[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Thermal Reaction of Styrene with Ethyl Thioglycolate; Evidence for the Termolecular Thermal Initiation of Styrene Polymerization

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The kinetics of the reaction of styrene and ethyl thioglycolate in the absence of added initiators has been made reproducible and measured. The results support the third-order mechanism for the thermal initiation of styrene polymerization. Certain implications are discussed, including the role of strong inhibitors in increasing the thermal initiation of styrene polymerization.

Introduction

In 1952, Zimm and Bragg[1] published calculations, based on existing data, which showed inadequacies in the currently accepted mechanism for thermal initiation of styrene polymerization; *i.e.*, the view that two styrene molecules unite to form a diradical capable of adding monomer units at both ends.[2] In the course of subsequent attempts by other investigators to provide a more satisfactory mechanism, some disagreement has arisen over the kinetic order of this initiation reaction. The common belief that it was of second order in styrene, engendered by the work of Schulz,[3] and of Suess[4] was questioned by Mayo,[5] who found the thermal polymerization of styrene in bromobenzene best described by third-order initiation of chains. However, as later pointed out by Burnett and Loan,[6] Mayo, in his calculations, did not consider the kinetic significance of the extra termination reactions introduced by the presence of "solvent" radicals. These investigators derived a steady state equation for polymerization in a solvent allowing for three termination reactions and showed that the "apparent molecularity" in monomer of the over-all reaction could be substantially influenced by just such factors.

Since the work of Suess[4] and of Schulz[3] could be criticized equally well on this basis, it seemed desirable to obtain further information bearing on the kinetics of polymerization of styrene in a solvent with an efficient and well defined chain transfer reaction. The large numbers of "solvent" radicals produced should necessitate use of the Burnett–Loan equation to correlate the data, and there should result an unambiguous indication of the kinetic order of the thermal formation of radicals from styrene.

Choice of Reaction

The reaction of styrene with ethyl thioglycolate in the presence of chain initiators or oxidizing agents has received previous study. With the use of minute amounts of thiol, the chain transfer constant C_{tr} for reaction with the polystyryl radical was found to be 58 ± 4 at 60°.[7] Nearly equal quantities of the reactants produced only the 1:1 adduct,[8] ethyl β-phenylethylthioglycolate, by a chain reaction with the propagation sequence

$$\mathrm{EtO_2CCH_2S\cdot + CH_2{=}CHC_6H_5 \longrightarrow EtO_2CCH_2SCH_2\dot{C}HC_6H_5} \quad k_2 \quad (2)$$

$$\mathrm{EtO_2CCH_2SCH_2\dot{C}HC_6H_5 + EtO_2CCH_2SH \longrightarrow EtO_2CCH_2S\cdot + EtO_2CCH_2SCH_2CH_2C_6H_5} \quad k_3 \quad (3)$$

The normally competing polymerization reaction,

$$\mathrm{EtO_2CCH_2SCH_2\dot{C}HC_6H_5 + CH_2{=}CHC_6H_5 \longrightarrow EtO_2CCH_2SCH_2CH(C_6H_5)CH_2\dot{C}HC_6H_5} \quad k_4 \quad (4)$$

is predicted to be insignificant by the chain transfer constant of the mercaptan in styrene polymerization, although this value is probably not strictly identical with k_3/k_4.

In the absence of extraneous initiators, there is no reaction of styrene with ethyl thioglycolate at room temperature.[9] However, it was found that carefully purified and degassed styrene and ethyl thioglycolate underwent slow but reproducible reaction at 100°, the exclusive product of which was ethyl β-phenylethylthioglycolate. This was not unexpected since at least one mechanism for the production of free radicals, that prevalent in thermal styrene polymerization, must operate. Assuming this to be the only source of radicals, the reaction scheme is completed by five equations in addition to 2, 3 and 4.

$$n\mathrm{CH_2{=}CHC_6H_5 \longrightarrow 2\ radicals,\ R\cdot} \quad k_1 \quad (1)$$

$$\mathrm{R\cdot + EtO_2CCH_2SH \longrightarrow RH + EtO_2CCH_2S\cdot} \quad k_{1a} \quad (1a)$$

$$\mathrm{2\ EtO_2CCH_2SCH_2\dot{C}HC_6H_5 \longrightarrow (EtO_2CCH_2SCH_2CHC_6H_5)_2} \quad k_5 \quad (5)^{10}$$

$$\mathrm{EtO_2CCH_2SCH_2\dot{C}HC_6H_5 + EtO_2CCH_2S\cdot \longrightarrow EtO_2CCH_2SCH_2CH(C_6H_5)SCH_2CO_2Et} \quad k_6 \quad (6)^{10}$$

$$\mathrm{2\ EtO_2CCH_2S\cdot \longrightarrow (EtO_2CCH_2S)_2} \quad k_7 \quad (7)^{10}$$

If the kinetic chains are long, reaction 1a may be neglected in comparison to reaction 3. Then in the manner of Burnett and Loan, neglecting no termination reactions and assuming a steady state, a four parameter expression for the rate of disappearance of mercaptan is obtained. Here M is con-

$$\text{rate} = -\mathrm{d}S/\mathrm{d}t = k_3S\left[\frac{k_1M^n}{k_5 + k_6\dfrac{k_3}{k_2}\dfrac{S}{M} + k_7\left(\dfrac{k_3S}{k_2M}\right)^2}\right]^{1/2} \quad (8)$$

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(1) B. H. Zimm and J. K. Bragg, *J. Polymer Sci.*, **9**, 476 (1952).

(2) P. J. Flory, THIS JOURNAL, **59**, 241 (1937).

(3) G. V. Schulz, A. Dinglinger and E. Husemann, *Z. physik. Chem.*, **B43**, 385 (1939).

(4) H. Suess, K. Pilch and H. Rudorffer, *ibid.*, **A179**, 361 (1937); H. Suess, A. Springer, *ibid.*, **A181**, 81 (1937).

(5) F. R. Mayo, THIS JOURNAL, **75**, 6136 (1953).

(6) G. M. Burnett and L. D. Loan, *Trans. Faraday Soc.*, **51**, 214 (1955).

(7) R. A. Gregg, D. M. Alderman and F. R. Mayo, THIS JOURNAL, **70**, 3740 (1948).

(8) M. S. Kharasch, "Inst. intern. chim. Solvay 8e Conseil chim., Univ. Bruxelles, Mecanisme de l'oxydation, Rapp. et disc.," 1950, p. 177, as reported in *C. A.*, **47**, 3253 (1953).

(9) M. S. Kharasch, A. T. Read and F. R. Mayo, *Chemistry & Industry*, **57**, 752 (1938).

(10) The kinetics would be unaffected by the partial or total occurrence of termination by hydrogen transfer instead of coupling as indicated.

centration of monomer (styrene) and S is "solvent" (mercaptan) concentration.

The object of the investigation reported here was to measure rates of the thermal reaction of styrene with ethyl thiolglycolate over a sufficient range of concentrations to determine the parameters of equation 8, with especial regard to n. No solvent other than the reactants was used; the formation of a homogeneous, non-polymeric product offered the advantage over polymerization that rates could be measured over a considerable extent of reaction.[11]

Experimental

Purification of Materials and Preparation of Runs.—At first, considerable difficulty was experienced in obtaining reproducible rates. Very thorough degassing was the most obvious precaution, but fractional distillation of both reactants immediately prior to use, elimination of contact of distilled reactants with the atmosphere, and acid soaking of the reaction cells prior to use also appeared to be necessary.

Thioglycolic acid, Eastman Grade 2, was esterified by the method of Baker, *et al.*,[12] and the ester fractionally distilled at reduced pressure, the fraction used boiling at 55.6–56.1° at 15 mm. Just prior to a kinetic run, the mercaptan was redistilled at that pressure. A 15-ml. middle cut, boiling at 56.0°, was collected, frozen, and degassed at 10^{-5} mm. and distilled into one or more reaction vessels. Samples of this material showed 99.5–99.7% of the theoretical reducing power by iodine titration.

After being washed with dilute aqueous sodium hydroxide to remove *t*-butyl catechol, Dow N-99 styrene was distilled under reduced pressure through a 100-cm. Fenske packed column. A middle cut of 20–30 ml. was collected, frozen and degassed at 10^{-5} mm. The desired amount then was distilled into reaction vessels, on top of the frozen mercaptan.

The reaction vessel consisted of a bulb with a long sidearm to which were sealed a number of small tubes. After the reactants had been distilled in and frozen, the flask was again evacuated, then sealed and disconnected from the vacuum line. The reactants were warmed to room temperature, thoroughly mixed, and decanted into the sidearm, filling the ampoules, which were then sealed and removed from the superstructure. The set of ampoules was placed in a constant temperature bath regulated to ±0.01°, and covered to prevent entrance of light. Withdrawals were made periodically and the samples chilled in Dry Ice–acetone.

Certain of the runs were made with pre-reacted materials. In these the procedure was the same except that the reaction mixture was heated at 100° *in vacuo* for 12 hours and the unreacted materials then distilled into new reaction vessels for rate measurements.

Determination of Rates.—The extent of reaction in each ampoule was measured by iodine titration of a weighed aliquot in 90% acetic acid. Styrene present in the solution was found to have no effect on the mercaptan titer. In most of the runs, the initial styrene concentration was calculated by difference, and equal amounts of the two reactants were assumed to have reacted thereafter. In reactions where mercaptan was in large excess, and its concentration change during the run small, the styrene concentration was determined directly as well as by measurement of its ultraviolet absorption at 291.5 mμ, with the use of weighed aliquots diluted with 95% ethanol.

Owing to a noticeable volume decrease during reaction, it was necessary to apply a small correction to the values found by the above method to obtain molar concentrations. The densities of ethyl thioglycolate and ethyl β-phenylethylthioglycolate were found to be 1.0049 and 1.0205, respectively, at 100.9°, where most of the runs were made. With 0.8354 being assumed for the density of styrene (interpolated from published data[13]), it was found that volumes of the three-component mixtures were additive. Densities of reaction mixtures could thus be calculated from a knowledge of the molal concentrations of the constituents.

At temperatures other than 100.9°, similar corrections were made, with the assumption that the thermal density gradients of ethyl thioglycolate and ethyl β-phenylethylthioglycolate were equal to that of styrene.

From 7 to 23 points were taken per run, over a percentage of reaction varying from 10 to 99. Curves of mercaptan concentration *vs.* time were plotted, and the instantaneous rate at each point determined from the slope of the curve.

Product Study.—Approximately equal quantities of styrene and ethyl thioglycolate, purified and degassed as for a kinetic run, were heated *in vacuo* for 30 days at 60°. Vacuum distillation of the product through a 40-cm. metal spiral column gave 1.4 g. of styrene, 30° (6 mm.); 3.2 g. of ethyl thioglycolate, 35–39° (6 mm.) and 16.5 g. of a substance boiling at 125–129° (0.1 mm.). There was no pot residue, although with styrene in excess some telomers should of course be formed. The high boiling material was hydrolyzed to an acid which on sublimation gave white needles, melting at 58–59°. Authentic ethyl β-phenylethylthioglycolate was prepared by reaction of styrene with ethyl thioglycolate induced by benzoyl peroxide. The infrared spectrum was identical with that of the oil obtained from the thermal reaction. Hydrolysis gave an acid which melted at 58–60° (lit. 56–58°[14]) and gave no depression on mixed melting point with the acid from thermal reaction.

Results

In all, 15 kinetic runs were carried out, two at 80.0°, one at 140.0° and 12 at 100.9°, in the course of which the measured ratio of mercaptan to styrene varied from 0.08 to 250. Typical reaction curves are shown in Fig. 1. In many of the runs small induction periods were noted, comparable to those observed by Goldfinger and Lauterbach[15] for the thermal polymerization of styrene. In accord with their findings prereaction of the materials effectively eliminated the initial slow reaction, but the rates obtained did not differ appreciably from the post-induction rates of the non-prereacted runs (Fig. 2.)

At the outset it was necessary to know whether free radicals were being produced from styrene–styrene interactions alone, since a contribution by mercaptan seemed plausible by the following reaction or a variant. Of the two runs made at 80°

$$\mathrm{EtO_2CCH_2SH + CH_2{=}CHC_6H_5 \longrightarrow EtO_2CCH_2S\cdot + CH_3\dot{C}HC_6H_5} \quad (9)$$

one was induced by 2.0×10^{-3} molar 2,2′-azobisisobutyronitrile. Use of this compound, whose rate of decomposition and efficiency of chain initiation in mercaptan solutions has been measured,[16] permitted calculation of $-\mathrm{d}S/\mathrm{d}t(V_i^{1/2}S)^{-1}$ for each point of the run. Examination of Table I shows that this value is a constant, equal by equation 8 to $k_3(k_5 + k_6k_3/k_2 + k_7k_3^2/k_2^2)^{-1/2}$, (since S/M is approximately unity throughout the reaction).

The kinetic chain length in this run, determined as moles of mercaptan used per mole of initiator decomposed, was equal to 660. Transferring of the average value of $-\mathrm{d}S/\mathrm{d}t(V_i^{1/2}S)^{-1}$ to the thermal reaction enables one to calculate rate of initiation of chains there (Table II). The rate of

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(11) This amounts, of course, to running the reaction in a constantly changing medium. However, the property of a solvent which is most important in the present problem is its chain transfer constant. The assumption is made that in this respect the product is inert in comparison with ethyl thioglycolate, as is the case with polystyrene.

(12) B. R. Baker, M. V. Querry, S. R. Safir and S. Bernstein, *J. Org. Chem.*, **12**, 138 (1947).

(13) R. H. Boundy and R. F. Boyer, "Styrene, Its Polymers, Copolymers, and Derivatives," Reinhold Publishing Corp., Baltimore, Md., 1952, p. 55.

(14) B. Holmberg, *J. prakt. Chem.*, **141**, 93 (1934).

(15) G. Goldfinger and K. E. Lauterbach, *J. Polymer Sci.*, **3**, 145 (1948).

(16) G. S. Hammond, J. N. Sen and C. E. Boozer, THIS JOURNAL, **77**, 3244 (1955).

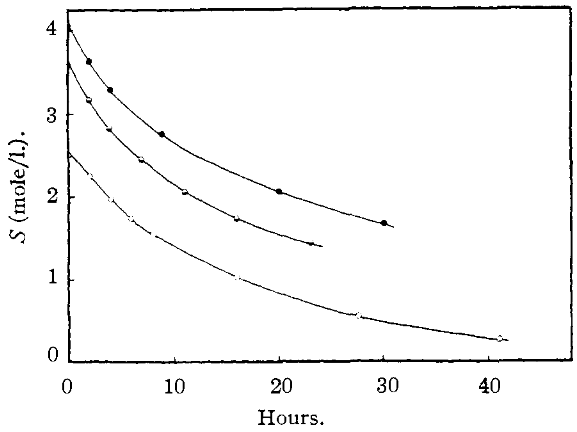

Fig. 1.—Thermal reaction of styrene with ethyl thioglycolate at 100.9°; typical sealed tube runs showing variation of mercaptan concentration with time: ◒, run 10-B; O, run 11-B; ●, run 12-B.

thermal initiation of styrene polymerization at 80° may be calculated from Mayo's "k_{3i}" to be 4.4×10^{-6} mole./l.hr.[5] and from the computations of Russell and Tobolsky[17] to be 5.4×10^{-6} mole./l.hr.

TABLE I

THE REACTION OF STYRENE WITH ETHYL THIOGLYCOLATE AT 80°, INDUCED BY 2,2'-AZOBIS-ISOBUTYRONITRILE; RUN 9

Time, min.	S, moles/l.	M, moles/l.	$V = -ds/dt$, moles/l. hr.	$V/V_i^{1/2}S$,[a] moles, l., hr.
0	3.74	4.62	1.75	9.2
10	3.44	4.33	1.56	9.4
20	3.23	4.13	1.34	9.0
30	2.99	3.89	1.20	9.4
40	2.76	3.76	1.07	9.4
50	2.66	3.56	0.97	9.4
60	2.47	3.39	.89	9.8
70	2.34	3.26	.78	9.6
82	2.15	3.07	.72	9.9
92	2.04	2.97	.65	10.1
110	1.87	2.80	.56	10.6
			Av.	9.6 ± 0.3

[a] $V = dS/dt$, $V_i = 3.6 \times 10^{-4} A_0 \exp(-1.8 \times 10^{-4} t)$, t = time in sec. and A_0, initial concn. of azo compound = 2.0×10^{-3} molar; V determined graphically.

TABLE II

ESTIMATION OF THERMAL INITIATION RATE FOR THE REACTION OF STYRENE WITH ETHYL THIOGLYCOLATE AT 80°

Time, hr.	S, moles/l.	M, moles/l.	V, mole/l. hr.	V_i found = $(V/9.6\ S)^2$ $\times 10^7$ moles/l. hr.	Calcd. $V_{i,3}$ $\times 10^7$[a] moles/l. hr.	Calcd. $V_{i,2}$ $\times 10^7$[b] moles/l. hr.
0	3.70	4.66				
18	3.50	4.46	0.0244	5.3	7.0	15.9
43	3.00	3.96	.0188	4.3	4.9	12.5
67	2.58	3.54	.0135	3.0	3.6	10.1
91	2.31	3.27	.0099	2.0	2.7	8.5
139	1.84	2.80	.0071	1.6	1.8	6.3

[a] Using Mayo's k_{3i}. [b] Using Mayo value for pure styrene but assuming second-order initiation.

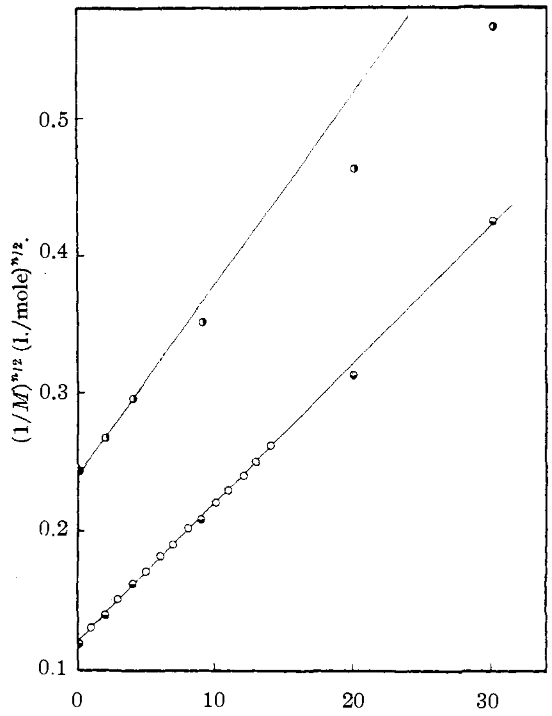

Fig. 2.—Thermal reaction of styrene with ethyl thioglycolate at 100.9°; initial concentrations of reactants equal; runs 12-B and 15-A plotted for the equation: $1/S^{n/2} = 1/M^{n/2} = (n/2A)t$; ◑, run 12-B, n = 2; ◒, run 12-B, $n = 3$; O, run 15-A, $n = 3$. Components in run 12-B were purified by pre-reaction.

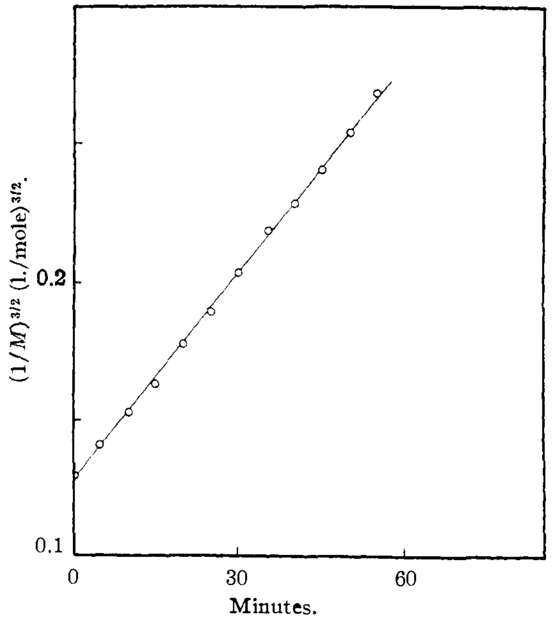

Fig. 3.—Thermal reaction of styrene with ethyl thioglycolate at 140.0°; initial concentrations of reactants equal; run 15-B plotted for the equation: $1/S^{3/2} = 1/M^{3/2} = (3/2A)t$.

By regarding the ethyl thioglycolate and the product ester as inert diluents, we can calculate the rate of thermal initiation due to this same mechanism in our reaction, assuming on the one hand bimolecular and on the other termolecular initiation. The initiation of mercaptan addition

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(17) K. E. Russell and A. V. Tobolsky, THIS JOURNAL, **76**, 395 (1954).

cannot in any case be *slower* than this generation of radicals from the styrene present. It might, of course, be faster if there is another initiation mechanism superimposed.

In Table II are listed the initiation rates at different times in run 8, as determined by applying the factor $V/V_i^{1/2}S$ = 9.6 mole$^{-1/2}$ l.$^{-1/2}$ hr.$^{-1/2}$ from Table I. For comparison are listed the rates of thermal initiation to be expected from styrene alone, according to Mayo,[5] first with the assumption of termolecular, then of bimolecular initiation. It appears that the rates predicted on the assumption of bimolecular initiation are greater than correspond to the experimental facts, and cannot be correct. The rates of third-order initiation are on the average only 20% greater than those deduced from experiment and would appear to be based on the correct assumption. In any case there is no other important chain initiation for the mercaptan addition beside that which it has in common with the polymerization of styrene.[18]

An independent test for the molecularity of the initiation is gained from the runs where initial concentrations of styrene and mercaptan were the same. In these circumstances equation 8 may be integrated to give

$$1/S^{n/2} = At, \text{ where } A \text{ is simply a constant}$$

Figures 2 and 3, with three runs, two at 100.9° and one at 140° plotted for $1/S^{n/2}$, *vs.* t both for $n = 2$ and $n = 3$, offers a convincing demonstration that termolecular initiation does indeed obtain.

It was found subsequently that, within experimental error, runs with initial S/M ratios from 0.44 to 1.64 and final S/M ratios from 0.08 to 2.47 were satisfied throughout their measured length by the expression $-\mathrm{d}S/\mathrm{d}t = AM^{3/2}S$. The spread of concentrations and ratios of S/M was considered wide enough to exclude any correlation of the rates with $MS^{3/2}$ or with $M^{1/2}S^2$ (expected results if one or two thiol molecules, respectively, participated in a termolecular initiation).

The runs carried out at 100.9° are listed in Table III, each with its average value of A and its internal average deviation.

TABLE III

AVERAGE VALUES OF $-\mathrm{d}S/\mathrm{d}t/M^{3/2}S$ FOR THE REACTION OF STYRENE WITH ETHYL THIOGLYCOLATE AT 100.9°

Run	S/M Initial	S/M Final	$-100\mathrm{d}S/\mathrm{d}t/M^{3/2}S = 100A$
10-A	0.82	0.68	0.60 ± 0.06
10-B	.77	.58	.68 ± .03
11-A	.55	.20	.61 ± .07
11-B	.44	.08	.59 ± .07
12-B	.97	.93	.70 ± .04
13	1.08	1.16	.60 ± .03
14	1.05	1.08	.65 ± .02
15-A	1.00	1.00	.65 ± .03
16-A	1.64	2.47	.64 ± .04
		Av.	0.64 ± 0.04

Mode of Chain Termination.—In the polymerization of styrene in the absence of solvent the only important mode of chain termination is the union of two polystyrene radicals in the process corresponding to k_5 in the present scheme. The figures in Table III, interpreted in the light of equation 8, show that the interaction of two styrene-type radicals, with the rate constant k_5, must be the dominant if not the only mode of chain termination also in the styrene–mercaptan addition reaction. If either of the other modes of chain termination were dominant, the value of "A" must vary by two- or threefold as the ratio S/M changed through such a range. The most probable reason for the dominance of the coupling of styrene radicals with each other is that reaction 2, in which a thiyl radical attacks styrene, must be much faster than reaction 3, in which the styrene radical attacks mercaptan, even though this latter reaction is in turn much faster than the attack of a styrene radical upon styrene. Thus the greater population of styrene-type radicals ensures their interaction with one another to the virtual exclusion of modes of termination involving thiyl radicals.

Table IV consists of the runs at very low styrene concentration, where rates of reaction were uniformly higher than predicted for termolecular (or bimolecular) initiation. In runs 16C and D, where the thiol concentration was essentially constant throughout, the rate varied linearly with $M^{1/2}$. It would appear that this is the result not only of the change in initiation mechanism mentioned above, but also of change in the dominant mode of termination. In terms of equation 8, k_5 is now smaller than k_6k_3S/k_2M. From the value of S/M where reaction 6 becomes prominent, the ratio of k_5 to k_6k_3/k_2 may be estimated to be about 10.

TABLE IV

EXPERIMENTS AT HIGH MERCAPTAN/STYRENE RATIO

Run	S/M Initial	S/M Final	$-100\ \mathrm{d}S/\mathrm{d}t/M^{3/2}S$ Initial	$-100\ \mathrm{d}S/\mathrm{d}t/M^{3/2}S$ Final
16-B	4.63	12.7	0.75	3.68
16-C	9.4	167	1.41	29.1
16-D	12.4	250	1.67	33.2

Discussion

It has been shown that the rate of disappearance of mercaptan in heated solutions of ethyl thioglycolate and styrene is proportional to $M^{3/2}S$ over a wide range of reactant concentrations (S/M 0.08–2.49). Taken alone, this indicates only that initiation of chains is termolecular, the molecular species involved being dependent on which *one* of possible termination reactions is predominant. It is the close coincidence of the measured rate of initiation of chains with that calculated from thermal polymerization data for termolecular reaction of styrene monomer that eliminates from consideration radical formation involving mercaptan, and establishes the mode of termination as reaction of two carbon radicals, and the mechanism of initiation as reaction of three molecules of styrene.

In the light of these conclusions, corroborating those of Mayo, the objections of Burnett and Loan must be re-examined. Apparently termination reactions involving "solvent" radicals are important neither in the bromobenzene–styrene system, the

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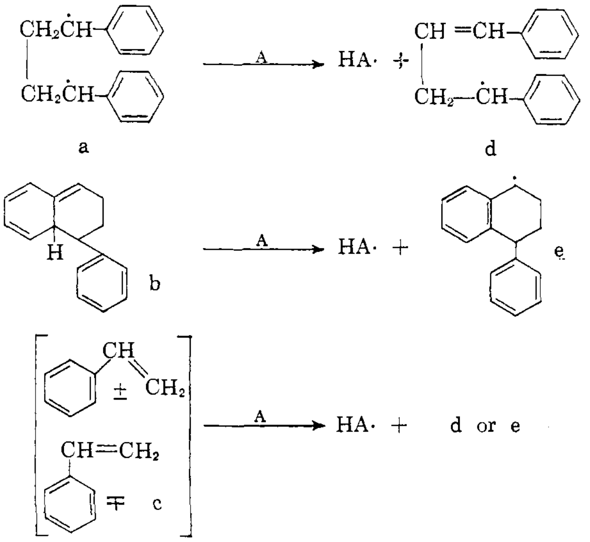
[18] An exception to this statement appears to be provided by the runs in which the styrene concentration is very low and that of mercaptan is very high. This special case is discussed later in this paper.

ethyl thioglycolate–styrene system,[19] nor, according to Sivertz, *et al.*,[20a,b] in the system *n*-butyl mercaptan–styrene.

This simplicity of termination probably does not arise from a k_5 significantly larger than k_6 or k_7, cross-termination in general being favored, but from the relative stability, derived from its benzyl-type resonance, of the styrene-type radical. Even with as potent a hydrogen atom donor as ethyl thioglycolate, the reaction to destroy styrene-type radicals (run 3) is much less favorable than the reaction creating them (run 2). Sivertz has shown that for *n*-butyl mercaptan with styrene the ratio k_3/k_2 is less than 1/100. Qualitative changes in this ratio can be predicted from consideration of chain transfer constants; for ethyl thioglycolate it should be somewhat larger than 1/100, for bromobenzene, considerably smaller.

The third-order initiation which the thermal mercaptan addition has in common with the thermal polymerization of styrene can be formulated in several ways. If a third-order reaction proceeds at a measurable rate despite a substantial activation energy, this is likely to be due to the existence of a reversibly formed association product of two of the three reacting molecules, equivalent to greatly prolonged binary collisions and an increased frequency of the ternary collisions on which reaction depends. The binary association product in the case of styrene might be (a) the classical Flory diradical, with the provisos that it attains equilibrium with styrene and that it can readily donate, but not accept, a hydrogen atom; (b) an addition product of Diels–Alder type in equilibrium with two styrene molecules[21]; (c) a charge transfer complex reversibly formed preliminary to the formation of a or b. Any of these species might react with a hydrogen atom acceptor (styrene in this case) to yield the monoradical d or e, together with the hydrogen transfer product HA·(α-phenylethyl radical). Although this behavior is possible for the diradical a, a species so constituted would be expected to be able to accept hydrogen as well as to donate it; the formulations b and c are therefore to be preferred for a species with the properties here required. There are other distyrene monoradicals which might be postulated (compare ref. 5), but both d and e have the advantage of being simply formed and of having an energy close to that of the chain carriers in the addition and polymerization reactions.



It now becomes possible to discuss the discrepancies observed at low styrene concentration. As styrene concentration decreases, initiation based on its concentration cubed dwindles rapidly, so that at [M] = 0.5 molar it becomes insignificant compared to another mode of initiation, unnoticeable at higher styrene concentrations. The rate dependence on $M^{1/2}$ under these conditions allows at least two interpretations. Hydrogen atom donation by ethyl thioglycolate to styrene could be the source of a small number of free radicals, according to equation 9 above. Here $-\mathrm{d}S/\mathrm{d}t$ should equal $M^{1/2}S^{1/2}$, the dependence on S being masked by its invariance over the course of the run.

It seems likely, however, that at very high ratios of thiol to styrene, the cross-termination reaction would become perceptible and even dominating. The $M^{1/2}$ in the numerator of the rate expression would then be provided by the term $k_6k_3/k(S/M)$ of equation 8, and initiation must necessarily be styrene independent. Free radicals might arise from thermal dissociation of small amounts of diethyl dithiodiglycolate, formed in the ethyl thioglycolate before degassing had been completed. If the mercaptan is assumed to contain 0.4% disulfide, (its average deviation from total purity as determined by iodine titration), a dissociation with a half-life of three years would be sufficient to account for the amount of radical formation observed.

The termolecular character of the thermal initiation step in styrene polymerization has several implications for the behavior of styrene-containing systems which have been investigated. In thermal copolymerization[22,23] the initiation due to styrene alone must be less than is assumed on the basis of second-order initiation. The cross initiation is therefore greater than previously calculated. If cross initiation is also of the third order, the polar differences between two monomers may favor cross initiation in at least two ways. The unsymmetrical counterpart of the complex I may be favored by a more pronounced donor–acceptor difference between the partners; and the actual hydrogen atom transfer may be to that member of the copolymerizing pair which is the better atom acceptor.

The facts presented in Table V are also suggestive. In at least six cases it has been possible

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[19] It is possible that a small and undetected amount of two-to-one product was formed, neglect of which could contribute to the simplicity of the rate expression. The data are being recalculated by computer techniques to ascertain the magnitude of such errors. It appears unlikely that this could result in gross changes in the conclusions reached here.

[20] (a) R. Back, G. Trick, C. McDonald and C. Sivertz, *Can. J. Chem.*, **32**, 1078 (1954); (b) M. Onyszchuck and C. Sivertz, *ibid.*, **33**, 1034 (1955).

[21] This suggestion has been made by F. R. Mayo (private communication). He has found both 1-phenyltetralin and 1,2-diphenylcyclobutane among several other dimers in inhibited polymerizations of styrene.

[22] C. Walling, THIS JOURNAL, **71**, 1930 (1949).

[23] C. Walling, "Free Radicals in Solution" John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 184, 195.

to compare either directly the rate of chain initiation or at least the rate of inhibitor disappearance in a styrene solution of a strong polymerization inhibitor, with the rate of thermal initiation of chains in the absence of inhibitor. In every case there appears to be greatly increased thermal chain initiation in the presence of the inhibitor. The explanation of this increased rate of initiation cannot be the same in all cases. For example, the fast initiation by iodine is known to lead to β-iodo-α-phenylethyl radicals,[24–26] while a similar first radical in the case of sulfur does not seem reconcilable with the quantitative study of the products.[27] There is enough quantitative divergence indicated in the third column of Table V to indicate that if interception of diradicals is the explanation in one case (Ref. *a*, Table V) it is not so in all cases. However, it can be seen that all these inhibitors are excellent hydrogen-atom acceptors, and in the absence of a still easier mechanism these substances might be able to take the place of the third styrene molecule in the initiation process. A number of these inhibitors have been used successfully to determine the rate of chain initiation by peroxides and azo compounds, but they are inherently and probably quite generally unsuitable for the counting of thermally initiated chains because of their possible participation in the initiation process.

TABLE V

"INITIATION" BY STRONG INHIBITORS IN THE POLYMERIZATION OF STYRENE

Inhibitor Z	Temp., °C.	$-d(Z)/dt$ R_i	Ref.
DPPH	60	85	[a]
Benzoquinone	60	61	
	100	21	[a,b]
Sulfur	80.9	22	[c]
Oxygen	50	38[g]	[d,f]
Iodine	25	$\sim 10^5$	[e]

[a] K. E. Russell and A. V. Tobolsky, THIS JOURNAL, **75**, 5052 (1953). [b] J. W. and H. L. Breitenbach, *Z. physik. Chem.*, **A190**, 361 (1942). [c] P. D. Bartlett and D. S. Trifan, *J. Polymer Sci.*, **20**, 472 (1956). [d] A. A. Miller and F. R. Mayo, **78**, 1017 (1956). [e] G. Fraenkel, Thesis, Harvard Univ., 1957. [f] F. R. Mayo and R. A. Gregg, THIS JOURNAL, **70**, 1284 (1948). [g] This figure represents the relative rates of thermal *initiation* with and without oxygen, estimated directly by comparison of rates of polymerization and oxidation in the presence and absence of AIBN.

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[24] D. S. Trifan, Thesis, Harvard University, 1949.

[25] G. Fraenkel, Thesis, Harvard University, 1957.

[26] P. D. Bartlett and G. Fraenkel, forthcoming publication.

[27] P. D. Bartlett and D. S. Trifan, *J. Polymer Sci.*, **20**, 472 (1956).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Formation and Certain Condensations of the Dicarbanions of Dibenzyl Ketone and Dibenzyl Sulfone by Means of Potassium Amide in Liquid Ammonia[1,2]

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Both the α- and α′-hydrogens of dibenzyl ketone were ionized by means of two molecular equivalents of potassium amide in liquid ammonia to form a red dicarbanion. This dicarbanion underwent exclusive monobenzylation with one equivalent of benzyl chloride and dibenzylation, with two equivalents of this halide. It underwent almost quantitative conjugate addition to ethyl cinnamate. The monocarbanion of dibenzyl ketone gave a mixture of products with an equivalent of benzyl chloride and failed to react with ethyl cinnamate under the conditions used with the dicarbanion. Both the α- and α′-hydrogens of dibenzyl sulfone were ionized by means of two equivalents of potassium amide in liquid ammonia to form a pale yellow dicarbanion. This dicarbanion underwent monobenzylation with one equivalent of benzyl chloride and dibenzylation, with two equivalents of this halide. The mono- and dibenzylation products underwent β-elimination reactions with excess potassium amide in ether to form stilbene. The monocarbanion of dibenzyl sulfone gave a mixture of products with an equivalent of benzyl chloride.

It is well known that sodium amide or potassium amide can effect the essentially complete ionization of an α-hydrogen of a ketone[4,5] or of a sulfone such as benzylmethyl[6] or dibenzyl[7] sulfone to form the corresponding sodio or potassio derivatives, which can be alkylated with alkyl halides or condensed with other reagents.

It now has been found that potassium amide in liquid ammonia can effect the ionization of not only an α-hydrogen but also an α′-hydrogen of dibenzyl ketone and dibenzyl sulfone to form the corresponding dipotassio derivatives, which can be mono- or dialkylated or condensed with certain other reagents.[8]

Results with Dibenzyl Ketone.—The twofold ionization of the α- and α′-hydrogens of this ketone was indicated by adding a solution of two molecular equivalents of potassium amide in liquid am-

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[2] Reported before the Southeastern Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14–16, 1957, and the 133rd Meeting of the American Chemical Society in San Francisco, Cal., April 13–18, 1958.

[3] National Science Foundation Predoctoral Fellow, 1956–1958.

[4] See E. E. Royals, "Advanced Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., pp. 829–931, 1954.

[5] See C. R. Hauser, F. W. Swamer and J. T. Adams, "Organic Reactions," Vol. VIII, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 63.

[6] J. Buchi, M. Prost, H. Eichenberger and R. Lieberherr, *Helv. Chim. Acta*, **35**, 1527 (1952).

[7] J. de Pascual Teresa and H. Sanchez, Bellido, *Anales real soc. espan. fis. y quim.* (*Madrid*), **50B**, 71 (1954).

[8] A preliminary communication was made by C. R. Hauser and T. M. Harris, THIS JOURNAL, **79**, 6342 (1957).