persed. But the increased susceptibility at liquid-air temperatures shows that the average chromium–chromium spacing is a little larger than that in pure crystalline chromic oxide.

The same general conclusions apply to so-called "copper chromite," namely, that the active black catalyst is not a spinel. This is established through the absence of characteristic X-ray diffraction and by the very different magnetic properties. This catalyst is, however, characterized by a very remarkable ferromagnetism which is found at liquid air temperatures. The Curie temperature for this substance lies between liquid air temperature and room temperature because not a trace of ferromagnetism is observable at 25°. Further work is in progress to find the exact Curie point. This ferromagnetism is not found in the adequately calcined catalyst, although prolonged heating is necessary to make the catalyst revert completely to copper chromite spinel. The ferromagnetism of this catalyst recalls that found for the chromic oxide gel. It is not clear that there is necessarily any relationship between the ferromagnetism and the catalytic activity. But the existence of ferromagnetism must be remarkably sensitive to rather minor changes in structure, and it is possible that such structural changes do have a relationship to catalytic activity.

It is well known that the copper oxide–chromium oxide black catalyst undergoes a change when it is heated in hydrogen. The black form is believed to contain divalent copper, while the reduced form contains either univalent copper or copper metal.[5] The reduced form was found in these experiments to show no trace of ferromagnetism. In fact the susceptibility dropped to a value not greatly different from that for the corresponding active zinc catalyst. Zinc ions are, of course, diamagnetic, as are both cuprous ions and copper atoms. The magnetic evidence is, therefore, not inconsistent with the view that the reduced catalyst contains cuprous ions or metallic copper, together with a rather slightly dispersed form of chromic oxide.

The magnetic results on the nickel–chromium oxide are a little surprising as it was thought, by analogy, that this catalyst would also be ferromagnetic at low temperatures. The absence of any ferromagnetism also implies the absence of metallic nickel. This is not unexpected, although nickel-containing catalysts not infrequently give magnetic evidence of some metallic nickel, even though the presence of metal would not have been predicted on consideration of the previous treatment of the catalyst. Further study of this catalyst may throw some light on the problem as to whether reduced copper–chromium oxide contains metallic copper or cuprous ions.

It is a pleasure to acknowledge a grant-in-aid of research from the Shell Development Company. The investigation was also supported by a grant from the Abbott Fund of Northwestern University.

Summary

Magnetic susceptibility measurements have been made on catalytically active solids consisting of chromic oxide supported on γ-alumina, on molybdenum dioxide supported on γ-alumina, and on a group of so-called "chromite" catalysts. It has been shown that the magnetic properties of a supported transition group oxide approach those of a magnetically dilute compound. This effect is expected to be useful in studying the structure of active solids, in estimations of dispersion and of surface area, and of the oxidation state of the activating agent.

EVANSTON, ILLINOIS RECEIVED JUNE 10, 1946

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

Regulator Theory in Emulsion Polymerization.[1] I. Chain Transfer of Low Molecular Weight Mercaptans in Emulsion and Oil-Phase

BY W. V. SMITH

In a general consideration of the mechanism of vinyl polymerization, Flory[1a] suggested that growing polymer free radicals might react with solvent molecules, producing inactive polymer molecules and solvent free radicals; and that this transfer reaction might explain the effectiveness of some solvents in reducing the molecular weights of polymer produced in them. More recently, Mayo[2] has discussed this idea quantitatively and has interpreted the molecular weights of polystyrene produced in various solvents in terms of the ratios of the rate constants for chain growth and chain transfer with the solvent. Early in the current synthetic rubber program it was proposed that the effectiveness of mercaptans in improving the processing characteristics of GR-S was due to their ability to reduce or "regulate" the molecular weight of the polymer produced in their presence; since it was found that mercaptan would reduce the molecular weight of emulsion polystyrene.[3] It was then shown that the

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[1] These papers, Parts I, II and III, were presented at the High Polymer Forum of the Chicago meeting of the American Chemical Society, Sept., 1946.

[1a] P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

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

[3] R. H. Ewart, private communication.

molecular weights of both polybutadiene and polyisoprene produced in emulsion in the presence of mercaptans were determined by the rates of reaction of the mercaptans, and that the molecular weight of the initial polybutadiene was such that there was one molecule of polymer formed for each molecule of reacted mercaptan.[4] It has also been shown that there is one molecule of polymer produced for each molecule of mercaptan reacted in the copolymer of butadiene and styrene.[5] The concept of chain transfer serves as the fundamental basis for interpreting regulator action both in emulsion and oil-phase polymerization.

It is assumed that a growing polymer radical, $M_n^{\cdot}$, reacts by either of two principal reactions: with monomer, M, by the chain growth reaction $M_n^{\cdot} + M \xrightarrow{k_2} M_{n+1}^{\cdot}$, giving a growing polymer radical with one more unit; or with regulator, R, by the chain transfer reaction $M_n^{\cdot} + R \xrightarrow{k_3} M_n + R^{\cdot}$, giving inactive polymer M_n and a free radical, $R^{\cdot}$, derived from the regulator. The specific reaction rate constants for these two reactions may be called k_2 and k_3 (reserving k_1 for the chain initiation rate constant which need not be considered here). It is evident that, under conditions in which practically all of the inactive polymer molecules are formed by this chain transfer, the number of polymer molecules formed will be just equal to the number of regulator molecules reacted. Furthermore, the chain length of polymer formed at any instant will be given by the ratio of the rate of monomer reaction to that of regulator reaction or

$$\overline{M}'_n = \mathrm{d}m/\mathrm{d}R \qquad (1)$$

where $\overline{M}'_n$ is the number average molecular weight of polymer formed at any instant and $\mathrm{d}m/\mathrm{d}R$ is the ratio of grams of monomer to moles of regulator reacting. In an homogeneous system such as oil-phase polymerization the rate law governing the disappearance of monomer and regulator may be expected to be

$$\frac{\mathrm{d}\ln R}{\mathrm{d}\ln m} = \frac{k_3}{k_2} = C \qquad (2)$$

Mayo[2] has called this ratio of rate constants the transfer constant and has given it the symbol, C.

In an inhomogeneous system, such as is present in emulsion polymerization, one might expect a more complicated equation than (2) to govern the relative rates of mercaptan and monomer reactions, $\mathrm{d}\ln R/\mathrm{d}\ln m$. However, it will be shown that under suitable conditions the same law holds and that the transfer constant, C, has practically the same value in emulsion and oil-phase. A succeeding paper will show that under other conditions the value of $\mathrm{d}\ln R/\mathrm{d}\ln m$ may be less in emulsion than in oil-phase due to control of the rate of regulator reaction by diffusion of the regulator through the aqueous phase and that under these conditions the law governing the rate is more complicated than 2.

Experimental

Materials.—The styrene was distilled from a commercial grade of about 99% purity, the distillation being carried out under reduced pressure just prior to use of the styrene. Methyl methacrylate was also distilled from a commercial grade just prior to use. Tertiary butyl mercaptan was fractionated from a commercial sample (fraction used: b. p. 63.9–64.4° (763 mm.)). The *n*-amyl mercaptan was an Eastman Kodak Co. sample. The stearic acid was specially treated to remove unsaturation. A commercial sample was soaked in concentrated sulfuric acid, washed with water, crystallized several times from toluene, washed with alcohol and finally distilled twice *in vacuo* (molecular weight from potassium hydroxide titration, 278 g.; calcd., 284.5). The potassium persulfate was a C. P. grade. The potassium hydroxide solution was prepared by diluting a 50% solution with oxygen-free water. This master solution was stored under nitrogen. All water used in these polymerizations was treated to remove oxygen, by distilling and condensing in a stream of nitrogen, after which it was stored under nitrogen.

Emulsion Polymerization.—In each series the individual runs were prepared from two master solutions. A typical hydrocarbon solution consisted of: stearic acid 3.95 g., *t*-butyl mercaptan 0.2 cc., monomer to make 100 cc., while a typical aqueous solution consisted of potassium persulfate 0.175 g., potassium hydroxide (12.1% solution) 3.51 cc., oxygen-free water to make 100 cc. The individual runs were carried out in 2-oz. glass-stoppered reaction bottles. A charge consisted of 10 cc. of hydrocarbon solution and 15 cc. of aqueous solution. Oxygen-free conditions were used in filling the bottles; *i. e.*, the reaction bottles were swept out with tank nitrogen and the addition of the solutions was done in an atmosphere of nitrogen. (The presence of oxygen was avoided to minimize inhibition.) The polymerization reaction was carried out with mild end-over-end agitation in a water-bath thermostated at 40 or 50°.

The bottles were withdrawn at the end of the reaction period, opened and, after vigorous shaking of the contents, a portion of the latex was poured out and weighed for mercaptan titration; the remainder of the latex was coagulated by adding it to a solution consisting of 50 cc. of water, 2 cc. of 5% hydroquinone solution, and 2 cc. of 6 *N* sulfuric acid, after which the unreacted monomer was removed by steam distillation. The coagulated polymer was purified by dissolving in benzene and precipitating with methanol, then redissolving in benzene, freezing and drying on a vacuum line and finally weighing to determine polymer yield.

The mercaptan titration was carried out amperometrically with silver nitrate using a method developed by Kolthoff.[6] The method consisted essentially of adding a few grams of the latex to 100 cc. of ethyl alcohol with vigorous stirring. One cc. of 0.1 *N* ferrous sulfate solution in 1 *N* sulfuric acid was then added. After standing for a few minutes, 2 cc. of concentrated ammonia solution was added and the amperometric titration with 0.005 *N* silver nitrate carried out. In the titration a rotating platinum electrode was used in conjunction with a half-cell prepared by dissolving 4.2 g. of potassium iodide and 1.3 g. of mercuric iodide in 100 cc. of satd. potassium chloride solution and placing mercury in a pool at the bottom of the solution.

Oil-Phase Polymerization.—In making the oil-phase polymerizations the charges consisted only of mercaptan

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(4) R. H. Ewart, W. V. Smith and G. E. Hulse, private communication.

(5) R. H. Snyder and F. T. Wall, private communication. See H. R. Snyder, J. M. Stewart, R. E. Allen and R. J. Dearborn, THIS JOURNAL, **68**, 1422 (1946); and F. T. Wall, F. W. Banes and G. D. Sands, *ibid.*, **68**, 1429 (1946).

(6) I. M. Kolthoff and W. E. Harris, *Ind. Eng. Chem., Anal. Ed.*, **18**, 161 (1946).

TABLE I

t-BUTYL MERCAPTAN IN STYRENE

Emulsion, 40°, monomer containing 0.2% mercaptan

Time, min.	20	40	60	80	110	140
Polymer yield, %	0.9	3.0	5.2	7.4	10.8	15.6
Mercaptan reacted, %	6.5	13.5	22.9	27.8	39.5	50.8

Oil-phase, 62.5°, monomer containing 0.1% mercaptan

Time, hr.	0	19.3	47.5	94.3	165.5	237.5
Refractive index	1.5462	1.5480	1.5495	1.5522	1.5560	1.5600
Polymer yield, %	0	3.1	5.7	10.4	16.9	23.8
Mercaptan reacted, %	0	6.0	19.8	41.0	53.8	63.0

Oil-phase, 100°, monomer containing 0.05% mercaptan

Time, hr.	3	4.5	6	8
Polymer yield, %	8.2	11.7	14.6	19.2
Mercaptan reacted, %	27.4	33.9	45.0	51.5

n-AMYL MERCAPTAN IN STYRENE

Emulsion, 40°, monomer containing 0.4% mercaptan (1/2 usual amount of persulfate used)

Time, min.	19	28	40	50	60	70
Polymer yield, %	0.9	3.0	4.5	7.5	11.3	14.2
Mercaptan reacted, %	32.8	54.5	73.7	84.0	92.75	97.08

Oil-phase, 62.5°, monomer containing 0.4% mercaptan

Time, hr.	0	20	44	66.5	90
Refractive index	1.5463	1.5488	1.5510	1.5529	1.5544
Polymer yield, %	0	4.3	8.1	11.4	14.0
Mercaptan reacted, %	0	57.2	80.1	87.6	92.88

n-AMYL MERCAPTAN IN METHYL METHACRYLATE

Emulsion, 50°, monomer containing 0.8% mercaptan

Time, min.	20	40	49	62	79
Polymer yield, %	4.1	28.2	38.8	52.7	66.0
Mercaptan reacted, %	8.5	24.2	37.0	43.8	54.5

Oil-phase, 100°, monomer containing 3.0% mercaptan

Time, min.	0	45	80	210	250	305	395
Refractive index	1.4152	1.4260	1.4265	1.4282	1.4312	1.4406	1.4431
Polymer yield, %	0	13.2	13.8	15.9	19.5	31.0	34.0
Mercaptan reacted, %	0	11.6	13.0	15.5	18.0	28.0	31.3

About 0.002 g. of benzoyl peroxide was added to the charge of 100 cc. after taking out the 210-minute sample, and 0.005 g. added after taking out the 250-minute sample.

and monomer. Most of the polymerizations were made at a temperature of 62.5°, while one experiment was run at 100°. The charges were made up in 100-ml. glass-stoppered volumetric flasks. A flask was first swept out with nitrogen, then the desired amount of mercaptan added, after which the monomer, which had had nitrogen bubbled through it, was added. These flasks were clamped in a thermostated water-bath. Samples of solution were removed from time to time to determine mercaptan concentration and polymer concentration. After the removal of each sample the flasks were swept out again with nitrogen and the reaction allowed to continue.

The samples for mercaptan determinations were added to alcohol with vigorous stirring and titrated with silver nitrate as above. It was found, however, that in the case of the higher conversion runs (those above about 10%) an appreciable amount of mercaptan remained in the precipitated polymer and did not react with the silver nitrate during the titration. This source of error was corrected for by taking out the polymer after the titration, dissolving it in benzene, then adding the benzene solution to another portion of alcohol and titrating again.

Polymer yields were determined from the refractive index of a sample of solution from the reaction flask. In order to convert the refractive index measurements to polymer yield the following relationships were used: for styrene $\Delta c = 1.73 \times 10^3 \Delta n^{20}_{\mathrm{D}}$, and for methyl methacrylate $\Delta c = 1.22 \times 10^3 \Delta n^{20}_{\mathrm{D}}$, where c is the concentration of polymer in weight per cent., n^{20}_{D} is the refractive index at 20° for the sodium D line.[7]

Solution Viscosity.—The solution viscosities of these polymers were determined in benzene, using an Ostwald viscometer. A single concentration of polymer was used, such that the specific viscosity, η_{sp} would be about 0.3. The intrinsic viscosity was then calculated from the relation

$$\eta_{sp}/c_v = [\eta] + 0.375\,[\eta]^2 c_v$$

where c_v is the concentration of the polymer in grams per 100 cc. of solution.[8]

Results

Three different systems were studied in this investigation: *t*-butyl mercaptan in styrene, *n*-amyl mercaptan in styrene, and *n*-amyl mercaptan in

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(7) These relations were obtained from the refractive indices of known solutions of polymer in monomer; the data for methyl methacrylate were kindly supplied by C. T. Walling.

(8) The use of this equation is based on a study of the intrinsic viscosities of benzene solutions of polystyrene by H. C. Tingey in these Laboratories.

methyl methacrylate. For each system polymer yields and mercaptan consumptions were determined in both emulsion and oil-phase polymerization. The data are given in Table I.

These data are plotted in Fig. 1, in which the logarithm of % mercaptan remaining is plotted against the function, 2-log % monomer remaining. This particular function is chosen so that increase in values of the abscissa corresponds to increasing values of the polymer yield and the negative slopes of the lines correspond to the transfer constants as defined by equation 2.

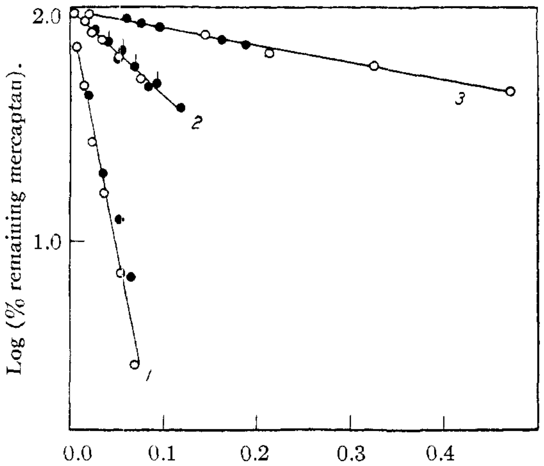

Fig. 1.—Curve 1, *n*-amyl mercaptan in styrene; curve 2, *t*-butyl mercaptan in styrene; curve 3, *n*-amyl mercaptan in methyl methacrylate; ○, emulsion polymerization; ●, oil phase polymerization at 62.5°; ●, oil phase polymerization at 100°. The slopes of the lines correspond to transfer constants of 20, 4 and 0.8, respectively.

In examining these data, the first thing to note is that variation in temperature has a very small effect on the slope of the lines given in Fig. 1, as is illustrated by the data on oil-phase polymerization of the *t*-butyl mercaptan in styrene system, which were obtained at the two temperatures, 62.5 and 100°. This variation in temperature gave only a slight variation in the slope of the line. Thus, while the oil-phase data were obtained at different temperatures from the emulsion data in order to have more convenient rates of reaction, the two types of polymerization can be compared directly since the temperature coefficient is small. In making such a comparison between the oil-phase and the emulsion data it is evident that, in all three systems studied, there is practically no difference between oil-phase and emulsion.

In addition to the above data, the intrinsic viscosities of many of these polymers were determined, also the intrinsic viscosities of polymers prepared under rather widely varying ratios of mercaptan to monomer. These data are given in Table II.

Table II

Intrinsic Viscosity of Polymers Prepared by Emulsion Polymerization

Styrene regulated with *t*-butyl mercaptan, 40°, 2.1×10^5 grams styrene per mole of mercaptan

Time, min.	20	40	60	90	120	150
Polymer yield, %	3.7	8.3	13.1	18.6	29.8	42.8
$[\eta]$	0.436	0.416	0.438	0.471	0.562	0.725

4.3×10^5 grams styrene per mole of mercaptan

Time, min.	20	40	60	120	150
Polymer yield, %	3.0	7.3	12.8	34.5	45.5
$[\eta]$	0.62	0.66	0.71	0.99	1.19

8.4×10^5 grams styrene per mole of mercaptan

Time, min.	20	40	60	90	120	150
Polymer yield, %	3.3	8.4	14.4	26.2	34.5	48.7
$[\eta]$	1.08	1.13	1.19	1.46	1.72	2.24

1.7×10^6 grams styrene per mole of mercaptan

Time, min.	20	40	60	80	100	120
Polymer yield, %	2.8	9.8	16.1	25.0	34.4	41
$[\eta]$	1.74	1.86	1.98	2.33	2.75	3.24

3.0×10^6 grams styrene per mole of mercaptan

Time, min.	15	30	45	60	75	90
Polymer yield, %	0.6	0.8	6.9	10.9	18.0	23.6
$[\eta]$	2.69	2.07	2.83	2.92	3.31	3.75

Styrene regulated with *n*-amyl mercaptan, 40°, 6.7×10^5 grams styrene per mole of mercaptan

Time, min.	85	105	125	145
Polymer yield, %	4.7	11.8	9.0	16.1
$[\eta]$	0.43	0.88	0.76	1.49

3.2×10^6 grams styrene per mole of mercaptan

Time, min.	20	30	40	50	65	80
Polymer yield, %	0.5	2.0	3.2	3.8	7.9	12.8
$[\eta]$	0.83	1.01	1.29	1.28	1.82	2.89

Methyl methacrylate regulated with *n*-amyl mercaptan, 50°, 7.4×10^4 grams of methyl methacrylate per mole of mercaptan

Time, min.	20	30	40	50	65	80
Polymer yield, %	19.0	34.4	48.7	68	90	100
$[\eta]$	0.596	0.590	0.611	0.580	0.562	0.560

The intrinsic viscosities of polymer for the two systems, *t*-butyl mercaptan in styrene and *n*-amyl mercaptan in styrene, are plotted on a logarithmic scale against the polymer yield in Fig. 2. The upper portion of this figure is for the system with *t*-butyl mercaptan while the lower portion is for that with *n*-amyl. The different curves represent different initial ratios of monomer to mercaptan. In such a plot it is evident that for any given system parallel lines are obtained, while the slopes of the lines are different for the different systems due to different relative rates of mercaptan and monomer reaction.

Discussion

These data can be interpreted satisfactorily using the picture of emulsion polymerization proposed by Harkins,[9] which is essentially that in emulsion polymerization the principal loci of reaction consist of the micelles during the early stages of the reaction and the swollen polymer particles during the later stages. The emulsified monomer droplets serve as reservoirs for supplying both monomer and mercaptan to these principal reaction loci. In such a picture, if both the

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

monomer and the regulator can diffuse from the reservoirs through the aqueous medium rapidly enough to keep the system substantially in equilibrium with respect to monomer and regulator, then it is reasonable to suppose that the ratio of regulator to monomer in the reaction loci will be the same as this ratio in the reservoirs, which in turn will be simply the over-all ratio of regulator to monomer. It also seems likely that the transfer constants in the reaction loci will be about the same as those determined in oil-phase polymerization. Under these conditions the values of d ln R/d ln m should be the same in emulsion polymerization as in oil-phase polymerization. The above data show this to be the case in the three systems investigated, which involve low molecular weight mercaptans. That this is not always the case will be shown in a succeeding paper where d ln R/d ln m is found to be less for emulsion than for oil-phase polymerization, when the regulator is a high molecular weight mercaptan.

The intrinsic viscosities of these polymers are related to the molecular weights and, consequently, it should be possible to relate them to the rate of regulator reaction through equations 1 and 2. By treating C in equation 2 as a constant, this equation can be integrated and a value of dm/dR obtained as a function of polymer yield, P. This, in turn, determines the molecular weight, $\overline{M}_n'$, by equation 1. The result is

$$\overline{M}_n' = \frac{m_0}{R_0C}(1 - P)^{1-C} \qquad (3)$$

where m_0/R_0 is the initial ratio of grams of monomer to moles of regulator and P is the fraction of monomer converted to polymer.

This molecular weight may be related to the intrinsic viscosity through the experimental law

$$[\eta] = K\overline{M}_v^a \qquad (4)$$

where K and a are constants and $\overline{M}_v$ is the viscosity average molecular weight,[10] if an assumption is made concerning the relation between the number average and viscosity average molecular weight. The most reasonable such assumption may be expressed by

$$\overline{M}_v' = \alpha\,\overline{M}_n' \qquad (5)$$

where $\overline{M}_v'$ and $\overline{M}_n'$ are viscosity and number average molecular weights, respectively, and the primes indicate that these refer only to polymer produced during a small increment of conversion; α is a constant which must be greater than unity for heterogeneous polymer. The assumed constancy of α is equivalent to assuming that the shape of the molecular weight distribution curve for polymer produced during a small increment of conversion is the same at all times irrespective of the average value of the molecular weight or of the degree of conversion. Equations 4 and 5 give

$$[\eta]' = K\alpha^a(\overline{M}_n')^a = K'(\overline{M}_n')^a \qquad (6)$$

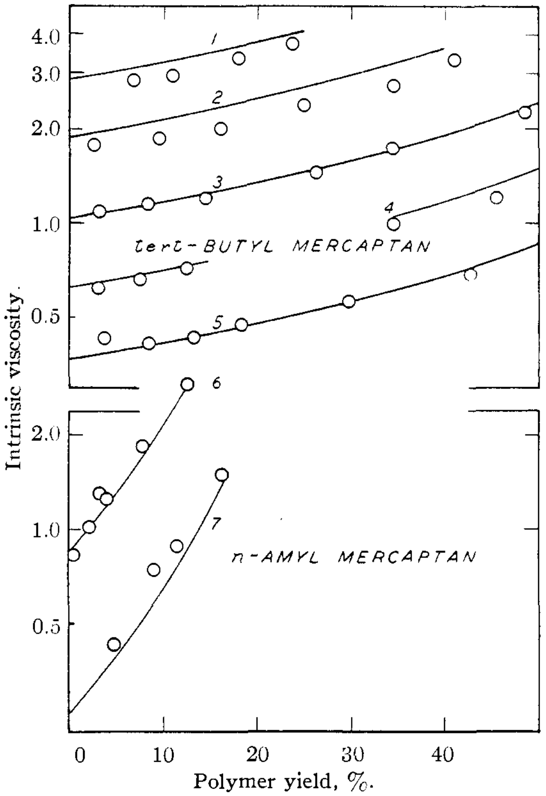

Fig. 2.—Intrinsic viscosity of polystyrene prepared in emulsion with mercaptan regulators: curve 1, 3.0 × 10^6 g. styrene/mole mercaptan; curve 2, 1.7 × 10^6 g./mole; curve 3, 8.4 × 10^5 g./mole; curve 4, 4.3 × 10^5 g./mole; curve 5, 2.1 × 10^5 g./mole; curve 6, 3.2 × 10^6 g./mole; curve 7, 6.7 × 10^5 g./mole. All curves are calculated from equation (8).

where $[\eta]'$ is the intrinsic viscosity of polymer produced during a small increment of conversion and K' is a constant greater than K. Thus from 3

$$[\eta]' = K'(m_0/R_0C)^a(1 - P)^{a(1-C)} \qquad (7)$$

The intrinsic viscosity of the total polymer, $[\eta]_T$, can then be obtained from the integration

$$[\eta]_T = \frac{1}{P}\int_0^P [\eta]'\mathrm{d}P$$

which gives

$$[\eta]_T = K\left(\frac{m_0}{R_0C}\right)^a\left[\frac{(1 - P)^{-\beta} - 1}{P\beta}\right] \qquad (8)$$

where $\beta = a(C - 1) - 1$.

The constants K' and a in 8 may be taken to be $K' = 7.54 \times 10^{-5}$ and $a = 0.783$ from the relation

$$[\eta] = 7.54 \times 10^{-5}\,\overline{M}_n^{0.783} \qquad (9)$$

found by Ewart, Tingey and Wales[11] for unfractionated oil phase polystyrene prepared with an excess of relatively inert regulator. The use of these constants in 8 is based on the assumption that the molecular weight distribution for the initially formed emulsion polymer is the same as that for the oil phase polymer samples studied by the above.

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[10] P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

[11] R. H. Ewart, H. C. Tingey and M. Wales, unpublished data obtained in these laboratories.

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

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

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.), $n^{20}\mathrm{D}$ 1.4569; *n*-dodecyl mercaptan, b. p. 153.7–153.9° (20.5 mm.), $n^{20}\mathrm{D}$ 1.4589; *n*-tetradecyl mercaptan, b. p. 179.8–180.9° (20.0 mm.), m. p. 7.0°, $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 1.4588; *n*-tridecyl mercaptan, b. p. 169.6–171.7° (22 mm.), $n^{20}\mathrm{D}$ 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).