations was specified in previous sections.^{1,2,3}

Dosage of 1-Chloro-1,3-butadiene

Accurately weighed pure 1-CB was dissolved in chloroprene and dosed directly into the polymerization charge.

Testing Methods

Dilatometric determination of polymer crystallinity, solubility, Defo plasticity, Mooney viscosity, and physical and mechanical properties were described in previous parts of this series.^{1,2,3}

RESULTS AND DISCUSSION

Effect of 1-Chloro-1,3-butadiene on the Kinetics of the Emulsion Polymerization of Chloroprene

It has been proved in many polymerization experiments that 1-CB has no influence on the rate of the emulsion polymerization of chloroprene in amounts up to about 5% 1-CB. The difference between individual polymerization curves was not greater than 1% conversion.

The latices prepared in the emulsion polymerization of chloroprene in the presence of 1-CB did not differ from one another in their polymer particle size, stability, and other colloidal properties.

Effect of 1-Chloro-1,3-butadiene on Polychloroprene Properties

No differences were found in intrinsic viscosity and solubility of the polychloroprene samples prepared in the presence of various amounts of 1-CB. In order to determine the values after aging of the samples during storage, the intrinsic viscosity and solubility data were measured after 12 and 32 months of storage at room temperature (about 25°C). The results obtained are summarized in Tables I and II.

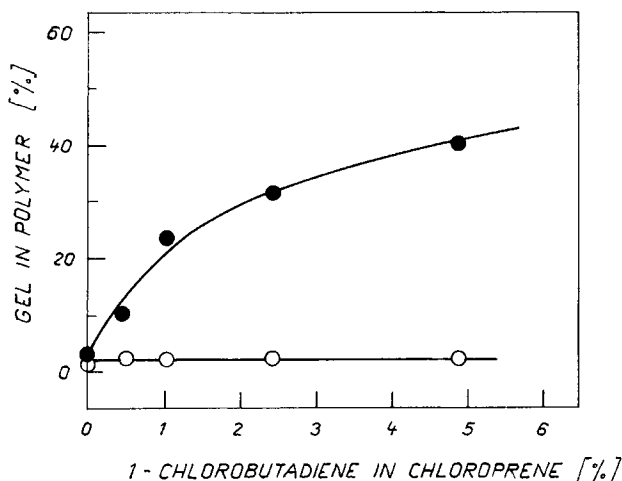


Fig. 1. Increase in amount of gel after aging polychloroprene samples prepared in presence of various amounts of 1-chloro-1,3-butadiene: (O) freshly prepared polymers; (●) after 32 months at 25°C.

Freshly prepared polymers do not differ from one another in solubility or intrinsic viscosity; but some changes occur during aging. In samples prepared with 2.44% 1-CB or higher, apparent crosslinking reactions were evident after 12 months, which gave rise to the "loose" gel (turbid polymer solutions). After prolonged storage of the samples, further crosslinking

TABLE I
Effect of 1-Chloro-1,3-butadiene on Solubility
and Aging Stability of Polychloroprene

Concentration of 1-CB in monomer, %	Polymer solubility, %		
	Freshly prepared polymers	After 12 months of aging	After 32 months of aging
0	99	100	97
0.49	98	99	90
1.03	98	97	77
2.44	98	95 ^a	69
4.90	98	98 ^a	61

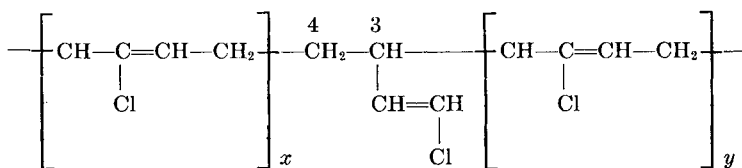
^a Polymers containing filterable gel (turbid polymers solutions).

TABLE II
Effect of 1-Chloro-1,3-butadiene on Intrinsic Viscosity
of Polychloroprene

Concentration of 1-CB in monomer, %	Intrinsic viscosity [η]		
	Freshly prepared polymers	After 12 months of aging	After 32 months of aging
0	1.59	1.40	1.52
0.49	1.60	1.45	1.55
1.03	1.58	1.47	1.58
2.44	1.62	1.55	1.65
4.90	1.58	1.52	1.28

caused formation of a considerable portion of gel in the polymer, even at 1-CB concentrations as low as about 1% (Fig. 1).

The decreased stability of polychloroprene prepared in the presence of 1-CB may be attributed to the introduction of 1-chloro-1,3-butadiene units in the 3,4-position into the basic polychloroprene chain:



Vinylly bonded chlorine is the most stable type of bonded chlorine, and its splitting off is not apt to occur. It may be expected, however, that during the oxidative aging of polymer the chain is first attacked on the

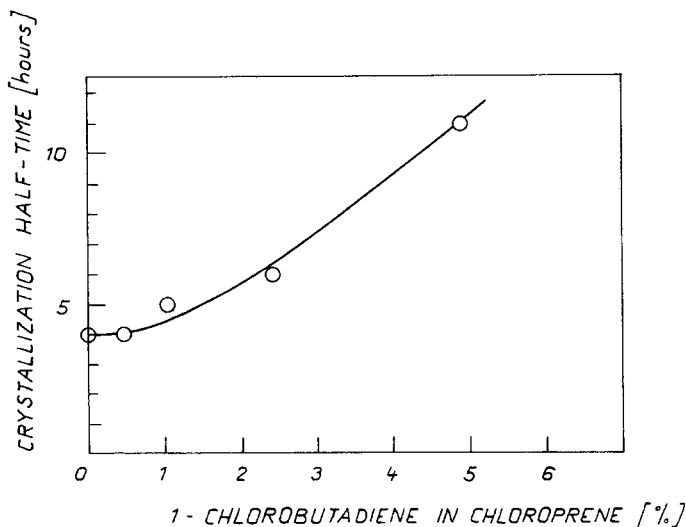


Fig. 2. Effect of 1-chloro-1,3-butadiene in monomer on crystallization rate of polychloroprene.

side-vinyl groups and that the crosslinking reaction in copolymers of chloroprene-1-chloro-1,3-butadiene takes place just in these points. The infrared spectra of the samples did not succeed in identifying any absorption bands corresponding to carbonyl groups, which could indicate an oxidation of polychloroprene.²⁵

The presence of 1-CB in the polymerization system resulted in a slightly increased crystallization rate of the polychloroprene obtained. The dependence of the crystallization half-time of homogenized (mill mixed, 3 min) polymer samples on the concentration of 1-CB in monomer is shown in Figure 2. It is evident that in the presence of 1-chloro-1,3-butadiene,

TABLE III
Dependence of Physical and Mechanical Properties of Polychloroprene
on Amount of 1-Chloro-1,3-butadiene in Chloroprene

	Vul- caniza- tion time, min	Numerical values of properties				
		0%* 1-CB	0.49% 1-CB	1.03% 1-CB	2.44% 1-CB	4.90% 1-CB
Scorch (for $\Delta 5^\circ\text{ML}$ at 140°C), min		30	30	29	30	23
Tensile strength, kg/cm ²	10	198	190	192	193	173
	20	201	190	200	202	168
	30	182	200	190	190	175
	40	205	195	192	182	149
Elongation at break, %	10	—	—	—	—	—
	20	970	850	1000	980	980
	30	980	850	1030	1000	1000
	40	980	780	940	840	850
500% Modulus, kg/cm ²	10	16	18	20	20	21
	20	19	23	22	22	22
	30	22	25	23	23	24
	40	20	27	23	24	26
Permanent set, %	10	18	14	18	19	18
	20	14	10	14	14	14
	30	14	10	14	14	12
	40	14	8	10	12	8

* Concentration of 1-chloro-1,3-butadiene in monomer.

copolymerization reactions of the two monomers occur. The regularity in the polychloroprene chain arrangement is affected by the introduction of the 3,4-structural units, and thus the crystallization of the polymer is limited. The decrease in crystallization rate caused by 1-CB is roughly the same as that observed in copolymers of chloroprene-styrene at comparable compositions of polymerization charges.²⁶

Estimating thermal stability of the polymer samples, no differences were observed between samples polymerized in the presence and in the absence of 1-CB. Thermal stability was measured at 120°C for 8 hr (Mooney viscosity, intrinsic viscosity, color of polymers).

The determination of physical and mechanical properties of polychloroprenes prepared in the presence of 1-CB proved that 1-chloro-1,3-butadiene decreases the tensile strength of the elastomer and the scorch times, though only at relatively high concentrations (Table III).

CONCLUSIONS

Some influence of 1-chloro-1,3-butadiene in the emulsion polymerization of chloroprene could be observed only at relatively high concentrations of this compound (approximately at 5%) in the monomer. The most significant changes found are decrease in tensile strength, increase in scorch rate, and moderate decrease in the crystallization rate of polychloroprene. Polymers prepared in the presence of 1% 1-chloro-1,3-butadiene tend to crosslink after aging. All these changes may be attributed to the copolymerization of 1-chlorobutadiene with chloroprene and to the introduction of some chlorine-substituted vinyl groups into the polymer chains. The polymerization rate was not influenced by up to 5% 1-chloro-1,3-butadiene in chloroprene.

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