

Effects of Monomer Impurities on the Emulsion Polymerization of Chloroprene and Properties of Polychloroprene. III. Effect of Divinylacetylene

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Synopsis

The presence of small amounts of divinylacetylene in the monomer during the emulsion polymerization of chloroprene results in substantial increase of the molecular weight, gel formation, and in corresponding changes of physical and mechanical properties of vulcanizates. These changes appear at concentrations of divinylacetylene as low as 0.05% in chloroprene. The polymerization kinetics of chloroprene are influenced to a relatively small extent.

INTRODUCTION

The purity of the monomer used is one of the main factors in all polymerizations, predetermining the properties of the polymer formed. In this respect chloroprene belongs to the most sensitive monomers. Frequently, the presence of some impurities in chloroprene is the reason of nonreproducibility of the polymerization process and undesirable changes in polychloroprene properties.

Together with the complicated roles of oxygen and chloroprene peroxides, the presence of impurities in chloroprene is also the reason why certain basic theoretical relationships in the radical polymerization of chloroprene were not studied until lately and why the kinetic constants of the elementary reactions in the emulsion polymerization of chloroprene were not determined.¹

In the preceding papers,^{2,3} the roles of methyl vinyl ketone and monovinylacetylene in the emulsion polymerization of chloroprene were described and their effects on polychloroprene properties and polymerization kinetics were demonstrated.

Divinylacetylene is another by-product often contaminating the industrial chloroprene monomer prepared in the most common process, i.e., by the dimerization of acetylene and hydrochlorination of the monovinylacetylene formed. This compound is usually present only in some very low concentrations (mostly from 10^{-4} to $10^{-1}\%$), which are rather difficult to be precisely determined analytically. In spite of this, some striking changes in polymer properties were observed in the presence of relatively small quantities of divinylacetylene.

It is the purpose of this study to define the properties of polychloroprene which are influenced by divinylacetylene, estimate quantitatively the influence of divinylacetylene on these properties, and to establish the requirements for the purity of the monomer used for the emulsion polymerization of chloroprene.

An adverse effect of divinylacetylene on the polymerization of chloroprene was mentioned by Klebanskyi⁴ who determined its influence on the Carrer plasticity and on the heat stability of the polychloroprene the molecular weight of which was regulated by the sulfur-tetramethylthiuram disulfide system.

The emulsion polymerization in the presence of dodecylmercaptans as regulators is in general more sensitive to the presence of any reactive compound present in the polymerization system.

EXPERIMENTAL

Polymerization of Chloroprene

The technique of the emulsion polymerization of chloroprene at 40°C with $K_2S_2O_8$ as an initiator and *n*-dodecyl mercaptan as a regulator was described in detail in the first part of this series.² Polymerizations were short-stopped at a conversion of $69 \pm 2\%$.

Materials

Chloroprene. The only impurity in the chloroprene used for experiments was 1-chloro-1,3-butadiene in concentrations less than 0.2% by weight. The maximum content of peroxidic compounds was 10 ppm active oxygen in monomer. The purification and preparation of chloroprene for polymerizations were described previously.²

Divinylacetylene (DVA). Crude DVA in the form of 50% solution of technical-grade DVA in xylene was rectified under reduced pressure in a nitrogen atmosphere (column length 50 cm, Cu coils with diameter 3 mm). It yielded a fraction enriched in DVA, which was stabilized with 0.5% *p*-tertiary butylcatechol and 0.5% phenothiazine. From this fraction, chromatographically pure divinylacetylene (bp 83.5°C⁵) was prepared by means of preparative gas chromatography. Divinylacetylene was stored for only a short period before use at Dry Ice temperature in order to prevent its spontaneous polymerization.

Dosage Divinylacetylene

Divinylacetylene was added to chloroprene in the form of 20–30% solution in thiophene-free benzene. Calculated portions of the solution were weighed with an accuracy of ± 0.0002 g and then transferred from the weighing bottles directly into the polymerization charge.

Testing Methods

The methods for the determination of solubility, Mooney viscosity, crystallinity, physical and mechanical properties of the polymer, and infrared analysis of polychloroprene were described in previous papers.^{2,3}

RESULTS AND DISCUSSION

Effect of Divinylacetylene on Polymerization Rate

In many experiments it was found that divinylacetylene slightly decreases the rate of the emulsion polymerization of chloroprene. This retarding effect is not very significant; with 0.25% DVA in chloroprene, the polymerization rate near 60% conversion is slower by about 5–10% than in the absence of DVA (Fig. 1). The retardation by DVA has an effect

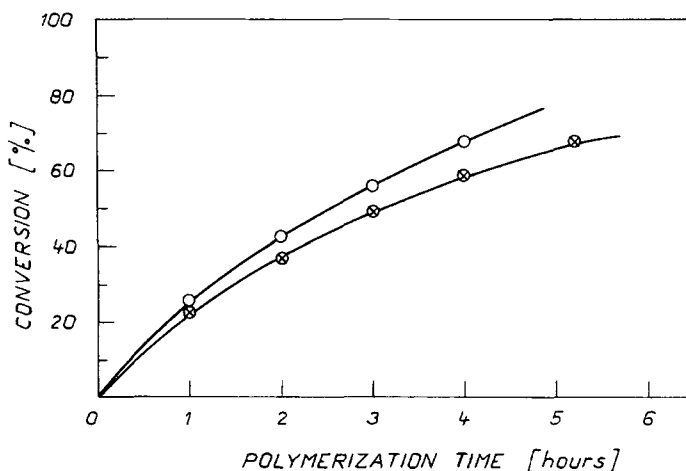


Fig. 1. Effect of divinylacetylene on rate of emulsion polymerization of chloroprene. Concentrations of DVA in chloroprene: (O) 0%; (⊗) 0.26%.

similar to what was observed in the case of monovinylacetylene;³ this is in good agreement with the general tendency of acetylenic monomers to retard free-radical polymerizations of vinyl monomers.⁶

Effect of Divinylacetylene on Properties of Polychloroprene

The effect of divinylacetylene was observed in almost all the properties studied. Divinylacetylene causes crosslinking of the polymer, indicated by the insolubility of polychloroprene samples (Fig. 2) and in an increase of molecular weights (Fig. 3).

It may be seen from Figure 2 that the solubility of the polymer remains essentially unchanged up to 0.075% DVA. In the region of these low

concentrations, DVA is probably built into polychloroprene chains in the same way as at the higher concentrations, i.e., by copolymerizing with polychloroprene radicals on one of its vinyl groups, while the second, "free" vinyl group can form a cross-intermolecular bond with another chain.

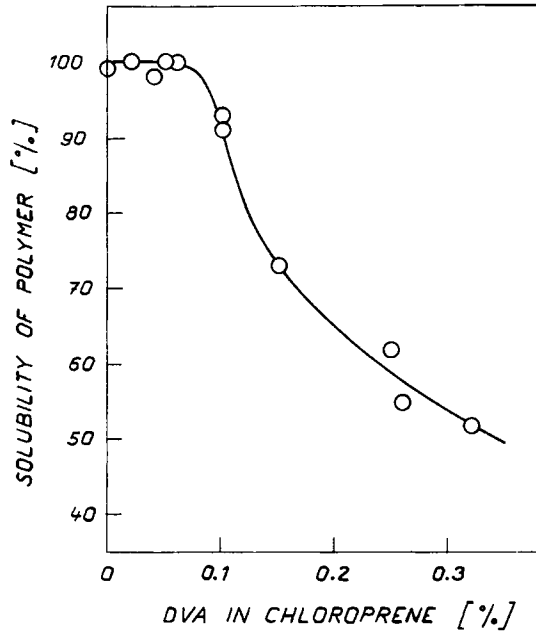


Fig. 2. Solubility of polychloroprene vs. DVA concentration in chloroprene.

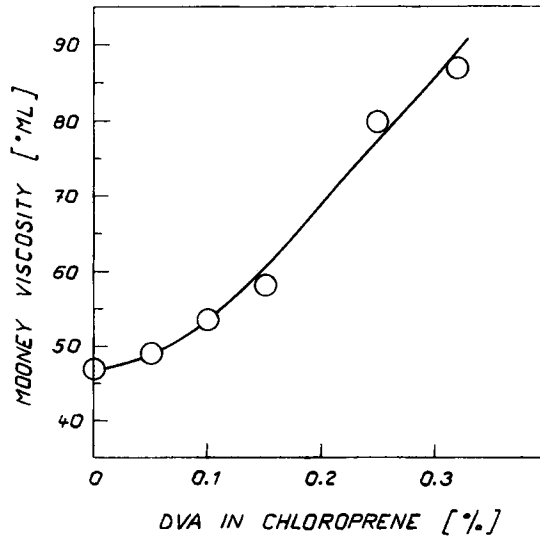


Fig. 3. Dependence of Mooney viscosity of polychloroprene on concentration of divinylacetylene in monomer.

However, at very low concentrations of DVA, these crosslinks are rather isolated and can form only the "loose gel" (or microgel) not detectable by filtering polymer solutions in the usual method for the determination of polymer solubility. A portion of divinylacetylene units could possibly act also as branching points, and the crosslinks need not necessarily be formed. Anyway, the incorporation of divinylacetylene units into the polychloroprene chains always causes some increase in the molecular weight; this effect was confirmed by the viscosity dependence on the DVA concentration in the polymerization charge (Fig. 3).

We have not succeeded in proving the presence of divinylacetylene units in the polychloroprene by infrared spectrophotometry. The concentrations of DVA in chloroprene were relatively very low; and, in addition, the intensity of the bands in the IR spectrum corresponding to the $\text{—C}\equiv\text{C—}$ group are extremely weak, contrary to the $\text{—C}\equiv\text{CH}$ groups which could be easily determined in the case of monovinylacetylene.²

The extent of the polymer oxidation might be indicated by the intensity of keto bands in the infrared spectrum. By measuring the IR spectra in the

TABLE I
Effect of Divinylacetylene Concentration on Properties of
Polychloroprene Vulcanizates

	Vul- caniza- tion time, min	Numerical values of properties					
		0% ^a DVA	0.05% DVA	0.10% DVA	0.15% DVA	0.25% DVA	0.32% DVA
Scorch (by Mooney vis- cosity measured at 140°C):							
Time for $\Delta 5^\circ$ ML, min		30	29	31	16	10	10
Minimum plasticity, °ML		43	41	59	67	75	76
Shrinkage on calendaring, % at 50°C		331	493	443	298	294	274
Tensile strength, kg/cm ²	5	179	236	216	196	185	160
	10	210	251	180	199	155	135
	15	190	207	146	147	175	137
Elongation at break, %	5	1020	1005	920	940	900	752
	10	930	960	850	835	750	640
	15	830	840	730	750	780	605
300% Modulus, kg/cm ²	5	10	17	19	16	18	40
	10	14	17	20	20	34	39
	15	16	19	24	19	20	35
500% Modulus, kg/cm ²	5	21	29	42	36	43	80
	10	26	37	38	46	73	82
	15	32	39	51	45	42	84
Permanent set, %	5	13	14	10	10	10	9
	10	8	10	8	8	9	7
	15	6	8	6	7	8	6

^a Concentration of divinylacetylene in monomer.

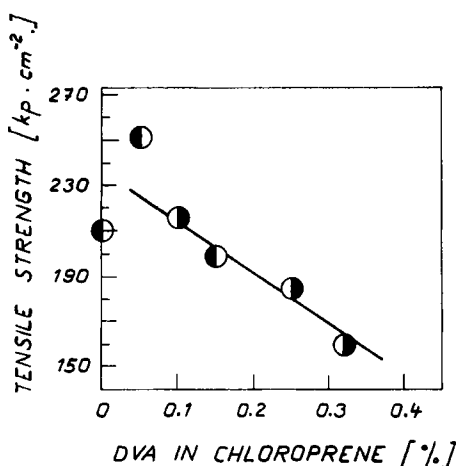


Fig. 4. Effect of divinylacetylene on maximum tensile strength of polychloroprene vulcanizates. Values after 5 min (●) and 10 min (○) of vulcanization are plotted.

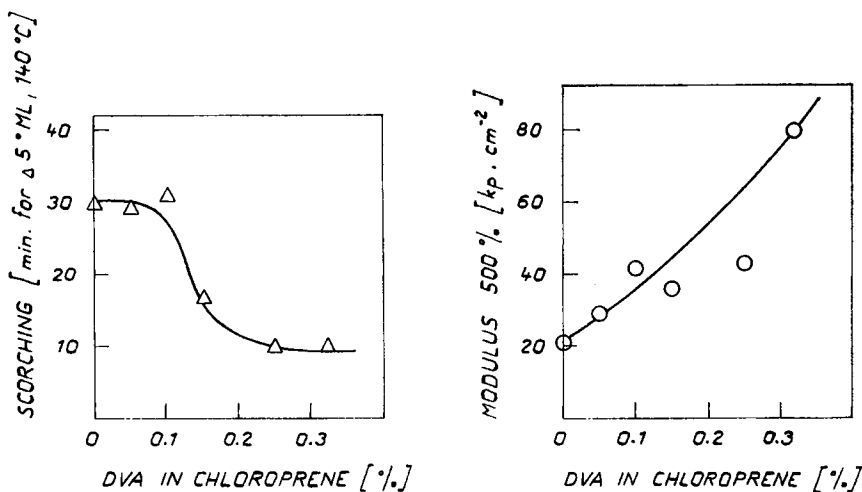


Fig. 5. Effect of divinylacetylene on scorch and 500% modulus of polychloroprene vulcanizates (vulcanization time 5 min).

corresponding region, we have tried to verify the observation of Klebanskyi⁴ that DVA activates the oxidation of chloroprene by air oxygen, which then results in a decrease in thermo-oxidative stability of polychloroprene. However, when comparing the intensity of the bands corresponding to the —C=O group, i.e., near 1450 and 1690 cm^{-1} , no dependence on the amount of DVA in the polymerization charge was found.

Measured crystallization rates of the polymers prepared from the chloroprene containing up to 0.3% DVA did not show any differences between individual samples. The influencing of the crystallization kinetics

would probably take place only at some higher concentrations of DVA in the monomer, i.e., at a substantially greater number of irregularities in polymer chains. In the case of low concentrations of DVA, the crystallization could be affected perhaps only by the crosslinking effect of divinylacetylene.

The effect of divinylacetylene was very markedly reflected by the physical and mechanical properties of chloroprene polymers and vulcanizates. Selected values are given in Table I. In all other properties measured, e.g., Shore hardness, resilience, brittleness at low temperatures, and color changes after irradiation of white vulcanizates with a Hg lamp, no changes were found.

The values given in Table I show a decrease in tensile strength and elongation at break with increasing concentration of DVA in the monomer, while the values of modulus increase. The results characterizing the increasing scorch rates with DVA content in chloroprene are of considerable practical importance. The changes of some selected values with DVA concentration are illustrated in Figures 4 and 5.

CONCLUSIONS

Experimental results show a very strong effect of divinylacetylene on the properties of polychloroprene, especially on polymer solubility (gel formation), its molecular weight (as indicated by the plasticity and viscosity of polychloroprene), tensile properties, and scorch.

The results have indicated that the principle of the DVA effect consists in copolymerization reactions with chloroprene which lead to the formation of crosslinks between polychloroprene chains.

Divinylacetylene has the most pronounced effect on the properties of polychloroprene of all the chloroprene impurities studied. Monomer used for the emulsion polymerization of chloroprene should preferably contain no divinylacetylene; or, at least, its concentration should be below 0.05% by weight.

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