

Effects of Monomer Impurities on the Emulsion Polymerization of Chloroprene and Properties of Polychloroprene. I. Effect of Methyl Vinyl Ketone

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Synopsis

The influence of small amounts (up to 2%) of methyl vinyl ketone in chloroprene on properties of polychloroprene and kinetics of the emulsion polymerization of chloroprene with mercaptans as regulators has been studied. Methyl vinyl ketone causes a substantial increase in molecular weight of polymer, which results in increased viscosity, gel formation, lowered plasticity of polymer, deterioration of processability, decreased tensile strength, and high modulus of vulcanizates. Methyl vinyl ketone interferes with the regulation of molecular weight by both primary and tertiary dodecylmercaptan; some differences are due to lower reactivity of tertiary dodecylmercaptan. In the presence of diisopropyl xanthogene disulfide as a molecular weight regulator the polychloroprene properties are not affected by methyl vinyl ketone. All changes in polymer properties have been proved to be caused by the addition reaction of dodecylmercaptan on methyl vinyl ketone, yielding 1-dodecylthiobutan-3-one. This compound itself has no influence on the polymerization of chloroprene. Methyl vinyl ketone has a marked promoting effect on polymerization rates, which accounts for its high reactivity and solubility in the water phase. A fast polymerization of methyl vinyl ketone takes place in the water phase of emulsion polymerization system simultaneously with the reaction of methyl vinyl ketone with dodecylmercaptan.

INTRODUCTION

The properties of polymers depend to a great extent on the amount and character of impurities in monomers. Further, the polymerization kinetics and reproducibility of polymerization are known to be usually affected by monomer impurities. Investigation of the influence of monomer impurities on emulsion polymerization of some dienes¹⁻⁶ has confirmed the extreme importance of high purity of monomers for the practical control of the polymerization process and for obtaining polymers of the required characteristics.

The emulsion polymerization of 2-chloro-1,3-butadiene (chloroprene) has some difficulties, and it is extremely sensitive to many factors. The effect of some impurities, which are usually present in chloroprene, has not been systematically studied.

Chloroprene prepared in the most usual process, i.e. by the dimerization of acetylene and hydrochlorination of vinylacetylene formed, may particu-

larly contain divinylacetylene, monovinylacetylene, methyl vinyl ketone, 1-chloro-1,3-butadiene, and 1,3-dichloro-2-butene. Besides these compounds small amounts of many other substances may be found in chloroprene, e.g., 4-chloro-1,2-butadiene, vinyl chloride, acetaldehyde, peroxides, and dimers of chloroprene. The amount of these impurities depends on conditions of monomer production technology.

It is the purpose of the present study to show the influence of methyl vinyl ketone on kinetics of the emulsion polymerization of chloroprene and on properties of polychloroprene elastomer.

An adverse effect of carbonyl-type impurities such as acetaldehyde and methyl vinyl ketone was mentioned by Daniels.⁷ He found that small amounts of methyl vinyl ketone in chloroprene caused the lowering of the polymer plasticity.

Methyl vinyl ketone alone polymerizes very easily in aqueous solutions,⁸ especially in the presence of free-radical initiators, and thus can polymerize under conditions of the emulsion polymerization of chloroprene in the water phase. Theoretical values of copolymerization reactivity ratios for chloroprene (M_1) and methyl vinyl ketone (M_2) which are $r_1 = 10.4$ and $r_2 = 0.06$, calculated from published Q and e values,⁹ are comparable, for instance, to the reactivity ratios⁹ for chloroprene and styrene copolymerization ($r_1 = 8.11 \pm 0.034$ and $r_2 = 0.052 \pm 0.01$). Accordingly, methyl vinyl ketone can be expected to copolymerize rather easily with chloroprene. Such copolymers were prepared;¹⁰⁻¹² their properties depend on the composition of copolymer.

Considering relatively very low concentrations of methyl vinyl ketone usually present in chloroprene, it can be assumed that a forming of homopolymers or copolymers of methyl vinyl ketone has no or negligible effect on polychloroprene properties.

A direct reaction of methyl vinyl ketone with chloroprene monomer, analogous to that of methyl vinyl ketone with butadiene,¹³ isoprene,¹⁴ fluoroprene,¹⁵ and other dienes,¹⁶⁻¹⁸ is not likely to occur under the conditions of emulsion polymerization of chloroprene.

These considerations made us search for some connection between the effects of methyl vinyl ketone and the process of molecular weight regulation of polychloroprene.

EXPERIMENTAL

Polymerization of Chloroprene

Chloroprene was polymerized in alkaline aqueous emulsion at 40°C. The ratio of water and monomer phases was 1:1. Persulfate (0.5 parts per 100 parts chloroprene) was used as an initiator and primary (0.20 part) or tertiary (0.77 part) dodecylmercaptan was used as a molecular weight regulator; the emulsifier was sodium salt of disproportionated rosin (2.5 parts). The alkalinity of the water phase was adjusted to pH 12.6 by sodium hydroxide. Polymerizations were carried out in 1000-ml glass

or stainless-steel bottles provided with a special screw cap with self-sealing gaskets that permitted removal of samples by means of a hypodermic syringe. The bottles placed in a constant-temperature water bath maintained at $40 \pm 0.5^\circ\text{C}$ were rotated end over end at a speed of 35 rpm. Oxygen was removed from the water phase, and polymerizations were conducted under a nitrogen atmosphere. The course of the polymerization was followed by removing samples and determining their total solids content. The samples removed were inhibited, and the total solids content was corrected for salts present in the polymerization recipe and for the inhibitor added. Polymerization was short-stopped at a conversion of $70 \pm 3\%$ by adding an emulsion of a toluene solution of phenothiazine and 2,2'-methylenebis(4-methyl-6-*t*-butylphenol). Unreacting chloroprene was removed by distillation under reduced pressure at $60\text{--}70^\circ\text{C}$. The latex was then stabilized by the addition of the solution of sodium salt of a formaldehyde-naphthalenesulfonic acid condensation product and acidified by 10% acetic acid solution to pH 5.5. Polymer was isolated by freezing a thin layer of latex at -20°C . The frozen sheet was washed by warm, distilled water and then dried in a stream of hot air for 1 hr at 90°C .

In polymerizations with diisopropyl xanthogene disulfide (0.52 part) as a regulator of molecular weight the same polymerization system was used in which dodecylmercaptan was omitted.

Polymerization of Methyl Vinyl Ketone

The polymerization of methyl vinyl ketone in aqueous solutions (the water phase for polymerization of chloroprene) was performed by the precise dilatometric method. The dilatometer, of a total volume of 30.3 ml, was charged with a water phase (26.7) of the same composition as that for the polymerization of chloroprene. It was heated to 40°C , and then the freshly distilled methyl vinyl ketone (3.0 g) was added by means of a long hypodermic needle into the center of the solution in the dilatometer. The initial reading was made immediately after adding methyl vinyl ketone. The total volume of the dilatometer capillary was 1.0 ml; its length was 110 mm.

Materials

Chloroprene. The chloroprene, CP (technical product of Duslo Chemical Works, Šála, Czechoslovakia) was purified by rectification under reduced pressure through a 120 cm column packed with Cu helices. Rectified chloroprene was inhibited by 1% of phenothiazine and stored at -20°C . Immediately before polymerization it was distilled, to remove inhibitor and accumulated peroxides and dimers. All the distillations were performed in the absence of air; apparatuses were flushed with nitrogen. The only impurity in the purified chloroprene found by gas chromatographic analysis was 1-chloro-1,3-butadiene in concentrations below 0.2% by weight. The content of peroxidic compounds determined by the polarographic method varied from 1 to 10 ppm active oxygen in chloroprene.

Methyl Vinyl Ketone. The methyl vinyl ketone, MVK (prepared at the Research Institute of Pharmacology and Biochemistry, Prague), contained (after gas chromatography) less than 0.1% impurities, essentially chloroprene and water. It was distilled *in vacuo* immediately before using.

Primary Dodecylmercaptan. Primary dodecylmercaptan (*n*-DDM), a distilled product of Glynn Brothers Ltd., London (b.p. 138–140°C at 6–8 mm, n_D^{20} 1.4591, D_4^{20} 0.8462) showed by amperometric titration a purity of 95.9%.

Tertiary Dodecylmercaptan. Tertiary dodecylmercaptan (*t*-DDM), a product of Light & Co., England, was purified by distillation (b.p. 119–121°C at 3–4 mm, n_D^{20} 1.4651, D_4^{20} 0.8550) showed by amperometric titration a purity of 95.7%.

Other Materials. Sodium salt of disproportionated rosin was Dresinate 731, product of Hercules Powder Co., U.S.A.; solutions of this emulsifier were adjusted to pH 10.5. Diisopropyl xanthogene disulfide (VEB, Chemische Werke Buna, Schkopau, Germany) was recrystallized from isopropanol (m.p. 58.5°C.) 2-Methyl propenal (methacrolein) was prepared at Technical University, Prague; after rectification it contained more than 91% methacroleine. Mesityloxide was a distilled product of the British Drug Houses Ltd. Persulfate and all other components of the polymerization recipe were of pure or reagent grade.

Additions of Methyl Vinyl Ketone

MVK was put in bottles charged with the chloroprene and the water phase under inert atmosphere by means of a special 1 ml hypodermic syringe. The syringe was weighed with an accuracy of ± 0.001 g before and after injection into the polymerization charge. In some experiments methyl vinyl ketone sealed in small thin-walled glass ampules was added, which were broken in bottles by rotating. All concentrations of methyl vinyl ketone are given in percentage by weight based on chloroprene in the charge.

Testing Methods

A regulation efficiency, molecular weights, and degree of polymer cross-linking were evaluated by data on intrinsic viscosity, solubility of polymer, Mooney viscosity, and Defo plasticity. Toluene (50 ml) was added to a polychloroprene sample (0.3 g); after 48 hr. the solution was filtered, and toluene was added to 100 ml of total volume. Solubility of polymer was determined from the total solids content of solution; intrinsic viscosity was measured at 30°C in an Ubbelohde viscosimeter.

Defo plasticity was measured at 80°C in Defo testing apparatus on specially prepared cylindrical test pieces (10 × 10 mm), the Defo plasticity value being the load in grams required to reduce the cylinder from 10 to 4 mm in 30 sec. Mooney viscosity was tested at 100°C in Mooney viscosimeter after 4 min.

Testing compound for determination of physical properties of polychloroprene vulcanizates had the following formulation (in parts by weight): polymer, 100; ZnO, 5; MgO, 4; Na-22, 0.5. The compound was mixed at 40–50°C and then cured at 145°C. The test pieces were 1 mm thick and 3.2 mm wide.

RESULTS AND DISCUSSION

Effect of Methyl Vinyl Ketone on Regulation of Molecular Weight of Polychloroprene

Mercaptans, particularly *n*-DDM and *t*-DDM, are the most widely used regulators of molecular weight in the emulsion polymerization of chloroprene and other dienes. Less common chain-transfer agents are dialkyl xanthogene disulfides, or the molecular weight is regulated on some other principle, e.g., by the reaction of thiuram disulfide with a copolymer of chloroprene and a small amount of sulfur built in polymer chains in the form of disulfidic or polysulfidic groups.^{19,20}

It was found that in the presence of dodecylmercaptans as regulators in the emulsion polymerization of chloroprene the presence of methyl vinyl ketone has a considerable effect on the regulation process. The molecular weight of polychloroprene rises with increasing concentrations of methyl vinyl ketone in monomer, as is indicated by the effect of methyl vinyl ketone on intrinsic viscosity of polychloroprene (Fig. 1).

In the case of *n*-DDM the marked rise of molecular weight appears at the range of MVK concentrations as low as 0.05–0.1%. Along with the increase in molecular weight a crosslinked polymer is formed. The pres-

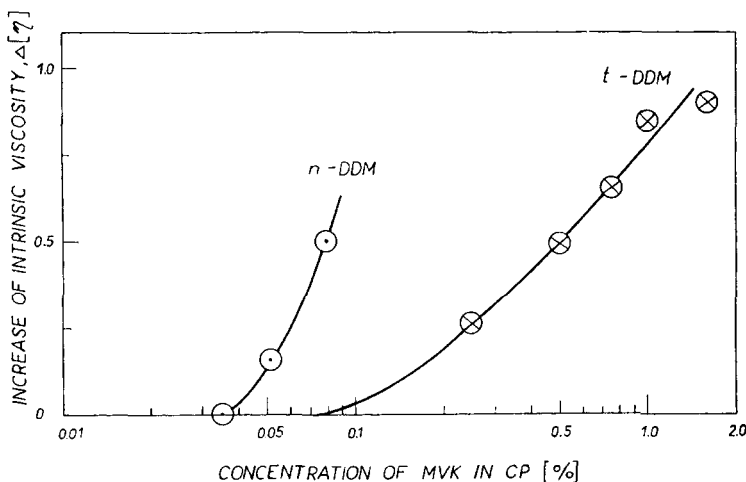


Fig. 1. Change in intrinsic viscosity of polychloroprene with concentration of MVK in monomer in the presence of (⊙) *n*-DDM and (⊗) *t*-DDM as molecular weight regulators. Initial values of $[\eta]$, in absence of MVK: *n*-DDM, 1.43; *t*-DDM, 1.46.

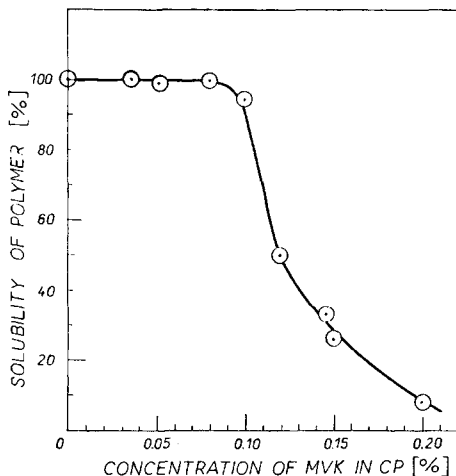


Fig. 2. The influence of MVK on the solubility of polychloroprene (*n*-DDM as regulator).

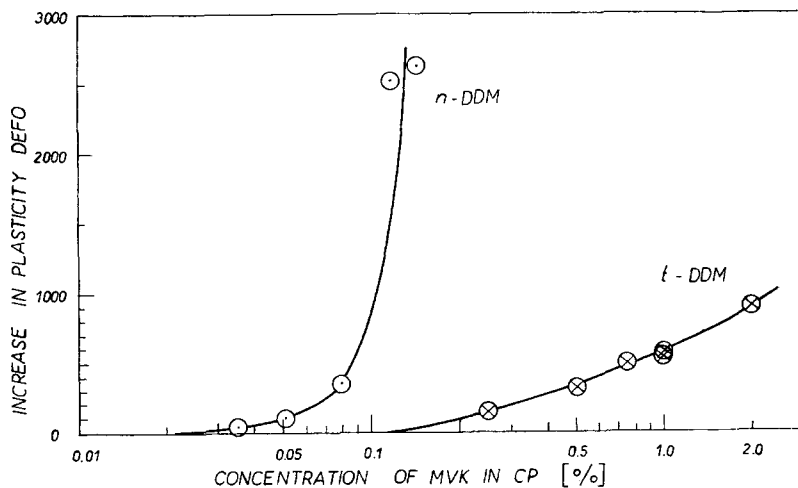


Fig. 3. Increase in plasticity of polychloroprene at various concentrations of MVK in the presence of (⊙) *n*-DDM and (⊗) *t*-DDM as molecular weight regulators. Initial values of Defo plasticity, in absence of MVK: *n*-DDM, 380; *t*-DDM, 300.

ence of gel causes reducing solubility of polychloroprene in this case (Fig. 2).

A noteworthy fact is that no decrease in solubility of polymer was observed in polymerizations with *t*-DDM as regulator, not even at concentrations of about 2% MVK in chloroprene.

The increase of molecular weight can be well demonstrated by the plasticity of polymer as a function of the amount of methyl vinyl ketone in chloroprene (Fig. 3). In the case of *n*-DDM the sharp rise of plasticity occurs at concentrations greater than 0.05% methyl vinyl ketone in

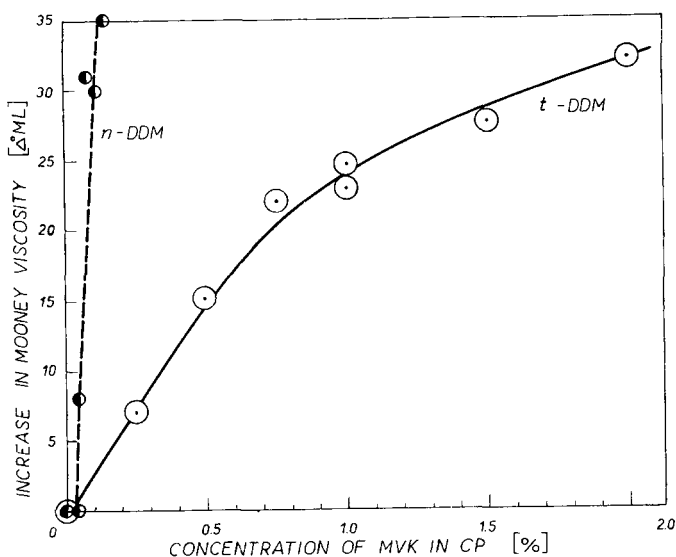


Fig. 4. Change in Mooney viscosity of polychloroprene with concentration of MVK in monomer in the presence of (○) *t*-DDM and (●) *n*-DDM as molecular weight regulators. Initial values of Mooney, in absence of MVK: *n*-DDM, 36; *t*-DDM, 37.

chloroprene; at more than 0.2% MVK the polychloroprene properties are similar to those of nonregulated polymer. In polymerizations with *t*-DDM as a regulator the adverse effect occurred at much higher concentrations of MVK.

A similar effect of MVK was observed when Mooney viscosity was measured as an indicator of a regulation efficiency of mercaptans (Fig. 4).

Consequently, MVK affects properties of polychloroprene both in the presence of *n*-DDM and *t*-DDM as regulators, but its effect on polymerization with *t*-DDM is less profound.

From the experimental results it may be seen that in the presence of MVK some reactions take place in the polymerization system that prevent the regulator from action as a chain-transfer agent.

To prove that this particular reaction of MVK and DDM causes all changes in properties of polychloroprene, a few polymerization experiments were carried out with regulators of different types. The properties of polychloroprenes, prepared in the presence of diisopropyl xanthogene disulfide as a regulator and various amounts of MVK, are given in Table I. These results indicate that in this system MVK had no effect on polymer properties up to about 1% MVK in chloroprene. It is apparent that MVK does not influence the regulation efficiency of diisopropyl xanthogene disulfide as in the case of mercaptans.

Differences in effects of MVK on polymer properties in the regulation of molecular weight by *n*-DDM and *t*-DDM are connected also with differences in regulation efficiency of both the dodecylmercaptans.

TABLE I
Properties of Polychloroprenes Polymerized in the Presence of Diisopropyl Xanthogene Disulfide as a Regulator at Various Concentrations of Methyl Vinyl Ketone

Concn. of MVK in chloroprene, %	$[\eta]$	Soly. of polychloroprene, %	Defo plast.	Mooney visc.
0	1.44	99	400	35
0.11	1.48	99	400	35
0.25	1.47	100	300	35
0.51	1.46	98	320	32
1.01	1.45	98	340	31

The relationship of polychloroprene plasticity and an amount of regulator (*n*-DDM and *t*-DDM) for the polymerization system used is shown in Figure 5. *n*-DDM is a substantially more effective regulator in the polymerization of chloroprene than is *t*-DDM. These results coincide closely

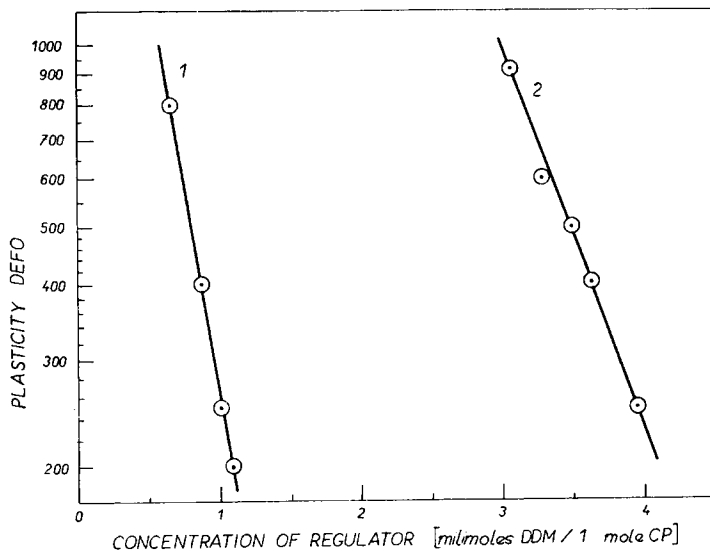


Fig. 5. Comparison of regulation efficiency of DDM in emulsion polymerization of chloroprene at 40°C: (1) *n*-DDM; (2) *t*-DDM.

with published data about kinetics of consumption of mercaptans in the emulsion polymerization of chloroprene^{21,22} and with the apparent chain-transfer constants²³ of *n*-DDM ($C = 1.0$) and *t*-DDM ($C = 0.24$).

Effect of Methyl Vinyl Ketone on Rate of Emulsion Polymerization of Chloroprene

It has been proved in many polymerization experiments at various concentrations of MVK that MVK substantially increases the rate of emulsion

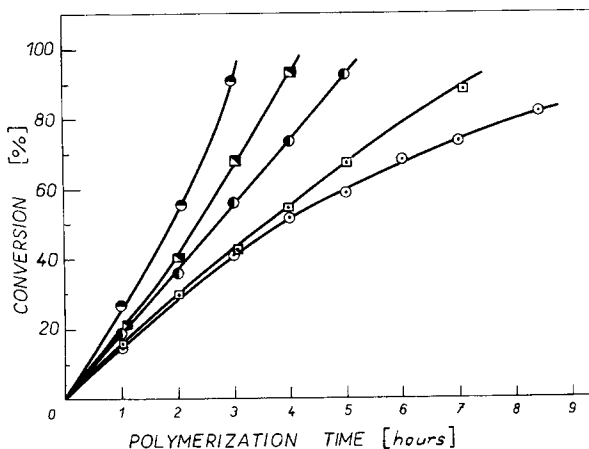


Fig. 6. Effect of MVK on rate of emulsion in chloroprene (%): polymerization of chloroprene (*n*-DDM as regulator). MVK (○) 0; (◻) 0.14; (●) 0.21; (◼) 0.28; (⊙) 1.03.

polymerization of chloroprene. The acceleration has occurred in polymerizations with both *n*-DDM and *t*-DDM as regulators. Polymerization curves obtained at various concentrations of MVK are plotted in Figure 6. Considerable acceleration of polymerization appears at concentrations of MVK as low as a few tenths of 1%, e.g., the difference in conversion between the polymerization in the presence of 0.21% MVK and the polymerization of pure chloroprene is about 34% after 5 hr of polymerization. The most powerful influence of MVK has been observed in the concentration range of 0.1–0.3% MVK. Additional increasing of MVK concentration then caused lesser increase in polymerization rate.

The promoting effect of MVK may be explained in several ways:

(1) MVK is very soluble in water; consequently, since it is miscible with chloroprene as well, in the emulsion system it will be distributed in a certain ratio between the monomer and the water phase. In the water phase, where the free-radical decomposition of initiator takes place, MVK free radicals can be formed, owing to the high concentration of primary radicals. These MVK free radicals may penetrate into monomer-polymer particles and there initiate polymerization or copolymerization of chloroprene, or they may initiate a homopolymerization of MVK in the water phase. A chance of application of this mechanism of the promoting effect of MVK depends on the ratio of reaction rates of the MVK polymerization and the considered reaction of MVK and DDM.

(2) The emulsion polymerization of pure chloroprene in the absence of DDM has been observed to proceed faster than the polymerization in the presence of DDM. If DDM is substantially consumed in a reaction with MVK, the polymerization rate should be higher, i.e. similar to that in the absence of DDM.

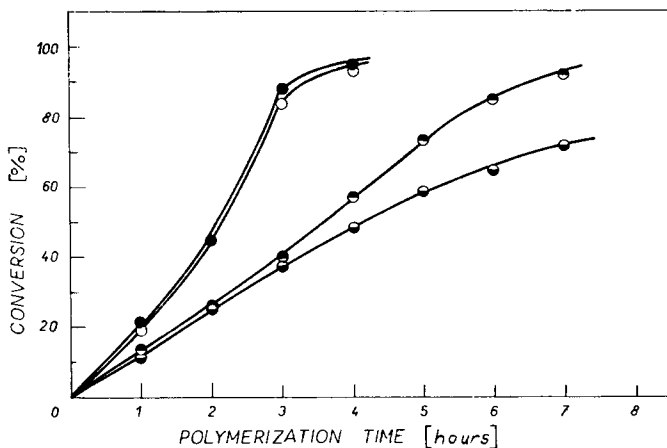


Fig. 7. Effect of DDM and MVK on rate of emulsion polymerization of chloroprene (CP): (●) pure CP, with *n*-DDM; (●) pure CP, in absence of *n*-DDM; (○) CP with 0.5% MVK, with *n*-DDM; (●) CP with 0.5% MVK, in absence of *n*-DDM.

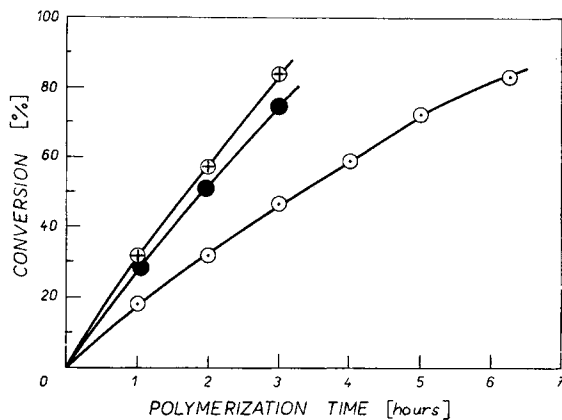


Fig. 8. Effect of MVK on rate of emulsion polymerization of chloroprene in presence of diisopropyl xanthogene disulfide as regulator. Percentage MVK: (○) 0; (●) 0.50; (⊗) 1.91.

The retarding effect of DDM in the emulsion polymerization of chloroprene is different from its effect in the emulsion copolymerization of butadiene and styrene, in which it acts as a promotor.²⁴ This difference may be attributed to differences in reactivities of monomeric radicals.

(3) Some copolymerization reactions of chloroprene and MVK may take place in the polymerization system and be able to affect the polymerization rate of chloroprene. However, considering those low concentrations in which MVK is likely to occur in chloroprene, we assumed this effect to be negligible.

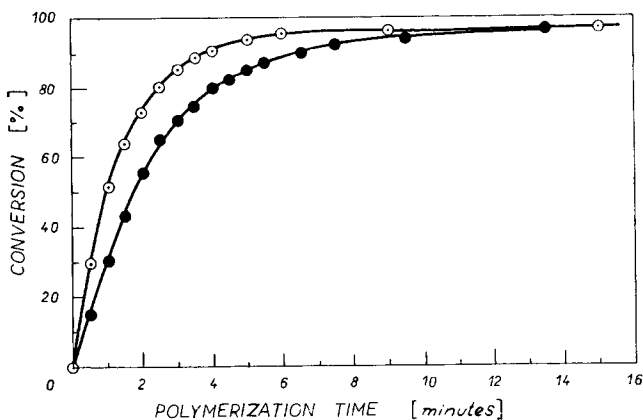


Fig. 9. Polymerizations of pure MVK in aqueous solutions of same composition as in chloroprene emulsion polymerization. MVK in solution (%): (○) 10; (●) 5.

Polymerization rates in the absence and in the presence of DDM for the polymerization of pure chloroprene and chloroprene containing MVK are shown in Figure 7. Apparently, MVK causes the same increase in polymerization rate both in the presence and in the absence of mercaptan. This increase is greater than the disappearance of DDM could cause.

In addition, it was observed that in the presence of diisopropyl xanthogene disulfide as a regulator MVK caused an increase of polymerization rate as well (Fig. 8). The polymerization of pure chloroprene in the presence of diisopropyl xanthogene disulfide runs more slowly than the polymerization in the absence of any regulator, but in this case no reaction of MVK's consuming regulator can be assumed.

Solution polymerizations of pure MVK in aqueous solutions of the same composition as the water phase in chloroprene emulsion polymerization system (water, emulsifier, NaOH, Na₂SO₃, persulfate) were performed to prove the high polymerization reactivity of MVK under the conditions of the emulsion polymerization of chloroprene. The experimental results, which are illustrated in Figure 9, show that the extraordinarily fast polymerization of MVK occurs at rather low concentrations of MVK in aqueous solution.

The results indicate that the promoting effect of MVK may be attributed to its great solubility in the water phase and its high reactivity. Some increase in polymerization rate may be due to the consumption of DDM in a reaction with MVK, but this effect is covered by the highly predominating effect of polymerization reactions of MVK in the water phase.

Effect of Methyl Vinyl Ketone on Polymer Properties

Vulcanizates of polychloroprene samples polymerized in the presence of various amounts of MVK were prepared. Their most important physical properties are summarized in Table II. *n*-DDM was used as a regulator.

TABLE II
Physical Properties of Polychloroprene Vulcanizates Polymerized in
the Presence of Methyl Vinyl Ketone

	Vulcaniz. time, min	Concn. of MVK in monomer			
		0	0.05	0.10	0.15
Tensile strength, kg/cm ² :	10	215	212	168	72
	20	195	205	95	45
	30	170	185	100	55
Elongation at break, %:	10	960	1040	630	300
	20	790	860	480	200
	30	720	840	500	230
500% modulus, kg/cm ² :	10	8	4	102	—
	20	18	15	—	—
	30	26	16	—	—
Permanent set, %:	10	11	15	11	2
	20	9	10	6	2
	30	5	8	4	2
Hardness (Shore A), °Sh	10	38	37	48	53
	20	44	42	49	55
	30	45	42	50	53

These results show that MVK in concentrations greater than 0.05% causes a marked decrease in tensile strength and elongation and a rise in modulus. The processability of polymers prepared in the presence of 0.10 and 0.15% MVK was worsened, and a considerable tendency to scorch was observed.

All the adverse changes in polymer properties can be explained by the increasing of molecular weight and crosslinking of polychloroprene, caused by the interference of MVK with the regulation of molecular weight.

Mechanism of Reaction of Methyl Vinyl Ketone and Dodecylmercaptan

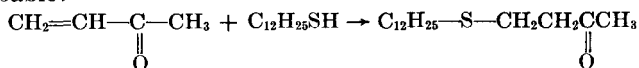
The experimental results indicate that the adverse effect of MVK on polychloroprene properties can be attributed to a reaction of MVK with DDM.

There are two possibilities of reacting MVK with DDM:

(1) A reaction of mercaptan with the carbonyl group of MVK, giving thiohemiacetal; such reactions of ketones and mercaptans occur very easily when the components are merely mixed;^{25, 26} reaction of thiohemiacetal with another molecule of mercaptan would require a catalyst.

(2) An addition of DDM on the vinylic double bond of MVK, giving ketosulfide.

Reactions of the first type are reversible, and thiohemiacetals are unstable substances.²⁶ Because of the high reactivity of the vinylic double bond of MVK, due to its conjugation with strongly polarized carbonyl double bond, the polar addition reaction of DDM on the vinylic double bond of MVK (giving 1-dodecylthiobutan-3-one) may be expected to be more probable:



This reaction is analogous to an addition of alcohols²⁷ and many other compounds on MVK;²⁸ it may be generally classed as a Michael reaction of α,β -unsaturated carbonyl compounds. Similar reactions of MVK with butylmercaptan and benzylmercaptan were described²⁹ as taking place under various conditions (with or without catalyst and irradiation).

We have succeeded in proving the assumption that in the emulsion system used for the polymerization of chloroprene just the addition of dodecylmercaptan on the vinylic double bond of MVK takes place.

Indirect Demonstration. Indirect demonstration was based on the consideration that in the case of reaction of the carbonyl group a similar effect on the molecular weight regulation would have to be observed in the presence of other (e.g., saturated) ketones, too. On the other hand, if mercaptans add on the vinylic double bond of MVK, a similar reaction should take place with other α,β -unsaturated carbonyl compounds, too.

Polymerizations of chloroprene in the presence of methyl ethyl ketone and acetone (0.3% ketone, *n*-DDM as regulator) showed no change either in polymer properties or in polymerization rates.

On the other hand, in the polymerization of chloroprene in the presence of methacrolein adverse effects of this compound were observed to be similar to those in the case of MVK. The most important results are given in Table III.

A considerable increase of polymerization rates in the presence of methacrolein was observed.

The results indicate that methacrolein react with DDM apparently in the same way as MVK.

Direct Demonstration. Direct demonstration of the proposed mechanism of reaction of MVK and DDM was performed as follows. First 0.1 mol of MVK and 0.1 mol of *n*-DDM were added to 100 ml of imitated emulsion polymerization system (chloroprene was replaced by benzene, initiator was omitted, the system was inhibited to prevent the polymerization of MVK). After 24 hr of standing the ethyl ether extract of the emulsion was evaporated, and a resulting oily liquid was crystallized to white needles. Infrared analysis of the recrystallized compound showed an absence of the group —C—OH; a strong band in the region of 1720 cm^{-1} proved the presence of the carbonyl groups.

The same substance was obtained by the direct reaction of MVK and *n*-DDM in benzene solution. Elementary analysis and molar refraction identified the compound as 1-dodecylthiobutan-3-one. This compound

TABLE III
Influence of Methacrolein on the Polymerization of Chloroprene

Methacrolein concn., %	Soly. of polymer, %	Defo plasticity
0	100	440
0.30	27	4500
1.01	14	7000

TABLE IV
Properties of the Reaction Product of the Addition of
n-Dodecylmercaptan on Methyl Vinyl Ketone

	Properties of 1-dodecylthiobutan-3-one	
	Found	Theor.
Elem. anal., %:		
C	70.75	70.52
H	11.66	11.84
S	11.45	11.77
Melting point, °C	27.8	—
Density at 30°C, D_{30}^{30} , g/ml	0.8998	—
Refractive index, n_D^{30}	1.466	—
Molar refraction	83.84	83.79

has not yet been described in the literature; its properties are given in Table IV.

A possibility of forming some other reaction products cannot be excluded. Dodecylthiobutanone could react with another molecule of MVK and give corresponding 1,5-diketone (as in the case of butylmercaptan,²⁹ it was observed), which may undergo an intramolecular cyclization³⁰ under suitable conditions. We believe that if such reactions occur at all in the emulsion polymerization system, their part is negligible.

An analogous reaction product was obtained with *t*-DDM and MVK. However, this reaction was less easy and had a lower yield than in case of *n*-DDM. These observations correspond closely to the effects of MVK on the regulation of molecular weight of polychloroprene by *n*-DDM and *t*-DDM. Properties of adduct with *t*-DDM were not determined, because the *t*-DDM used was a mixture of isomers.

Polymerizations of pure chloroprene in the presence of recrystallized dodecylthiobutanone (up to 1.2% in monomer) proved that this compound had no effect on either the polymer properties or the kinetics of emulsion polymerization. Therefore, the only cause of all changes in polychloroprene properties is the consumption of a regulator by its reaction with MVK.

Actual Reaction Situation in Emulsion Polymerization System

Because of the complicatedness of the emulsion system for the polymerization of chloroprene and the relatively slight concentrations of MVK and DDM it is very difficult to obtain any analytical data directly from the reacting system. However, it is possible to use some data on changes in polymer properties caused by MVK and results of regulation of molecular weight by DDM.

From the relationships of polymer properties and MVK concentration in monomer (Figs. 1-4) and from the results of regulation of molecular weight (Fig. 5) the amounts of MVK and either of the DDM's can be found

which are equivalent to each other as for the change in properties of polychloroprene.

The increase in Defo plasticity from 400 to 1000 (i.e., in practically the most important region) is caused by the addition of 1.256 mmol of MVK (based on 100 g of chloroprene) to the polymerization system with *n*-DDM as regulator (Fig. 3). The same change of plasticity also can be achieved by lowering the concentration of *n*-DDM by 0.326 mmol (based on 1000 g of chloroprene) in the emulsion polymerization of pure chloroprene (Fig. 5). Consequently, both the amounts of the two compounds are equivalent as regards the polymer plasticity change. If the reaction of MVK with DDM is the only cause of the change, then it follows that the two compounds react just in this ratio. Properties of polymer can be used here as an analytical indicator of reaction of organic compounds in polymerizing system.

The numerical data show that an average of 3.9 molecules of MVK are needed to be present in the system for the reaction of 1 molecule of *n*-DDM.

In the case of *t*-DDM the same change of Defo plasticity (from 400 to 1000) is attained by the addition of 17.121 mmols of MVK or by lowering the *t*-DDM concentration by 0.702 mmol. For a reaction of 1 molecule of *t*-DDM 24.4 molecules of MVK should be present in the polymerization system.

Assuming the equimolar reaction of DDM and MVK, the question arises why excess MVK does not react with another portion of mercaptan. Some possible explanations are the following:

(1) An extremely fast polymerization of MVK takes place in the aqueous phase of the system (Fig. 9). If the addition reaction with DDM will not proceed fast enough, then a part of MVK may polymerize before reacting with mercaptan.

(2) The reaction apparently does not reach high conversion under the given conditions; some parts of MVK and DDM do not react.

Considering the high polymerization reactivity of MVK, its fast polymerization in the water phase as a competitive reaction for the addition reaction of DDM is likely to be the principal cause of the disproportion mentioned. This consideration is confirmed by the substantially higher excess of MVK which is required for 1 molecule of *t*-DDM to react in comparison with the excess of MVK required for *n*-DDM; that is, if *t*-DDM reacts more slowly with MVK than *n*-DDM then MVK has a longer time to polymerize, and because of the greater polymerized portion the greater excess of MVK is necessary to the reaction of the same molar amount of mercaptan.

CONCLUSIONS

MVK reacts with DDM's used as regulators of molecular weight of polymer in the emulsion polymerization of chloroprene. This reaction is the main cause of all adverse changes of polychloroprene properties.

The principal cause of the promoting effect of MVK on the emulsion polymerization of chloroprene is its solubility in the water phase, where

MVK free radicals may initiate either the solution homopolymerization of MVK or polymerization and copolymerization of chloroprene in monomer-polymer particles.

The solution polymerization of MVK in the water phase is a competitive reaction to the addition of DDM on MVK. Since the addition reaction of tertiary *t*-DDM is slower than that of *n*-DDM, there is a greater chance for polymerization of MVK. In addition to the lower regulation efficiency of *t*-DDM this fact is the reason for the lower effects of MVK in the regulation of molecular weight by *t*-DDM.

References

1. R. L. Frank, C. E. Adams, J. R. Blegen, R. Deanin, and P. V. Smith, *Ind. Eng. Chem.*, **39**, 887 (1947).
2. R. L. Frank, J. R. Blegen, G. E. Inskeep, and P. V. Smith, *Ind. Eng. Chem.*, **39**, 893 (1947).
3. R. F. Dunbrook, *India Rubber World*, **117**, 203 (1947).
4. G. S. Whitby, *Synthetic Rubber*, Wiley, New York, 1954, pp. 260, 683, 684.
5. C. A. Uranek, A. E. Follett, and G. J. Kostas, *Ind. Eng. Chem.*, **47**, 1724 (1955).
6. V. Svoboda, *Chem. Prumysl*, **7**, 209 (1957).
7. G. H. Daniels, U.S. Pat. 2,494,087 (1950).
8. G. S. Whitby, M. D. Gross, J. R. Miller, and A. J. Constanza, *J. Polym. Sci.*, **16**, 552 (1955).
9. G. E. Ham, *Copolymerization*, Wiley, New York, 1964.
10. W. H. Carothers, A. M. Collins, and J. E. Kirby, U.S. Pat. 2,066,331 (1937).
11. S. Kiesskalt, W. Schaich, H. Brunotte, and K. Winnacker, Ger. Pat. 683,232 (1939); Ger. Pat. 687,387 (1940).
12. H. Brunotte, W. Schaich, and K. Winnacker, Ger. Pat. 695,177 (1940).
13. K. Adler and W. Vogt, *Ann.*, **564**, 109 (1949).
14. E. F. Lutz and G. M. Bailey, *J. Amer. Chem. Soc.*, **86**, 3899 (1964).
15. A. A. Petrov and A. V. Tumanova, *Zh. Obshch. Khim.*, **26**, 2744 (1956).
16. A. A. Petrov and N. P. Sopov, *Zh. Obshch. Khim.*, **22**, 591 (1952).
17. G. A. Ropp and E. C. Coyner, *J. Amer. Chem. Soc.*, **71**, 1832 (1949).
18. L. Reich and E. I. Becker, *J. Amer. Chem. Soc.*, **71**, 1834 (1949).
19. W. E. Mochel and J. H. Peterson, *J. Am. Chem. Soc.*, **71**, 1426 (1949).
20. A. M. Collins, U. S. Pat. 2,264,173 (1941).
21. L. G. Melkonjan and R. V. Bagdasarjan, *Armyansk. Khim. Zh.*, **19**, 253 (1966).
22. L. G. Melkonjan, R. V. Bagdasarjan, and R. A. Karapetjan, *Armyansk. Khim. Zh.*, **19**, 733 (1966).
23. J. W. McFarland and W. Pariser, *J. Appl. Polym. Sci.*, **7**, 675 (1963).
24. I. M. Kolthoff and W. E. Harris, *J. Polym. Sci.*, **2**, 47 (1947).
25. E. Baumann, *Ber.*, **18**, 885 (1885).
26. I. Ernest and S. Hermanek, *Preparativni reakce v organické chemii*, Vol. IV, NČSAV, Prague, 1959, p. 389.
27. N. Murata and H. Arai, *J. Chem. Soc. Japan, Ind. Chem. Section*, **56**, 628 (1953).
28. N. C. Ross, Ph.D. Thesis, Univ. Pittsburgh, 1959.
29. K. Yamagishi, *Nippon Kagaku Zasshi* **80**, 764, (1959).
30. J. Plešek and A. Zobacova, *Preparativni reakce v organické chemii*, Vol. V, NČSAV, Prague, 1960, pp. 256, 864.

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