

Effects of Monomer Impurities on the Emulsion Polymerization of Chloroprene and Properties of Polychloroprene. V. Effect of 1,3-Dichloro-2-Butene

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Synopsis

The emulsion polymerization of chloroprene in the presence of 1,3-dichloro-2-butene in various concentrations up to 5% was studied. In contrast to all other common chloroprene impurities, no influence of this compound on the kinetics of chloroprene polymerization and the properties of polychloroprene was found. 1,3-Dichloro-2-butene does not cause polymer chain transfer and it is not able to copolymerize with chloroprene under the given polymerization conditions.

INTRODUCTION

The influence of the most significant compounds that are usually present as impurities in chloroprene used for polychloroprene rubber production, i.e., methylvinyl ketone, monovinylacetylene, divinylacetylene, and 1-chloro-1,3-butadiene, on the emulsion polymerization process and polymer properties was investigated in the previous parts of this series.¹⁻⁴ Each of these compounds has shown a pronounced effect on the structure and physical properties of the resulting polymer product, and some of them have also affected the polymerization kinetics.

1,3-Dichloro-2-butene is another of the impurities usually found in technical chloroprene in small concentrations. It is formed as a by-product in the hydrochlorination of monovinylacetylene to chloroprene, when the addition of HCl to chloroprene results in the attachment of a chlorine atom onto the outer carbon atom, together with shifting of the remaining double bond.⁸ The major part of dichlorobutene formed can be easily removed by effective rectification of chloroprene.

No data concerning the influence of 1,3-dichloro-2-butene on chloroprene polymerization have been found. As for 1,3-dichloro-2-butene itself, it is known that in the presence of some Friedel-Crafts catalysts, it can undergo polycondensation reactions forming various low molecular weight polymers; e.g., $C_{68}H_{86}Cl_{13}$ polymers have been isolated.⁵ In the reaction of 1,3-dichloro-2-butene with chloroprene (or other dienes) in the presence of Friedel-Crafts catalysts, a telomerization takes place by cationic mech-

anism, in which one, two, three, or more molecules of chloroprene are added to one dichlorobutene molecule, e.g., Klebanskyi and co-workers⁶ prepared $C_{28}H_{36}Cl_4$ compounds.

Recently, it has been proved⁷ that 1,3-dichloro-2-butene cannot polymerize by the free-radical mechanism; however, it has also been found that it can enter a free-radical copolymerization reaction with vinyl acetate⁷ (reactivity ratios are $r_1 = 4.8 \pm 0.9$; $r_2 = 0.0$). At the same time, dichlorobutene acts as the chain transfer agent and causes moderate inhibition of copolymerization.

These observations indicate that 1,3-dichloro-2-butene is a monomer with very low polymerization activity, but that the possibility of its copolymerization with chloroprene cannot be excluded. In the copolymerization, a labile chlorine atom would be incorporated into polychloroprene chains which would result in lowered thermo-oxidation stability of polychloroprene.

EXPERIMENTAL

Polymerization of Chloroprene and Testing Methods

The technique of the emulsion polymerization of chloroprene as well as all the testing methods used were described in detail in the previous parts of this series.¹⁻⁴

Materials

Chloroprene. The chloroprene used for the experiments contained less than 0.2% by weight 1-chloro-1,3-butadiene. The content of peroxidic compounds varied in the range of 0-10 ppm active oxygen in monomer.

1,3-Dichloro-2-butene. This compound was obtained as a crude product from Duslo Chem. Co., Šala. It was purified by effective fractionation in a bubble tray column (60 apparent trays, heated jacket, reflux ratio 1:15 to 1:8). The boiling point of the fraction used was 127.0°-127.3°C at 755 mm Hg, and its refractive index was 1.4710 at 20°C, that is, in good agreement with published data.⁸⁻¹⁰ The purity of 1,3-dichloro-2-butene as estimated by gas-chromatographic analysis was 99.8% (mixture of *cis* and *trans* isomers). Dichlorobutene was charged into the polymerization emulsion similarly as in the case of 1-chloro-1,3-butadiene.⁴

Other Materials. The purity of all other chemicals used was specified in the first part of this series.¹

RESULTS AND DISCUSSION

Effect of Dichlorobutene on the Kinetics of the Polymerization of Chloroprene

No differences in the rates of emulsion polymerization of chloroprene were found in the presence of 1,3-dichloro-2-butene in concentrations up

to about 5% in monomer. The course of individual conversion curves did not differ more than 1% from the average conversion values.

Effect of Dichlorobutene on Properties of Polychloroprene

In order to verify that dichlorobutene does not transfer with polychloroprene chains—as was observed in the copolymerization of 1,3-dichloro-2-butene with vinyl acetate⁷—we measured the dependence of polymer intrinsic viscosity on the concentration of dichlorobutene in the monomer used. The values of intrinsic viscosity together with the data on Defo plasticity, Mooney viscosity, polymer solubility, and crystallization rate of the chloroprene polymers prepared in the presence of various amounts of dichlorobutene are summarized in Table I.

The experimental results show that none of the followed properties of polychloroprene was influenced by 1,3-dichloro-2-butene.

TABLE I
Effect of 1,3-Dichloro-2-butene on Properties of Polychloroprene

Dichloro- butene in chloro- prene, %	$[\eta]$	Polymer solubility, %	Defo plasticity, g	Mooney viscosity, ML 4/100	Crystallization half-time, hr
0	1.36	100	340	42	5.5
1.0	1.43	99	390	40	6.5
2.0	1.45	99	510	47	7.3
3.0	1.45	98	360	43	6.3
4.0	1.52	99	360	42	5.0
5.0	1.36	97	450	47	5.0

TABLE II
Effect of 1,3-Dichloro-2-butene on Properties of Polychloroprene and Vulcanizates

	Numerical values of properties					
	0% ^a	1.0%	2.0%	3.0%	4.0%	5.0%
Scorch (for $\Delta 5^\circ$ ML at 140°C)	30	20	30	27	30	30
Shrinkage on milling (50°C), %	189	171	211	216	182	152
Tensile strength, kg/cm ²	194	184	202	189	183	201
Elongation at break, %	920	950	920	850	860	900
300% Modulus, kg/cm ²	12	10	13	15	13	13
Permanent set, %	11	12	7	8	8	10
Shore hardness, °Sh	40	38	42	42	43	41
Elasticity Schopper	58	55	58	59	59	58
Light stability (white vulcanizate under Hg lamp)	approximately the same for all samples					

^a Concentration of 1,3-dichloro-2-butene.

The estimation of the chlorine content in the polymer samples could not contribute to solving the question whether the copolymerization of dichlorobutene with chloroprene takes place or not; after complete copolymerization of 5% dichlorobutene with chloroprene (100% conversion), the theoretical increase in chlorine content in the copolymer would be 0.9%. The sensitivity of the methods available for the determination of chlorine was not sufficient for determining such small concentration changes in the chlorine content in polymers.

The presence of dichlorobutene in the polymerization of chloroprene had also no effect on the thermo-oxidation stability of polychloroprene. All samples were completely soluble after 12 months, and their intrinsic viscosity values were equal and unchanged as well.

A summary of the physical and mechanical properties of the vulcanizates prepared from polychloroprene samples polymerized in the presence of various amounts of dichlorobutene is presented in Table II.

CONCLUSIONS

The experimental results indicate that 1,3-dichloro-2-butene is evidently not able to copolymerize with chloroprene under the conditions used. In contrast to all other impurities in monomeric chloroprene, it has no influence on the structure and molecular weight of polychloroprene or on the physical and mechanical properties of the vulcanizates.

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