In Fig. 2 the lines are calculated from equation 8, using the values of the constants discussed above. It is evident that these theoretical lines are in satisfactory agreement with the experimental points, with the possible exception of the two series having the highest molecular weight. For sufficiently high molecular weight (low regulator concentration) this theoretical equation should not be accurate because not all the polymer molecules will be formed by chain transfer. This agreement between theory and experiment indicates that the molecular weights of emulsion polystyrene regulated with either *t*-butyl or *n*-amyl mercaptan can be satisfactorily interpreted by the chain transfer hypothesis, providing there is sufficient regulator present.

## Summary

Experimental data on the rates of mercaptan reaction in both emulsion polymerization and oil-phase polymerization of the three systems, tertiary butyl mercaptan in styrene, *n*-amyl mercaptan in styrene and *n*-amyl mercaptan in methylmethacrylate, have been obtained. In each of the three systems the relative rates of mercaptan to monomer reactions are practically identical in emulsion polymerization and oil-phase polymerization.

Intrinsic viscosities obtained on these regulated polymers have been interpreted by the chain transfer theory of regulator action.

PASSAIC, NEW JERSEY RECEIVED MAY 7, 1946

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# Regulator Theory in Emulsion Polymerization. II. Control of Reaction Rate by Diffusion for High Molecular Weight Mercaptans

BY W. V. SMITH

In Part I[1] where the rate of reaction for low molecular weight mercaptans in oil-phase and emulsion was discussed, it was shown that the rate of reaction of the mercaptan relative to that of monomer was the same in emulsion polymerization as in oil-phase in each of the three systems studied. This can be interpreted satisfactorily in terms of Harkins'[2] theory of the loci of emulsion polymerization by assuming a rapid rate of diffusion of the mercaptan through the aqueous phase and by assuming that the transfer constant for the mercaptan is the same in the reaction loci of emulsion polymerization as in oil-phase. Harkins' theory is essentially that the principal reaction loci consist of the soap micelles in the early stages of polymerization and of the polymer particles during the later stages. The emulsion droplets serve chiefly as reservoirs for supplying these loci with monomer and regulator. While this theory is not essential to interpret the rates of reaction of low molecular weight mercaptans, the concept of the reaction loci being separated from the monomer reservoirs by an aqueous layer is essential for interpreting the rates of reaction of the higher molecular weight mercaptans. For these, the present study indicates that the rate of diffusion of mercaptan through the aqueous layer plays a predominant role in determining the rate of mercaptan reaction.

## Experimental

**Monomers.**—The butadiene was from a cylinder of commercial grade used in preparing GR-S. It was distilled just prior to use. The styrene was from a commercial grade of about 99% purity which was distilled under reduced pressure just prior to use.

**Mercaptans.**—The *n*-amyl, *n*-hexyl and *n*-heptyl mercaptans were Eastman Kodak Co. samples, the latter two having sulfur contents corresponding to 93 and 98.5% of theory, respectively. The *n*-octyl and *n*-nonyl mercaptans were samples obtained from Naugatuck Chemical Co.; they had sulfur contents of 96.0 and 91.0% of theory, respectively. The *n*-decyl, *n*-dodecyl and *n*-tetradecyl mercaptans were obtained by fractionating the commercial Naugatuck Chemical Co. regulator OEI. The fractions used were: *n*-decyl mercaptan, b. p. 126.5–126.8° (21.5 mm.), $n^{20}_{D}$ 1.4569; *n*-dodecyl mercaptan, b. p. 153.7–153.9° (20.5 mm.), $n^{20}_{D}$ 1.4589; *n*-tetradecyl mercaptan, b. p. 179.8–180.9° (20.0 mm.), m. p. 7.0°, $n^{20}_{D}$ 1.4607. The *n*-undecyl and *n*-tridecyl mercaptans were prepared from the corresponding alcohols obtained from Eastman Kodak Co. The alcohols were first treated with hydrogen bromide; the bromides obtained then reacted with thiourea and the product was hydrolyzed to give the mercaptans. These were fractionated, the portions used being: *n*-undecyl mercaptan, b. p. 139.9–140.0° (20 mm.), $n^{20}_{D}$ 1.4588; *n*-tridecyl mercaptan, b. p. 169.6–171.7° (22 mm.), $n^{20}_{D}$ 1.4595.

**Catalysts.**—The soap used in most of these runs was a commercial grade, designated S. F. Flakes. The potassium persulfate was a C. P. grade.

**Procedure.**—The work reported herein on the lower molecular weight mercaptans in butadiene (up to undecyl mercaptan) was done early in the course of this investigation, at which time a different technique was being used than that used more recently. Pressure bottles (citrate bottles) of about 380-cc. capacity were used as reaction vessels. For a typical charge the following were added to each bottle: butadiene 70 g., aliphatic mercaptan 0.1 to 2.0 cc., soap 3.5 g., potassium persulfate 0.21 g. and distilled water 120 g. The butadiene and mercaptan were added last after the other ingredients had been chilled in the reaction bottle by immersing in ice water. The chilled reaction bottle was tared on a balance and cold liquid butadiene poured in until the desired weight had been added, after which the bottle was immediately closed. The bottle was rocked in a water-bath thermostated at 50°. On completion of the desired reaction time, the bottle was again cooled with ice water, then opened, and 3 cc. dilute (5 *N*) hydrochloric acid solution was added. The unreacted butadiene was evaporated off by placing the bottle in warm water. After most of

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[1] W. V. Smith, THIS JOURNAL, **68**, 2059 (1946).

[2] W. D. Harkins, *J. Chem. Phys.*, **13**, 381 (1945).

the liquid butadiene had evaporated, 4 g. of ammonium sulfate was added and removal of the unreacted butadiene completed. Benzene was then added to the bottle to give a polymer solution which it was estimated would be about 10 to 20%. The contents of the bottle were transferred to a separatory funnel and the aqueous layer was drawn off and discarded. Two washes were made with 20-cc. portions of 60% aqueous acetic acid solution. The aqueous layer was then withdrawn as completely as possible and rejected. To a portion of the remaining hydrocarbon layer were added 10 drops of aniline and 30 cc. of glacial acetic acid. The mercaptan in this solution was then determined by titrating with a copper oleate solution in benzene containing about 1 mg. of copper per cc. The end-point was determined by the appearance of a green color due to unreacted copper oleate. The polymer yield was determined from a portion of the benzene solution taken out before the mercaptan titration. This solution was dried on a vacuum line and the polymer content determined by weight.

In the more recent experiments with butadiene smaller reaction vessels consisting of 1-oz. screw cap bottles containing Neoprene gaskets for sealing have been used. A typical charge in these consisted of: distilled water 10 cc., soap 0.35 g., potassium persulfate solution (2.1%) 1 cc., butadiene 7 g., 10% benzene solution of mercaptan 0.2 cc. Polymerization was carried out again in a water bath at 50° using end-over-end agitation. Separate bottles were used for the polymer yield determinations and for the mercaptan titrations since the volatility of the butadiene made representative sampling of the latex extremely difficult. For the mercaptan titrations the entire contents of a reaction bottle was poured into 150 cc. of ethyl alcohol which was then titrated with silver nitrate solution using the Kolthoff method described in Part I. For the styrene polymerizations the technique given in Part I[1] was used. In titrating the high molecular weight mercaptans it was found necessary to make successive approximations by separating the polymer after a titration, redissolving in benzene, then precipitating with alcohol and titrating this alcohol solution. Three approximations were found sufficient in practically all cases.

## Results

In Table I are summarized the polymer yields and mercaptan determinations for the eight mercaptans studied in butadiene and for the four mercaptans studied in styrene emulsion polymerization.

TABLE I

MERCAPTAN REACTION IN EMULSION POLYMERIZATION

BUTADIENE, 50°

| | *n*-Amyl mercaptan, 0.31% of monomer | | | | |
|---|---|---|---|---|---|
| Time, hr. | 0.17 | 0.67 | 1.0 | 1.33 | 5.00 |
| Polymer yield, % | .. | 0.03 | 0.37 | 1.18 | 5.65 |
| Mercaptan reacted, % | 27.5 | 33 | .. | 42.5 | 79 |

| | *n*-Hexyl mercaptan, 1.2% of monomer | | *n*-Heptyl mercaptan, 1.2% of monomer | |
|---|---|---|---|---|
| Time, hr. | 1.10 | 2.05 | 1.10 | 2.05 |
| Polymer yield, % | 0.22 | 0.60 | 1.11 | 2.82 |
| Mercaptan reacted, % | 9.0 | 15.4 | 26.8 | 42.2 |

| | *n*-Octyl mercaptan | | | | |
|---|---|---|---|---|---|
| | 1.2% of monomer | | | 0.6% of monomer | |
| Time, hr. | 0.15 | 2.22 | 4.22 | 1.10 | 3.03 |
| Polymer yield, % | 0 | 5.9 | 12.3 | 2.28 | 8.30 |
| Mercaptan reacted, % | 6 | 67.4 | 91.5 | 43.5 | 78 |

| | *n*-Nonyl mercaptan 0.6% of monomer | | | *n*-Decyl mercaptan 1.2% of monomer | |
|---|---|---|---|---|---|
| Time, hr. | 1.19 | 1.84 | 3.25 | 2.23 | 4.42 |
| Polymer yield, % | 2.84 | 5.30 | 9.85 | 6 | 13 |
| Mercaptan reacted, % | 40.5 | 62.4 | 84.3 | 67 | 92.2 |

| | *n*-Undecyl mercaptan, 1.2% of monomer | | |
|---|---|---|---|
| Time, hr. | 1 | 2 | 2 |
| Polymer yield, % | 3.1 | 6.0 | 13.1 |
| Mercaptan reacted. % | 27.3 | 48.0 | 70.4 |

| | *n*-Dodecyl mercaptan, 0.15% of monomer | | | | | |
|---|---|---|---|---|---|---|
| Time, hr. | 1 | 2 | 2.83 | 4 | 5.5 | 6.5 |
| Polymer yield, % | 2.1 | 5.0 | 7.9 | 11.2 | 17.4 | 19.8 |
| Mercaptan reacted, % | 16.3 | 25.1 | 29.3 | 34.5 | 44.4 | 52.1 |

| | *n*-Tridecyl mercaptan 3.1% of monomer | | | *n*-Tetradecyl mercaptan 3.1% of monomer | | | |
|---|---|---|---|---|---|---|---|
| Time, hr. | 1 | 6 | 6 | 1 | 1 | 6 | 6 |
| Polymer yield, % | 2.5 | 20.2 | | 2.5 | | 18.0 | |
| Mercaptan reacted, % | 7.6 | 23.5 | 25.4 | 4.3 | 6.0 | 12.8 | 12.3 |

High *p*H runs, 0.72 g. excess potassium hydroxide per 100 g. of water.

| | *n*-Dodecyl mercaptan | | | | | |
|---|---|---|---|---|---|---|
| | 1.2% of monomer | | | 0.6% of monomer | | |
| Time, hr. | 1 | 2.2 | 0.42 | 0.75 | 1.25 | 2.00 |
| Polymer yield, % | 3.66 | 9.03 | 1.27 | 2.41 | 4.30 | 6.75 |
| Mercaptan reacted, % | 38.9 | 64.2 | 15.5 | 27.5 | 41.8 | 47.2 |

| | *n*-Tetradecyl mercaptan, 2.5% of monomer | | | |
|---|---|---|---|---|
| Time, hr. | 0.20 | 1.03 | 2.05 | 3.82 |
| Polymer yield, % | ... | 3.62 | 6.43 | 10.57 |
| Mercaptan reacted, % | 1 | 13.4 | 20.6 | 24.3 |

STYRENE 40°

| | *n*-Amyl mercaptan, 0.4% of monomer, 0.5 normal amount of potassium persulfate | | | |
|---|---|---|---|---|
| Time, min. | 15 | 30 | 45 | 60 |
| Polymer yield, % | 0.32 | 1.9 | 4.1 | 7.9 |
| Mercaptan reacted, % | 28.6 | 50.8 | 70.9 | 84.7 |

| | *n*-Undecyl mercaptan, 0.3% of monomer | | | |
|---|---|---|---|---|
| Time, min. | 90 | 135 | 150 | 165 |
| Polymer yield, % | 1.7 | 6.2 | 10.2 | 20.5 |
| Mercaptan reacted, % | 7.3 | 20.0 | 27.7 | 55 |

| | *n*-Dodecyl mercaptan, 0.3% of monomer | | | | | |
|---|---|---|---|---|---|---|
| Time, min. | 90 | 110 | 130 | 150 | 170 | 190 |
| Polymer yield, % | 1.69 | 5.10 | 11.4 | 28.9 | 37.2 | 51 |
| Mercaptan reacted, % | 2.7 | 6.8 | 13.6 | .. | 30.5 | 43.0 |

| | *n*-Tridecyl mercaptan, 0.3% of monomer | | | |
|---|---|---|---|---|
| Time, min. | 80 | 80 | 165 | 165 |
| Polymer yield, % | 3.5 | 7.5 | 45.0 | 47.5 |
| Mercaptan reacted, % | ... | 0.5 | 14.8 | 15.4 |

High *p*H runs, 0.72 g. excess potassium hydroxide per 100 g. of water, (soap prepared from pure stearic acid)

| | *n*-Amyl mercaptan, 0.4% of monomer, no persulfate | | | |
|---|---|---|---|---|
| Time, min. | 15 | 35 | 55 | 75 |
| Polymer yield, % | 0.32 | 2.4 | 4.4 | 6.2 |
| Mercaptan reacted, % | 17.1 | 49.2 | 68.4 | 76.2 |

| | *n*-Dodecyl mercaptan, 0.6% of monomer | | | | |
|---|---|---|---|---|---|
| Time, min. | 20 | 40 | 60 | 80 | 100 |
| Polymer yield, % | 9.4 | 18.7 | 28.5 | 36.0 | 41.0 |
| Mercaptan reacted, % | 49.0 | 73.4 | 79.9 | 83.9 | 84.2 |

In Fig. 1 are shown the data for butadiene; the logarithms of the mercaptan remaining are plotted against 2 minus the log of the monomer remaining. It will be seen that the slope of the line determined by such a plot is practically the same for all the low molecular weight mercaptans up to decyl mercaptan; whereas, for those above decyl, the slope is less (in absolute amount) the greater the number of carbon atoms in the mercaptan.

In Fig. 2 the polymer yields are plotted against the polymerization time for the different mercaptans. It is seen that the rate of polymerization is about the same for all the high molecular weight mercaptans (those with 8 or more carbon atoms)

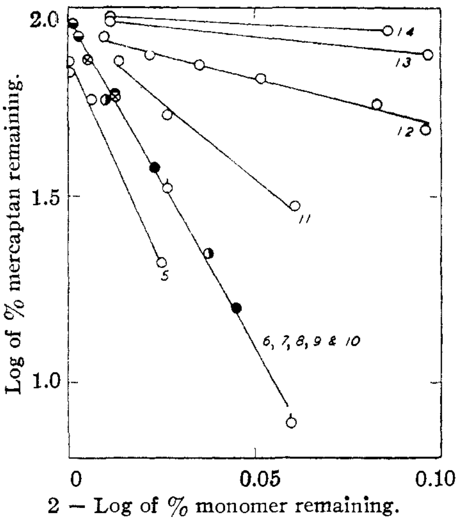

Fig. 1.—Relative rates of reaction of aliphatic mercaptan regulators in the emulsion polymerization of butadiene. The numbers refer to the no. of carbon atoms in the mercaptan: ◒, hexyl mercaptan; ⊗, heptyl mercaptan ◑, octyl mercaptan; ●, nonyl mercaptan; ȯ, decyl mercaptan.

but that it becomes definitely less for the low molecular weight mercaptans. This inhibition of the rate of polymer formation by the low molecular weight mercaptans is quite interesting in that it is unique for emulsion polymerization, since no such effect is found in oil-phase polymerization. This effect is illustrated further by Fig. 3 in which data on polymer yields are plotted against time for different initial concentrations of amyl mercaptan. Here it is seen that the higher the initial concentration of mercaptan, the slower the polymerization.

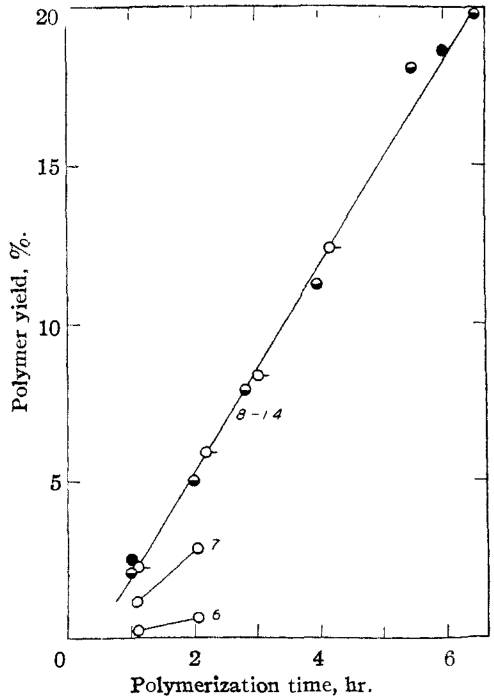

Fig. 2.—Butadiene polymerization in emulsion with different aliphatic mercaptan regulators; the numbers refer to the no. of carbon atoms in the mercaptan: o-, octyl mercaptan; ◒, dodecyl mercaptan; ●, tetradecyl mercaptan.

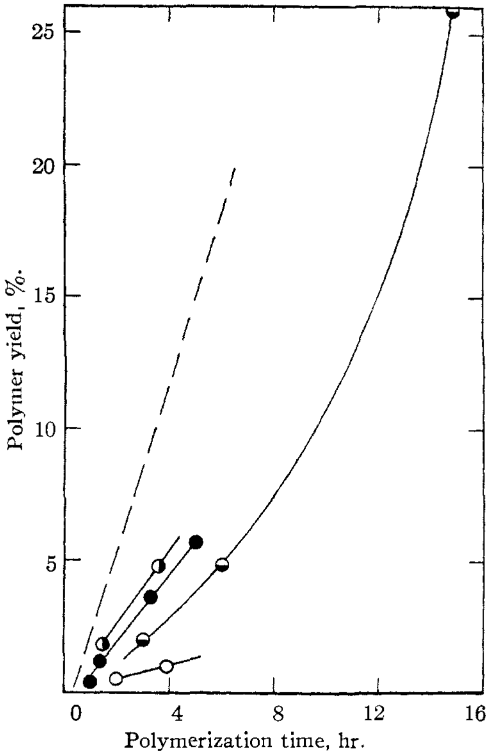

Fig. 3.—Emulsion polymerization of butadiene containing amyl mercaptan: ◑, 0.15%; ●, 0.3%; ◒, 0.6%; O, 1.2%. Dashed curve is that obtained when the mercaptan contains 8 or more carbon atoms.

The value of the quantity d ln $R$/d ln $M$($R$ = regulator remaining and $M$ = monomer remaining) determined from the slope of the curves in Fig. 1 is plotted as a function of the number of carbon atoms in the regulator in Fig. 4. This figure includes data for both butadiene and styrene. It is seen that the value of this quantity is substantially independent of the number of carbon atoms in the regulator up to 10 carbon atoms in the case of butadiene, and that additional carbon atoms successively make it smaller.

Another characteristic of emulsion polymerization pertains to the rates of reaction of high molecular weight mercaptans and is shown in Fig. 5. Here it is seen that the $p$H of the aqueous emulsion has an appreciable effect on the rate of reaction of dodecyl mercaptan in the emulsion polymerization of styrene (curves 2) but that there is no such effect of $p$H on the rate for the low molecular weight mercaptan, amyl (curve 1).

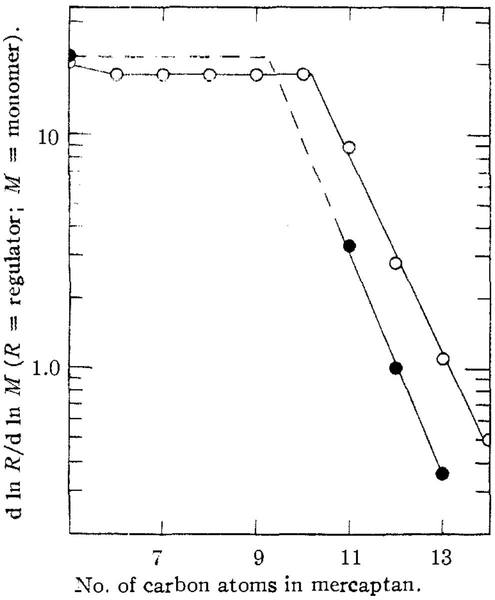

Fig. 4.—Relative rates of reaction of the normal aliphatic mercaptans from amyl to tetradecyl in the emulsion polymerization of butadiene (○) and of styrene (●).

## Discussion

In Part I[1] it was shown that the value of d ln $R$/d ln $M$ ($R$ = regulator and $M$ = monomer) for low molecular weight mercaptans is practically the same in emulsion as in oil-phase polymerization. However, examination of Fig. 5 shows that this is not the case for high molecular weight mercaptans, such as dodecyl mercaptan, for which the value of d ln $R$/d ln $M$ is much less in emulsion polymerization. This almost certainly indicates that with these high molecular weight mercaptans the ratio of mercaptan to monomer in the reaction locus must be less than the ratio in the emulsion droplet reservoirs. Thus there must be a lack of equilibrium of regulator in the system and, consequently, appreciable activity gradients of regulator. In view of the low water solubility of these mercaptans, the most likely location of the principal activity gradient appears to be the aqueous solution; the effect of the *p*H of the aqueous phase on the mercaptan reaction which will be discussed more fully shortly demonstrates the importance of the water solution.

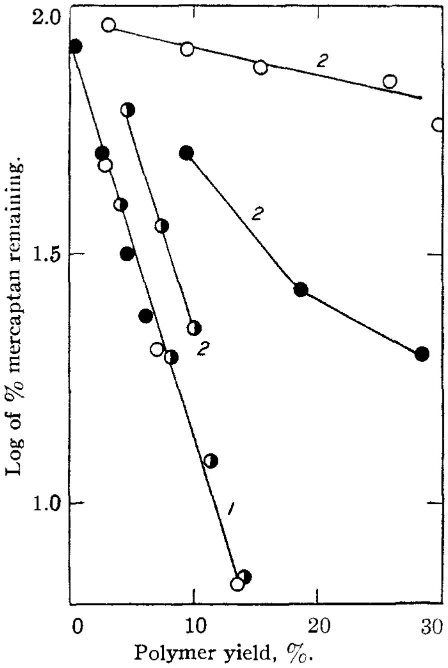

Fig. 5.—Effect of excess alkalies on rate of mercaptan reaction in emulsion polymerization of styrene for the low molecular weight mercaptan, amyl (curve 1), and for the high molecular weight mercaptan, dodecyl (curves 2): ○, emulsion with excess stearic acid; ●, emulsion with excess potassium hydroxide; ◑, oil phase.

The activity gradient of regulator in the water solution can occur in either of two principal manners representing two extremes. On the one hand, the reservoirs (emulsified monomer droplets) may be substantially in equilibrium with the aqueous phase around them, the principal gradient occurring in the water solution immediately surrounding each reaction locus (polymer particle). On the other hand, the reaction loci may be substantially in equilibrium with the aqueous phase around them, the principal gradient occurring uniformly in the water solution between reservoirs. More generally the situation will lie between these two extremes. At the very beginning of the polymerization when the surface of the reservoirs is large compared with that of the polymer particles, the situation represented by the first extreme may prevail, but as polymerization proceeds and the surface of the polymer particles becomes large with respect to that of the reservoirs, the other extreme should more closely represent the system. While it is relatively simple to discuss these two extremes in a quantitative manner, the more general intermediate case is more involved and a quantitative discussion will not be presented. However, a brief qualitative discussion of the effects of the principal variables of the system on the rate of regulator reaction will be given. The effectiveness of the water as a barrier to the transport of regulator from reservoir to reaction locus will be determined by the diffusion constant of regulator in the water and by the distribution coefficient of regulator between reservoir and water. The diffusion constants of the mercaptan regulators studied here should represent only minor variations. However, the distribution coefficients are very dependent on the number of carbon atoms in the mercaptan. For example, Yabroff[3] has determined the distribution coefficients of some aliphatic mercaptans between isoöctane and water and has found the coefficient to be decreased by a factor of about

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(3) D. L. Yabroff, *Ind. Eng. Chem.*, **32**, 257 (1940).

4.4 for each additional carbon atom in the mercaptan. This decrease is no doubt largely responsible for the large negative slopes of the portions of the two curves in Fig. 4 pertaining to mercaptans containing more than ten carbon atoms; these slopes correspond to a factor of about 3 for each additional carbon atom. The horizontal portion of these curves, for the mercaptans below nonyl or decyl, indicate large enough distribution coefficients to keep the mercaptan in the polymer particles substantially in equilibrium with that in the monomer reservoirs. Under these conditions the rate of mercaptan reaction relative to that of monomer is determined only by the transfer constant of the mercaptan in the polymer particles, as was discussed in Part I.[1]

Another factor important in determining the rate of transport of mercaptans through the water solution during the polymerization is the *p*H of the aqueous phase. Being weak acids, these aliphatic mercaptans ionize in high *p*H solutions giving mercaptide ions. Since both un-ionized mercaptan and mercaptide ion will diffuse through the water, increase in *p*H will aid in the transport of mercaptan through the water; this will in turn increase the regulating action of the high molecular weight mercaptans even though the mercaptide ion itself does not regulate. The ionization constant for aliphatic mercaptans in water is of the order of $10^{-11}$; Yabroff[3] gives $1.77 \times 10^{-11}$ for butyl mercaptan in water at 20°. So this effect should become important as the *p*H approaches 11 or greater. This effect of *p*H is illustrated in Fig. 5. In the case of dodecyl mercaptan (curves 2) the rate of the regulating reaction relative to that of monomer is much less in emulsion than in oil-phase, indicating that diffusion is a controlling factor, and with this mercaptan increase in the *p*H of the aqueous phase increases the relative rate of regulator reaction in emulsion. However, with amyl mercaptan where the relative rate of regulating reaction in emulsion is already as great as the relative rate in oil-phase, increasing the *p*H of the emulsion has no effect on the rate.

Other properties of the system which should influence the relative rate of regulator reaction when diffusion is a controlling factor are: size of the polymer particles (at low conversions), interfacial area of the reservoirs (at higher conversions), the transfer constant and the rate of polymerization per unit volume of aqueous phase (also at the higher conversions).

Since the primary importance of the rate of regulator reaction is that it determines the molecular weight of the polymer produced, it is worth while to make a few remarks about the effect of diffusion control of the regulator reaction on the molecular weight of the polymer. Of course, the primary effect is that insofar as diffusion controls the rate of regulator reaction it also controls the number average molecular weight of the polymer, since one polymer molecule is produced for each regulator molecule reacted. Aside from this primary effect, the question arises as to the nature of the molecular weight distribution of the polymer. It is probable that this distribution for polymer formed during any small increment of time in a particular locus of emulsion polymerization is the same as the distribution for oil-phase polymer. However, in emulsion the possibility arises that the ratio of regulator to monomer may vary from locus to locus when diffusion is a controlling factor; if this were the case it should lead to an unusually broad molecular weight distribution. Again in considering this problem it is convenient to discuss the two extreme cases separately. If the principal activity gradient is that around the individual polymer particles then the only broadening in molecular weight distribution expected to result from diffusion control of regulation should be that resulting from a distribution in the polymer particle sizes. In the other extreme, polymer particles located relatively near a reservoir should have a ratio of regulator to monomer greater than that for polymer particles relatively far away from a reservoir; this should result in a broadening of the molecular weight distribution which would be very large if the particles remained stationary and if $d \ln R / d \ln M$ were much less than the transfer constant. However, under normal conditions of emulsion polymerization the Brownian motion of the small polymer particles should be sufficient to cause them to move distances comparable to or greater than the average distance between reservoirs in a time of the order of that required for a single molecule to form. This Brownian motion should reduce the effect of diffusion control of regulation on the molecular weight distribution of the polymer. While broadening of the molecular weight distribution of polymer produced in emulsion has been looked for in these laboratories, no large effect has been found even when the value of $d \ln R / d \ln M$ was only 0.02 times the value of the transfer constant measured in oil-phase.

**Acknowledgment.**—The author gratefully acknowledges the constructive criticism of Dr. R. H. Ewart in preparing this paper.

## Summary

The effect of the chain lengths of aliphatic mercaptans on their regulating action in the emulsion polymerization of styrene and of butadiene has been investigated. It is found that the rate of reaction of regulator relative to that of monomer for the lower molecular weight mercaptans is practically the same in emulsion polymerization as this relative rate in oil-phase polymerization. For higher molecular weight mercaptans, however, this relative rate is less than the corresponding oil-phase rate, which is interpreted as indicating that the rate of diffusion of the high

molecular weight mercaptans through the aqueous phase is a controlling factor in determining the rate of regulator reaction.

PASSAIC, NEW JERSEY RECEIVED MAY 7, 1946

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[CONTRIBUTION FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

# Regulator Theory in Emulsion Polymerization. III. Regulator Reaction in Copolymerizing Systems

BY W. V. SMITH

The relative rates of reaction of two monomers during copolymerization have been discussed from both a theoretical and experimental standpoint.[1] The rate of reaction of a transfer agent or regulator in the polymerization of a single monomer has been discussed by Mayo.[2] It is the purpose of this paper to combine these two treatments and thus obtain the law governing the rate of reaction of a regulator during the copolymerization of two monomers. While the theory should apply either to oil-phase polymerization or to emulsion polymerization, the experimental portion is confined to emulsion polymerization.

## Theory

The following elementary reactions are assumed to account for chain propagation and chain transfer in a system in which the monomers A and B are copolymerizing in the presence of the regulator R

$$\mathrm{A\cdot} + \mathrm{A} \xrightarrow{k_1} \mathrm{A\cdot} \qquad (1)$$

$$\mathrm{A\cdot} + \mathrm{B} \xrightarrow{k_2} \mathrm{B\cdot} \qquad (2)$$

$$\mathrm{B\cdot} + \mathrm{B} \xrightarrow{k_3} \mathrm{B\cdot} \qquad (3)$$

$$\mathrm{B\cdot} + \mathrm{A} \xrightarrow{k_4} \mathrm{A\cdot} \qquad (4)$$

$$\mathrm{A\cdot} + \mathrm{R} \xrightarrow{k_5} \mathrm{P} + \mathrm{R\cdot} \qquad (5)$$

$$\mathrm{B\cdot} + \mathrm{R} \xrightarrow{k_6} \mathrm{P} + \mathrm{R\cdot} \qquad (6)$$

In the above system of reactions A· and B· designate growing polymer free radicals in which only the active ends are specified, since it is assumed that the nature of the rest of the free radical will have a negligible effect on the specific reaction rate constants involving the free radical. R is regulator, R· is the free radical derived from the regulator by chain transfer, and P is inactive polymer. The specific reaction rate constants for the six reactions considered are $k_1$ to $k_6$. Certain ratios of these rate constants can be measured by analytical methods, these are

$$k_1/k_2 = \sigma;\ k_3/k_4 = \mu$$

$$k_5/k_1 = C_{\mathrm{A}};\ k_6/k_3 = C_{\mathrm{B}}$$

The symbols are those used by Mayo in his treatment of copolymerization[1a] and of transfer constants.[2]

By reactions (5) and (6) the rate of regulator disappearance is given by

$$\mathrm{d}\ln R/\mathrm{d}t = k_5(\mathrm{A\cdot}) + k_6(\mathrm{B\cdot}) \qquad (1)$$

Letting (A) and (B) represent the molal concentrations of the two monomers, the rate of disappearance of monomer by reactions 1 to 4 is

$$\mathrm{d}((\mathrm{A}) + (\mathrm{B}))/\mathrm{d}t = k_1(\mathrm{A})(\mathrm{A\cdot}) + k_2(\mathrm{B})(\mathrm{A\cdot}) + k_3(\mathrm{B})(\mathrm{B\cdot}) + k_4(\mathrm{A})(\mathrm{B\cdot}) \qquad (2)$$

By using the steady state assumption of Mayo

$$k_2\,(\mathrm{B})(\mathrm{A\cdot}) = k_4(\mathrm{A})(\mathrm{B\cdot}) \qquad (3)$$

and replacing the individual $k$'s by the ratios given above, equations 1 and 2 give

$$\frac{\mathrm{d}\ln R}{\mathrm{d}((\mathrm{A}) + (\mathrm{B}))} = \frac{\sigma(\mathrm{A})C_{\mathrm{A}} + \mu(\mathrm{B})C_{\mathrm{B}}}{\sigma(\mathrm{A})^2 + 2(\mathrm{A})\,(\mathrm{B}) + \mu(\mathrm{B})^2} \qquad (4)$$

This can be put into a form which is in some respects more convenient to use by making the substitutions

$$\frac{(\mathrm{A})}{(\mathrm{A}) + (\mathrm{B})} = A \text{ and } \frac{(\mathrm{B})}{(\mathrm{A}) + (\mathrm{B})} = B$$

where $A$ and $B$ are the mole fractions of each unreacted monomer expressed on the basis of total unreacted monomer so that $A + B$ is 1 at all times. Then

$$\frac{\mathrm{d}\ln R}{\mathrm{d}\ln((\mathrm{A}) + (\mathrm{B}))} = \frac{\sigma A C_{\mathrm{A}} + \mu B C_{\mathrm{B}}}{\sigma A^2 + 2AB + \mu B^2} \qquad (5)$$

The quantity d ln $R$/d ln ((A) + (B)) may be considered to define the transfer function, $C$, in the copolymerizing system so

$$C = \frac{\sigma A C_{\mathrm{A}} + \mu B C_{\mathrm{B}}}{\sigma A^2 + 2AB + \mu B^2} \qquad (6)$$

In using this law, the units of $R$ are immaterial; however, $A$ and $B$ must be mole fractions. The use of mole fractions in the latter case is required due to use of the steady state assumption 3. The transfer function as defined above using molal units for expressing the monomer concentrations is satisfactory for relating degrees of polymerization with rate of regulator disappearance. However, for relating regulator disappearance with molecular weight, a more convenient definition of the transfer function would be one in which the monomer concentrations were in weight units; but as this would result in an ex-

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[1] (a) F. R. Mayo and F. M. Lewis, THIS JOURNAL, **66**, 1594 (1944); (b) F. M. Lewis, F. R. Mayo and W. F. Hulse, *ibid.*, **67**, 1701 (1945); (c) F. T. Wall, *ibid.*, **66**, 2050 (1944); (d) T. Alfrey, Jr., and G. Goldfinger, *J. Chem. Phys.*, **12**, 205, 322 (1944); (e) R. Simha and H. Branson, *ibid.*, **12**, 253 (1944).

[2] F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943).