Measurements were made at 300, 310 and 320 mμ. The average value for the equilibrium constant was 0.08 ± 0.08 where the standard deviation is the measure of the precision.

Complexes of this sort between an olefin and bromine would certainly be expected on the basis of recent work[18] on the 1:1 complexes of halogens acting as electron acceptors with various types of electron donors including olefinic compounds.[19] Ionization of some donor–acceptor halogen complexes also had been observed,[20] but as it has already been pointed out[2a] ionization of olefin–bromine complex is not necessary to explain most of the kinetic results obtained for bromine addition. In fact, in the present work the evidence shows that ionization is not a necessary step if the bromine–crotonic acid complex is an intermediate in the bromine addition in the presence of tribromide.

[18] See footnote 8, and R. S. Mulliken, THIS JOURNAL, **72**, 600 (1950); **74**, 811 (1952), for references.

[19] (a) R. J. Keefer and L. J. Andrews, *ibid.*, **74**, 1891 (1952); (b) S. Freed and K. M. Sancier, *ibid.*, **74**, 1273 (1952).

[20] (a) L. F. Audrieth and E. J. Birr, *ibid.*, **55**, 668 (1933); (b) R. A. Zingaro, C. A. VanderWerf and J. Kleinberg, *ibid.*, **73**, 88 (1951); (c) R. E. Buckles and N. A. Meinhardt, *ibid.*, **74**, 1171 (1952).

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Thermal Initiation of Styrene Polymerization

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When styrene polymerization is initiated by moderate concentrations of active monoradical-producing catalysts, the rate of initiation of polymer chains can be measured by the rate of consumption of the inhibitors, 2,2-diphenylpicrylhydrazyl and benzoquinone. However, the rate of consumption of these inhibitors during *thermal* polymerization of highly purified styrene is very much greater than the rate of initiation of polymer chains. It is suggested that diradicals are formed at a rapid rate in the thermal polymerization of styrene and that a high proportion, perhaps all, of these diradicals undergo self-termination to form small rings. While the rate of production of diradicals is very much greater than the rate of initiation of polymer chains, the actual weight fraction of the rings formed should be very small. A relation between the production of diradicals and the formation of high molecular weight polymer has not been established.

The relationship[1]

$$R_p^2 - R_{p,th}^2 = \frac{k_p^2[M]^2}{2k_t} R_i = 3 \times 10^{-2} R_i \qquad (1)$$

holds for the polymerization of styrene in bulk at 60°, initiated by monoradical-producing catalysts such as benzoyl peroxide and 2-azobisisobutyronitrile. In equation 1 R_p is the total rate of polymerization at 60°, $R_{p,th}$ is the rate of thermal polymerization and R_i is the rate of initiation of the polymer chains which started frrom catalyst fragments. The quantities k_p and $2k_t$ are the specific rate constants for propagation and termination, respectively, and [M] is the monomer concentration.[1] In this paper concentrations are expressed in moles/liter and time in seconds.

For moderate concentrations of active monoradical-producing initiators, the second term on the left-hand side of (1) can be neglected, giving

$$R_p^2 = 3 \times 10^{-2} R_i \qquad (2)$$

The constant in equation 2 has been determined by experimental measurements of R_p and R_i. The measurement of R_i was carried out by three independent methods, the results of which were all in close agreement.[1] The best value of the constant in equation 1 was evaluated from data from various sources.[2,3] It is highly improbable that the numerical value 3×10^{-2} is in error by more than 50%.

One of the most successful methods for measuring R_i in monoradical-initiated polymerization involves the use of the inhibitor 2,2-diphenylpicrylhydrazyl.[1,4,5] In the presence of this substance, there is an induction period in the polymerization during which the inhibitor is consumed. The rate of consumption of inhibitor R_{DPPH} is taken to be equal to the rate of initiation R_i which prevails with inhibitor absent. It is assumed that one molecule of inhibitor stops one radical chain. This assumption has been proved for the case where the initiation occurs *via* a fragment from an active monoradical-producing catalyst, by comparison of R_{DPPH} with R_i determined by two independent methods.[1]

If thermal polymerization proceeds with the same mechanisms of propagation and termination as does polymerization initiated by monoradical-producing catalysts, the following equation should apply

$$R_{p,th}^2 = 3 \times 10^{-2} R_{i,th} \qquad (3)$$

where $R_{i,th}$ represents the rate of initiation of growing polymer radicals produced thermally (a growing polymer diradical, if present, is considered as two growing polymer radicals). Equation 3 may be regarded as a definition of $R_{i,th}$ at 60°. $R_{p,th}$ at 60° has the value 2.0×10^{-6} mole/liter/sec.[6] so that $R_{i,th} = 1.3 \times 10^{-10}$ mole/liter/sec.

It is interesting to compare the value of $R_{i,th}$ defined by equation 3 with some other measured value of the rate of thermal initiation. To this end we determined R_{DPPH} in pure styrene at 60°. We found R_{DPPH} to be 1.1×10^{-8} mole/liter/sec. and

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[1] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951); *ibid.*, **71**, 497, 2610 (1949).

[2] D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952).

[3] A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, in press.

[4] P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).

[5] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

[6] F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

the rate was almost independent of the concentration of DPPH. In other words, the rate of initiation of radicals in pure styrene as measured by R_{DPPH} is some 85 times greater than $R_{i,th}$ derived from polymerization rate measurements and equation 3. From two experiments with styrene in benzene solution, it was concluded that the reaction is second order with respect to styrene.

Similar results are obtained when benzoquinone is used as an inhibitor in place of DPPH; this can be inferred from results given in the literature[7,8] and from our own measurements.

At 100° the monoradical relationship[3]

$$R_p^2 = 2.45 \times 10^{-1} R_i \qquad (4)$$

when applied to thermal polymerization leads to the result $R_{i,th} = 1.3 \times 10^{-8}$ mole/liter/sec. The rate of disappearance of benzoquinone in pure styrene at 100° is $R_{BZQ} = 2.7 \times 10^{-7}$ mole/liter/sec.[7] At 60°, $R_{BZQ} = 7.9 \times 10^{-9}$ mole/liter/sec.[7] for pure styrene, and this compares with $R_{i,th} = 1.3 \times 10^{-10}$ mole/liter/sec. (The results of Goldfinger, Skeist and Mark[8] extrapolated to 60° differ slightly from those quoted here, but this does not affect the general argument.) The conclusion is reached that both at 100 and 60°, benzoquinone is used up at a far greater rate than would be predicted from the rate of thermal polymerization; $R_{BZQ}/R_{i,th} = 21$ at 100° and $R_{BZQ}/R_{i,th} = 61$ at 60°.

On the other hand, when polymerization is initiated by monoradical-producing catalysts, the ratio R_{BZQ}/R_i is nearly unity. Measurements have been made on styrene at 60° containing 0.0444 mole/liter of benzoyl peroxide. In the absence of inhibitor this catalyst concentration produces an R_p value of 7.35×10^{-5}.[2] From equation 2 a value of $R_i = 1.8 \times 10^{-7}$ is obtained. The measured value of R_{BZQ} is 1.5×10^{-7}, obtained from an induction period of 4.5 hours when 0.00242 mole/liter of benzoquinone is present. While the induction period may not give an exact measure of the rate of consumption of benzoquinone, it is improbable that R_{BZQ} exceeds 3×10^{-7} mole/liter/sec. Thus the values of R_i and R_{BZQ} are approximately equal in the benzoyl peroxide-catalyzed polymerization of styrene in striking contrast with the case of thermal polymerization when $R_{BZQ}/R_{i,th} = 61$ at 60°. Our experimental results for benzoyl peroxide-catalyzed polymerization of styrene inhibited by quinone are in very close agreement with those of Cohen who made a more thorough study of the problem.[9] His conclusion was that one molecule of quinone is consumed for each molecule of benzoyl peroxide decomposed during the induction period; this is clearly quite similar to our conclusion since the effect of induced decomposition is small.[6] The problem was also studied by Melville at much lower levels of peroxide and quinone.[10] In this range Melville contends that benzoquinone acts more like a retarder than an inhibitor. For vinyl acetate polymerization initiated by monoradical-producing catalysts Matheson uses benzoquinone as a means of counting radical chains in the same way as DPPH is used.[1] His conclusion that each molecule of quinone counts one growing chain is in agreement with our result concerning the approximate equality of R_i and R_{BZQ} for styrene polymerization initiated by monoradical-producing catalysts.

The discrepancy between $R_{i,th}$ and R_{BZQ} at 100° has already been noted by Bartlett, *et al.*,[11] and by Mayo, *et al.*[12] Bartlett suggested that the radical formed when benzoquinone attacks a growing polymer radical might be capable of further reaction with monomer at 100°. Because of the relatively high activation energy of this process, he stated that such an effect could not be so marked at temperatures in the neighborhood of 60°. It has been shown here that the effect exists for thermal polymerization at 60 and 100°. Mayo put forward a reaction mechanism which assumed that a reactive quinone intermediate was formed either by chain transfer of a growing radical with a quinone molecule or by the addition of quinone to the chain. This is in agreement with the fact that many molecules of quinone are used up per *growing* polymer chain suppressed in thermal polymerization, but fails to explain why only one quinone molecule (approximately) is used up per growing polymer chain suppressed in monoradical-catalyzed polymerization.

It is clear that the results for R_{BZQ} and R_{DPPH} during thermal polymerization of styrene require an explanation not yet offered in the literature. One possible explanation of the fact that the rate of production of radicals as measured by DPPH or benzoquinone is far greater than the rate of initiation of long polymer chains is that the disappearance of these substances (*e.g.*, DPPH) is due to a direct reaction between DPPH and styrene. However, we find that the rate of DPPH disappearance is nearly zero order with respect to DPPH between concentrations of 3.6×10^{-4} and 1.2×10^{-4} mole/liter, and falls off only slightly below the latter concentration. This evidence argues against a simple direct attack of DPPH on molecular styrene.

A second possibility is that the reaction is affected by small amounts of oxygen. DPPH reacts very rapidly with styrene in the presence of oxygen, and the rates recorded here may be due to the presence of minute traces of dissolved gas. However, the great care taken in degassing the styrene and the excellent reproducibility of the results with different samples of styrene militate against such an explanation.

It has long been held that the initiation of thermal polymerization involves the production of diradicals.[13] We present here a tentative explanation of our results in terms of the reactions of diradicals. A minimum value for the rate of production of diradicals is given by $^1/_2 R_{DPPH}$ or $^1/_2 R_{BZQ}$. In the absence of inhibitors a high proportion, perhaps all, of the diradicals undergo self-termination to form small rings. Zimm and Bragg[14] have sug-

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[7] J. W. Breitenbach and H. L. Breitenbach, *Z. physik. Chem.*, **A190**, 361 (1942).

[8] G. Goldfinger, I. Skeist and H. Mark, *J. Phys. Chem.*, **47**, 578 (1943).

[9] S. G. Cohen, THIS JOURNAL, **69**, 1057 (1947).

[10] H. W. Melville and W. F. Watson, *Trans. Faraday Soc.*, **44**, 886 (1948).

[11] P. D. Bartlett, G. S. Hammond and H. Kwart, *Discs. Faraday Soc.*, **2**, 342 (1947).

[12] F. R. Mayo and R. A. Gregg, THIS JOURNAL, **70**, 1284 (1948).

[13] P. J. Flory, *ibid.*, **59**, 241 (1937).

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

gested that the long chain polymers which are formed in the thermal polymerization of styrene arise by chain transfer of a growing diradical to monomer before ring closure occurs, the monoradicals then growing in the normal way. Their calculations show that, on this mechanism, less than 0.1% of the diradicals originally formed are converted to long chain polymer molecules, and that 29% of the monomer is converted to low molecular weight rings. This latter result is in conflict with experimental evidence.

We have not demonstrated that the disappearance of DPPH (or benzoquinone) in styrene, even if a measure of the rate of production of diradicals, is related in any way to the production of thermal polymer. One can nevertheless estimate the weight fraction of ring compared to total polymer if it is assumed that DPPH can react with all the thermally produced diradicals before they have a chance to undergo any ring closure. In this case the weight fraction of rings $W(r)$ at 60° would be

$$W(r) = \frac{{}^1/_2 R_{\mathrm{DPPH}} x}{R_{\mathrm{p}}} = 2.8 \times 10^{-3} x \qquad (5)$$

where x is the average size of the rings. If an ***upper*** limit of 10 be assigned to x,[14] it is clear that the actual weight fraction of rings should be small.

It is of interest to note that R_{DPPH} for thermal polymerization of styrene has an estimated activation energy of 21 kcal./mole as obtained from measurements at 50, 60 and 75°. This compares with an activation energy for R_{BZQ} of 22 kcal./mole derived from the work of Breitenbach,[7] and 28 kcal./mole obtained by Foord.[15]

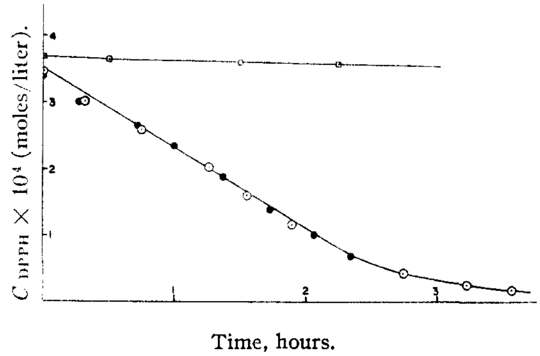

Fig. 1.—Disappearance of DPPH in styrene at 75°: ○, first sample of styrene; ●, second sample of styrene; □, blank run with benzene at 75°.

Experimental

Dow styrene N99 was distilled at a pressure of 18 mm. in an atmosphere of nitrogen. It was transferred to a vacuum apparatus, degassed three times and twice distilled. The reaction tubes were pumped out at a pressure of 10^{-4} mm. and filled with styrene by vacuum distillation. The concentration of DPPH was followed by means of a Fisher electrophotometer using a red filter (650 mμ). In a second series of experiments the styrene was subjected to fractional crystallization and an extra vacuum distillation in addition to the treatment described above. With both samples of styrene the rates of thermal polymerization at 60° were in the range 0.0068–0.0070 mole/liter/hour.

Typical results for the disappearance of DPPH in pure styrene are shown in Fig. 1, where the concentration of DPPH is plotted against time for measurements at 75°. The graph is essentially linear down to a DPPH concentration of 10^{-4} mole/liter, but the rate falls off at lower concentrations of DPPH. The reproducibility of the present work is demonstrated by the results for the second sample of styrene which are included on the same graph. A blank run in benzene was performed and a slight correction applied to the styrene results.

In the presence of oxygen the rate of disappearance of DPPH in styrene is very high, *e.g.*, for an initial DPPH concentration of 2×10^{-4} mole/liter, the disappearance of color in the presence of air at 60° is complete within 10 minutes. We have not attempted to elucidate the mechanism of this reaction which at first approach seems rather complex, but have attempted to measure R_{DPPH} in the complete absence of oxygen as discussed above. The excellent reproducibility shown in Fig. 1 argues against a role for oxygen in the thoroughly degassed systems. Furthermore, we have performed experiments during which residual oxygen, if directly entering the reaction between styrene and DPPH, would be completely consumed. For example, a solution of 0.008 g. of DPPH in 1 g. of styrene was prepared by the usual vacuum technique, and was heated to 100°. Visually the violet color of the DPPH disappeared after less than 12 hours, the time predicted by the present work. It is highly improbable that the styrene contains sufficient dissolved oxygen to cause the disappearance of this relatively high concentration of DPPH.

Two runs were made at 60° with styrene solutions in benzene at a concentration of 4.18 moles/liter. The reaction order for R_{DPPH} with respect to styrene monomer was found to be 1.7 from one experiment and 1.9 from the other. From these limited experiments the reaction appears to be second order with respect to monomer.

The DPPH used in this work was kindly donated by Dr. R. B. Mesrobian of the Polytechnic Institute of Brooklyn.

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[15] S. G. Foord, *J. Chem. Soc.*, 48 (1940).