

Consumption of Mercaptan Chain Transfer Agents in Chloroprene Polymerization*

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INTRODUCTION

Mercaptans can be employed in the polymerization of chloroprene as well as of other compounds for the regulation of molecular weight by a chain transfer mechanism. The rates of consumption of various types of mercaptans, such as primary, secondary, and tertiary, in butadiene-styrene copolymerizations have been rather thoroughly studied by Kolthoff and Harris.¹ One of the most important results of such investigations was the finding that the chain length within a class of mercaptans affected the rate of mercaptan consumption. The rate of consumption varied inversely as the mercaptan molecular weight varied.

The chemical literature is almost devoid of information on the kinetics of mercaptan modifiers in chloroprene polymerization. Morton and Piirma² measured the consumption of a tertiary mercaptan relative to the consumption of chloroprene. They found that the disappearance of tertiary mercaptan was very slow compared with that of chloroprene, and was independent of the rate of polymerization and temperature.

EXPERIMENTAL

The polymerizations were carried out in three-necked round-bottomed flasks fitted with a stirrer, specific gravity tube, and nitrogen inlet. The reagents were well emulsified prior to their introduction into the flask. The recipe used is shown in Table I. A relationship of specific gravity versus monomer conversion was established by the removal of latex samples at various specific gravities, addition of stabilizer, and precipitation of polymer with acetone. From the weight of dried polymer the per cent monomer conversion was determined.^{3,4}

The mercaptan present in the latex at various conversions of the chloroprene was determined by the amperometric titration method of Kolthoff

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TABLE I
Polymerization recipe (pH 11.8)

Constituent	
Water	113
Chloroprene	100
NaOH	0.55
Disproportionated abietic acid	3.0
Naphthalenesulfonic acid per formaldehyde condensation	0.40
Product	
Na ₂ SO ₃	0.30
K ₂ S ₂ O ₃	0.02
Sodium anthraquinone sulfonate	0.001
R—SH	Variable

and Harris¹ with 3–5 ml. samples of latex withdrawn during the polymerization.

The polymer was isolated by adding the latex to a stirred acetone solution containing 1% (based on polymer) of phenothiazine. The polymer was press-dried at ambient temperature, washed with water, and dried under vacuum. The intrinsic viscosity was measured by conventional methods with reagent-grade thiophene-free benzene as solvent.

RESULTS AND DISCUSSION

Effect of Mercaptan Chain Length

The disappearance of several primary mercaptans with respect to chloroprene at 40°C. is shown in Figure 1. Within the C₅–C₁₂ primary mercaptan range, the rate of mercaptan disappearance is independent of chain length. This result is in marked contrast to that of the styrene-butadiene system of Kolthoff and Harris.¹ However, the conditions of our polymerizations were different from theirs, which were nearly neutral (see Table I).

Not only do all primary mercaptans exhibit the same reaction rates, but all are consumed at very nearly the same relative rate as that of chloroprene. This is evident from inspection of Figure 1: the slope of the straight line equals -1 . This lack of dependence of mercaptan disappearance on mercaptan chain length suggests that the chain transfer reaction is not diffusion-controlled under the present reaction conditions.

Effect of Temperature on *n*-C₁₂H₂₆SH Consumption

The reaction rates changed with temperature in such a way that mercaptan was consumed a little more effectively (relative to chloroprene) at 10°C. than at 55°C., as is shown in Figure 2. The difference in the heat of activation between reactions of mercaptan and chloroprene appears to be 2–3 kcal./mole.

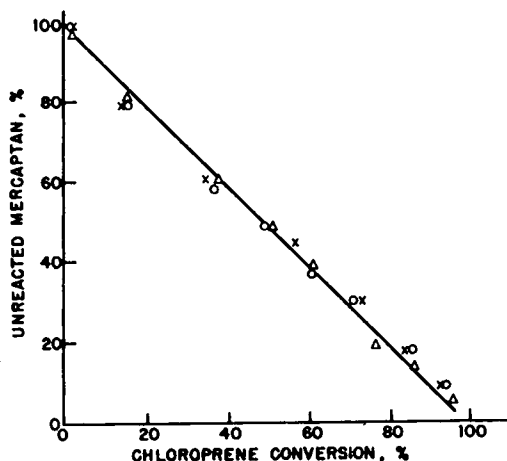


Fig. 1. Disappearance of primary RSH during chloroprene polymerization, 40°C., pH 11.8, 1.1 mmoles RSH per mole chloroprene, polymerization rate approximately 0.4% conv./min.: (O) $n\text{-C}_8\text{H}_{17}\text{SH}$; (X) $n\text{-C}_9\text{H}_{17}\text{SH}$; (Δ) $n\text{-C}_{12}\text{H}_{25}\text{SH}$.

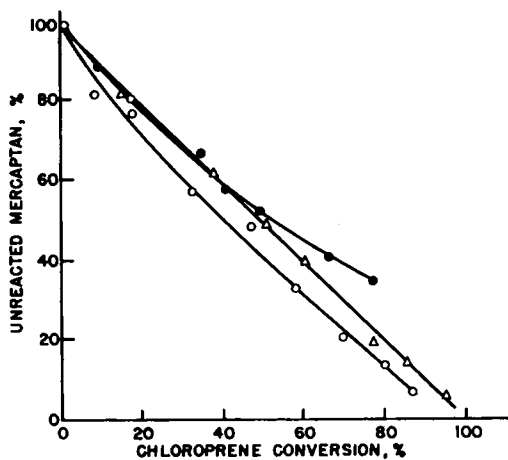


Fig. 2. Effect of temperature on $n\text{-C}_{12}\text{H}_{25}\text{SH}$ consumption, pH 11.8, 1.1 mmoles RSH per mole chloroprene: (●) 55°C.; (Δ) 40°C.; (○) 10°C.

Effect of Mercaptan Chain Structure

A comparison of the rates of the disappearance of tertiary dodecyl mercaptan and of primary dodecyl mercaptan is shown in Figure 3. As was reported by Morton and Piirma,² tertiary mercaptans react relatively slowly. When the chloroprene was almost completely polymerized, approximately one-half of the original mercaptan remained in the latex. Although no data were collected on secondary mercaptans, it may be expected that they would be intermediate between primary and tertiary in reactivity.

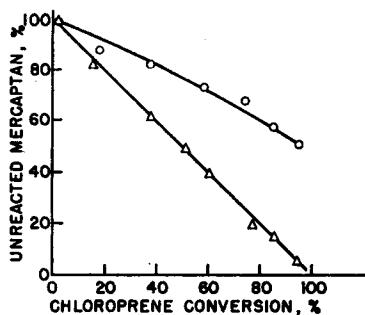


Fig. 3. Effect of structure on mercaptan consumption, 40°C., pH 11.8, 1.1 mmoles RSH per mole chloroprene: (Δ) $n\text{-C}_{12}\text{H}_{26}\text{SH}$; (\circ) $t\text{-C}_{12}\text{H}_{26}\text{SH}$.

Effect of Polymerization Rate on Relative Mercaptan Consumption Rate

The consumption of n -dodecyl mercaptan at two different chloroprene polymerization rates (0.6% conv. min. and 0.4% conv./min.) is shown in Figure 4. The polymerization rate was controlled by the rate of persulfate initiator addition. Over the range of polymerization rate, the relative rate of mercaptan consumption appears independent of polymerization

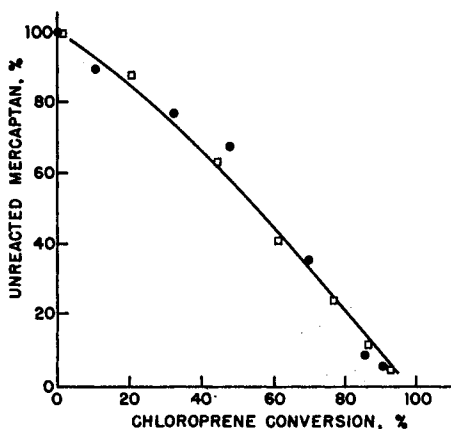
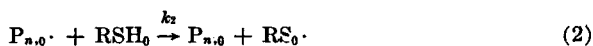


Fig. 4. Effect of polymerization rate on $n\text{-C}_{12}\text{H}_{26}\text{SH}$ consumption, 40°C., pH 10.5, 1.1 mmoles RSH per mole chloroprene: (\circ) 0.6% conv./min.; (\square) 0.4% conv./min.

rate. Similar results were obtained with the C_5 mercaptan. (It may be noted that the points in Figure 4 do not conform to a straight line as closely as those in Figure 1; this apparent discrepancy is probably largely within the experimental error; however, the runs in Figure 4 were carried out at a slightly lower pH and while the effect of pH was not investigated this may indeed be responsible for the difference.)

Mechanism

The following equations may be postulated, to account for the preceding observations:



where P_n is a polymer chain with n monomer units, M is monomer, the dot designates a radical, and "0" and "w" subscripts designate oil and water phases respectively.

Since the mercaptan and monomer are assumed to react only in the oil phase, it follows from eqs. (1), (2), and (3) that

$$d([RSH_0] + [RSH_w])/dt = -k_2[RSH_0][P_{n,0} \cdot] \tag{4}$$

where the square brackets designate concentrations. If we assume that the equilibrium (3) is very rapid relative to reactions (1) and (2), substitution of:

$$K \equiv k_3/k_{-3} \equiv [RSH_0]/[RSH_w] \tag{5}$$

into eq. (4) yields:

$$d(RSH_0)/dt = -k_2(K/1 + K)[RSH_0][P_{n,0} \cdot] \tag{6}$$

Furthermore, since the total amount of mercaptan, RSH , is directly proportional to $[RSH_0]$,

$$RSH = [RSH_0](V_0 + V_w/K)$$

where V_0 and V_w are the volumes of the oil and water phases, respectively, and are assumed to remain constant in time, Eq. (6) can equally well be written:

$$dRSH/dt = -k_2(K/1 + K)RSH[P_{n,0} \cdot] \tag{7}$$

Similarly:

$$dM/dt = -k_1M[P_{n,0} \cdot] \tag{8}$$

where M is the total amount of monomer and is taken to be entirely in the oil phase.

From eqs. (7) and (8):

$$dRSH/dM = (K/1 + K)(k_2/k_1)(RSH/M) \tag{9}$$

Integration of eq. (9), between initial amounts M_i and RSH_i and amounts at time t (designated by subscript t) gives:

$$RSH_t/RSH_i = (M_t/M_i)^{[K/(1+K)](k_2/k_1)} \tag{10}$$

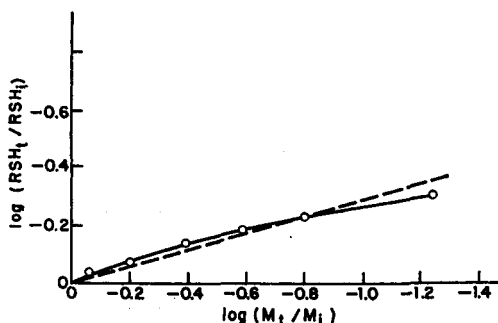


Fig. 5. Disappearance of $t\text{-C}_{12}\text{H}_{25}\text{SH}$ during chloroprene polymerization, 40°C ., pH 11.8 mmoles RSH per mole chloroprene; slope, 0.24.

If one plots log mole ratio $\text{RSH}_t/\text{RSH}_i$ against log mole ratio M_t/M_i , the slope of the curve is $(K/1 + K)(k_2/k_1)$, as is shown by eq. (10). Figure 5 is such a plot for the tertiary dodecyl mercaptan. A logarithmic plot is not required for primary mercaptans, since the slope is 1; this is clearly evident from Figure 1.

If K is large (that is, solubility in the aqueous phase is low), the slope of the curve is simply k_2/k_1 and becomes essentially independent of the solubility of the mercaptan in the water phase. The reactivity is then simply the reactivity of the mercaptan at the reaction site.

It was shown experimentally that K is indeed large when mercaptans in the $\text{C}_5\text{--C}_{12}$ range were used. Mercaptan was shaken with chloroprene, water, and sodium hydroxide (pH 11.8) at 40°C . for 1 hr. in the amounts ordinarily used in polymerizations. The two layers were separated and the mercaptan in the aqueous phase was titrated amperometrically with silver nitrate. In Table II are shown the percentages of the mercaptans which were found in the aqueous phase; K and $(K/1 + K)$ are also given. These results support the conclusion that $k_1 \cong k_2$ for primary mercaptans at 40°C .

TABLE II
Solubility of RSH in Aqueous Base (pH 11.8) at 40°C .

	$n\text{-C}_5$	$n\text{-C}_8$	$n\text{-C}_{12}$	$tert\text{-C}_{12}$
RSH in aqueous phase, %	7.8	6.6	3.8	3.0
K	11.8	14.2	25.3	32.3
$K(1 + K)$	0.92	0.93	0.96	0.97

The solubilities are quite low and not far apart for all mercaptans in the specified range. One could speculate that very low molecular weight mercaptans, such as methyl- or ethyl-, might deviate somewhat from those studied, because of their greater aqueous base solubility; similarly, diffusion effects would probably become important as the mercaptan molec-

ular weight were increased. We have not yet extended our investigations to below C_5 or above C_{12} mercaptans. However, it has been shown that *n*-propyl-SH is 25% soluble in the aqueous phase in measurements like those in Table II.

The slope of the curve for tertiary dodecyl mercaptan, as shown by Figure 5, is 0.24. Since the slope is essentially equal to k_2/k_1 , the reaction rate constant for the tertiary mercaptan is only about one-fourth that of chloroprene or the primary mercaptans.

Polymer Viscosity as a Function of Monomer Conversion

In Figure 6 are plotted intrinsic viscosities of polychloroprene at different monomer conversions with various primary mercaptans. As is consistent with their similar reactivities, the mercaptans gave similar curves practically within experimental error. The curves are flat to approximately 70% monomer conversion and then rise rapidly.

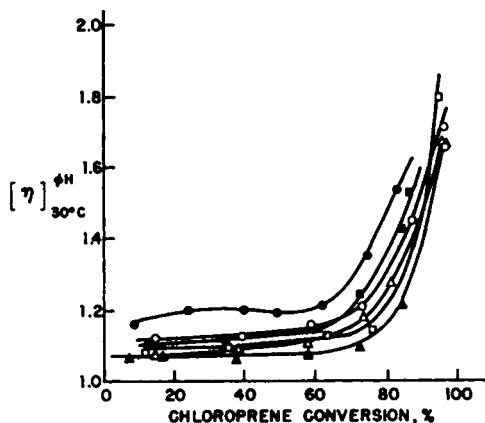
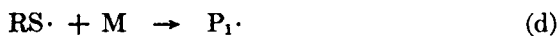
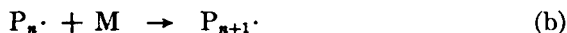


Fig. 6. Viscosity vs. chloroprene conversion, 40°C., pH 11.8, 1.1 mmoles RSH per mole chloroprene: (●) 1-pentanethiol; (Δ) 1-hexanethiol; (■) 1-heptanethiol; (□) 1-octanethiol; (○) 1-decanethiol; (▲) 1-Dodecanethiol.

Although the chloroprene/RSH ratio remains the same throughout the polymerization, it is not unexpected that the polymer viscosity increases during the latter stages. The following equations represent some of the reactions which may take place in the emulsion:



During the early stages of the polymerization, when monomer is in abundance, reaction (b) takes place in preference to (c), the latter representing the reaction of growing polymer chain $P_n\cdot$ with polymer molecule P_m . This can lead to crosslinked high-viscosity polymer. However, as polymerization proceeds and the polymer/monomer ratio becomes greater, reaction (c) becomes more important in affecting the molecular weight distribution and viscosity of the polymer.⁵

References

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Synopsis

The consumption of primary mercaptans from C_6 to C_{12} , and of tertiary dodecyl mercaptan, has been studied during chloroprene polymerization. All of the primary mercaptans disappeared with the same rate constant as did the chloroprene monomer. Tertiary dodecyl mercaptan disappeared more slowly. Equal molar concentrations of different primary mercaptans gave similar intrinsic viscosity polychloroprenes at any specific monomer conversion. Polymerization rate and temperature were shown to have little effect on relative mercaptan consumption over the limited conditions employed. The mercaptans studied were shown to have only slight solubilities in aqueous base solutions. The observations led to the conclusion that the mercaptan consumption is not diffusion- or solubility-controlled, but depends upon the inherent reactivity of a mercaptan at the polymerization site.

Résumé

On a étudié la consommation de mercaptans primaires de C_6 à C_{12} et du mercaptan *tert*-dodécylique au cours de la polymérisation du chloroprène. Tous les mercaptans primaires disparaissent avec la même constante de vitesse ainsi que le chloroprène monomère. Le mercaptan-*tert*-dodécylique disparaît plus lentement. Des concentrations molaires égales de différents mercaptans primaires donnent des polychloroprènes de viscosité intrinsèque semblable à chaque taux de conversion spécifique du monomère. On a montré que la vitesse de polymérisation ainsi que la température n'ont qu'un faible effet sur la disparition du mercaptan dans les conditions limites employées. On montre que les mercaptans étudiés n'ont qu'une faible solubilité dans des solutions aqueuses basiques. Les faits observés nous mènent à la conclusion que la consommation de mercaptan n'est pas contrôlée par la diffusion ou la solubilité mais dépend de la réactivité inhérente du mercaptan à l'endroit de la polymérisation.

Zusammenfassung

Der Umsatz von primären Merkaptanen von C_6 bis C_{12} und von *tert*-Dodecylmerkaptan während der Chloroprenpolymerisation wurde untersucht. Alle primären Merkaptane wurden mit der gleichen Geschwindigkeitskonstanten umgesetzt wie das monomere Chloropren. *Tert*-Dodecylmerkaptan reagierte langsamer. Gleiche molare Konzentration verschiedener primärer Merkaptane lieferte bei gleichem Monomerumsatz Polychloroprene mit ähnlicher Viskositätszahl. Es wurde gezeigt, dass Polymerisationsgeschwindigkeit und Temperatur in dem verwendeten Bereich an Reaktionsbedingungen wenig Einfluss auf den relativen Merkaptanverbrauch besitzen. Die untersuchten

Merkaptane zeigten nur eine geringe Löslichkeit in basischen wässrigen Lösungen. Die Ergebnisse führten zu dem Schluss, dass der Merkaptanverbrauch nicht diffusions- oder löslichkeitskontrolliert ist, sondern von der spezifischen Reaktivität eines Merkaptans am Polymerisationsort abhängt.

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