To the crude acid chloride obtained from 1 g. of the acid was added 15 ml. of one of the various reagents. After the times stated the reaction mixture was rapidly cooled if hot and extracted with ether, the ether removed, and the residue taken up in ethanol and treated with an excess of 2,4-dinitrophenylhydrazine solution. The precipitated 2,4-dinitrophenylhydrazone was dried, weighed, and characterized by melting point and in some instances by absence of depression in melting point in mixtures with authentic samples. From the alkaline mother liquors there were isolated on acidification α-(benzenesulfonamido)-phenylacetic acid and benzenesulfonamide as noted. One run using the chloride from 1.5 g. of acid was made in a closed system filled with air. The 130 ml. of evolved gas was collected over water. Of this gas, uncorrected for the air in the system, 55 ml. or 48% of the theoretical amount of carbon monoxide was soluble in acidic cuprous chloride.

Decomposition of α-(Benzenesulfonamido)-phenylacetic Acid in Pyridine and Acetic Anhydride.—This reaction was carried out as previously described[2] for the propionic acid derivative using 3 g. of acid. The yield of carbon dioxide evolved at the end of 10 minutes was 81% of theory. The reaction mixture was poured on ice and hydrochloric acid and extracted with ether. The ether extracts were washed with water and bicarbonate and divided into two portions. The ether was removed from one portion leaving a residue from which a 2,4-dinitrophenylhydrazone, m.p. 236–237°, was obtained. This showed no depression in melting point when mixed with an authentic sample of the benzaldehyde derivative. The yield corresponded to 53% of the theoretical amount of benzaldehyde. The other portion was extracted with sodium hydroxide. The alkaline extract was acidified and extracted with ether. The ether extracts on evaporation deposited less than 0.1 g., *ca.* 7%, of benzenesulfonamide, m.p. 152–153°. The alkali-extracted ether extract was evaporated to remove the ether and steam distilled to give *ca.* 0.05 g., *ca.* 5%, of diphenyl disulfide, m.p. 55°.

TABLE I

ALKALINE DECOMPOSITION OF α-(BENZENESULFONAMIDO)-PHENYLACETYL CHLORIDE

Reagent[a]	Time, min.	Yield,[b] %	Other products[c] (% yield)
5% NaOH	5	24	BSPA (10)
5% NaOH	5	33	BSPA (27)
15% NaOH (hot)[d]	5	43	BSA (15)
C_2H_5OH[e]	5	5	....
C_2H_5OH[e]	5	4	....
NH_4OH	4 hr.	..	BSPAM (50)
Pyridine	1 hr.	13	....
H_2O	20 hr.	3	BSPA (67)
5% NaOH (hot)[d]	3	65	BSA (54)
50% NaOH	1	0	....

[a] The reaction was run at room temperature (30°) except as noted. [b] Of the isolated 2,4-dinitrophenylhydrazone of benzaldehyde. [c] Yield in parentheses; BSPA, α-(benzenesulfonamido)-phenylacetic acid; BSPAM, amide of BSPA; BSA, benzenesulfonamide. [d] The reagent was heated to boiling and added to the chloride. [e] Reaction mixture tested for benzaldehyde directly.

LOUISVILLE 8, KENTUCKY RECEIVED JUNE 18, 1951

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Monoradical and Diradical Polymerization of Styrene[1]

BY D. H. JOHNSON AND A. V. TOBOLSKY

Relations between reciprocal number average degree of polymerization and rate of polymerization have been derived for monoradical and diradical initiation to account for the effects of termination of combination and disproportionation and also for the effect of chain transfer to catalyst. These equations were applied to experimental data on the polymerization of styrene at 60° initiated by various catalysts and by light. The chain transfer constant of styrene of 2-azo-bis-isobutyronitrile is effectively zero. The chain transfer constants of cumene hydroperoxide and *t*-butyl hydroperoxide are 0.063 and 0.035, respectively. The chain transfer constant for benzoyl peroxide calculated by our equation agrees closely with that reported by Mayo, Gregg and Matheson. The catalyst efficiencies for benzoyl peroxide and 2-azo-bis-isobutyronitrile are found to be nearly unity and the results indicate that the termination step occurs mainly by combination of radicals. Photopolymerization appears to proceed *via* chains growing in one direction only.

Introduction

In a recent paper by Mayo, Gregg and Matheson[2] a very careful analysis of the benzoyl peroxide catalyzed polymerization of styrene at 60° was made which enabled these authors to calculate the chain transfer constants to monomer and to catalyst, to evaluate the catalyst efficiency for benzoyl peroxide, and to conclude that the termination step probably occurs by recombination of radicals.

We present in this paper a similar series of experiments on the polymerization of styrene initiated by benzoyl peroxide, 2-azo-bis-isobutyronitrile, *t*-butyl hydroperoxide, cumene hydroperoxide and ultraviolet light. Our results offer an independent verification of the conclusions and results of Mayo, *et al.*, discussed above. In addition, we calculate the catalyst efficiency of 2-azo-bis-isobutyronitrile, the chain transfer constants for *t*-butyl hydroperoxide, cumene hydroperoxide, 2-azo-bis-isobutyronitrile, and show that photopolymerization proceeds *via* chains growing in one direction only. Our method of analyzing the kinetic data[3,4] is different from, but not contradictory to, the method of Mayo, *et al.*, and has, we think, attractive features of simplicity.

Chain Transfer Constants for Monoradical Catalyzed Polymerization.—Catalysts for vinyl polymerization such as benzoyl peroxide, 2-azo-bis-isobutyronitrile, *t*-butyl hydroperoxide and cumene hydroperoxide (which we shall hereinafter refer to as Bz_2O_2, Azo, *t*-BHP, and CHP, respectively) cleave to produce monoradicals, some of which initiate polymer chains. In the case of styrene (but not all vinyl monomers) there is in addition a spontaneous thermal initiation which occurs independently of the cata-

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(1) This paper was presented at the September, 1950, Meeting of the American Chemical Society in Chicago. Earlier results were presented at the September, 1949, meeting of the American Chemical Society in Atlantic City, N. J. See Abstracts of the A.C.S., September, 1949, Meeting at Atlantic City, p. 10 N; and Abstracts of the A.C.S., September, 1950, Meeting at Chicago, Ill., p. 2J.

(2) F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, 73, 1691 (1951).

(3) D. H. Johnson, A. Escoruela and A. V. Tobolsky, Princeton University Plastics Report 14A, Signal Corps Contract W-36-039-SC-32011, May 3, 1949. Copies may be obtained by writing to Plastics Laboratory, Princeton University.

(4) H. Mark and A. V. Tobolsky, "The Physical Chemistry of High Polymeric Systems," Interscience Publishers, New York, 1950, pp. 401–408.

lyst. It has been postulated, but never completely proven, that the thermal initiation proceeds *via* chains which start growing in two directions (*i.e.*, two monomer molecules collide to form a diradical which initates the polymerization). Since the rate of thermal initiation at 60° is small compared to the rates under discussion when catalysts are used, and since it is not yet proven that the thermally initiated chains are diradicals, we shall treat the kinetics as if all growing chains were monoradical chains when monoradical producing catalysts are used. Our results show that this assumption (or approximation) cannot be disproved or proved within the accuracy of our data or any existing data.

With this assumption the following equation was derived[3,4]

$$\frac{1}{P_n} = C_m + C_I\frac{[\mathrm{Cat}]}{[\mathrm{M}]} + AR_p \qquad (1)$$

where

$$C_m = k_{tr}/k_p;\ C_I = k_I/k_p;\ A = \frac{(2k_{td} + k_{tc})}{k_p{}^2[\mathrm{M}]^2} \qquad (2)$$

The nomenclature in the above equations conforms to that of reference (2). C_m is the chain transfer constant to monomer, C_I the chain transfer constant to catalyst, P_n the number average degree of polymerization, R_p the rate of polymerization, k_p, k_{td}, k_{tc}, k_{tr} and k_I are the specific rate constants for propagation, disappearance of radical pairs by disproportionation, disappearance of radical pairs by combination, transfer to monomer and transfer to catalyst, respectively. To compare with the notation in references (3) and (4), $k_p = k_2$; $k_{tr} = k_{TM}$; $k_I = k_{TC}$; $2k_{td} = k_d$; $2k_{tc} = k_c$.

Throughout this paper the units used are moles, liters and seconds. The concentration of pure monomer is taken to be 8.35 moles/liter, which is its actual value at 60°, rather than the value of 8.63 used in reference (2). In all cases when catalyst concentrations, [Cat], are introduced, we are referring to the initial concentration of catalyst which we assume remains approximately constant during polymerization to low conversion. We also assume [M] to be constant since the polymerizations were carried out to less than 10% conversion.

Equation (1) is identical with an equation that can be obtained from equation (11) and (14) of reference (2) if thermal polymerization is neglected in equation (11), or if it is assumed that it *proceeds via monoradicals*.

Melville and Valentine[5] have recently published an equation relating $1/P_n$ and R_p for each of the two modes of radical termination. Their equation predicts that in plotting $1/P_n$ *versus* R_p for $k_{td} = 0$ both the slope and the intercept of the line (neglecting chain transfer to catalyst) will be half the corresponding value for the same plot when $k_{tc} = 0$. This result differs from that expressed by our equation (1) and we believe Melville and Valentine to be in error.

The relation between catalyst concentration and rate of polymerization R_p for bulk polymerization will later be shown to be

$$R_p^2 = B_I[\mathrm{Cat}] \qquad (3)$$

where B_I is a different constant for each catalyst. Equation (1) can therefore be written as

$$\frac{1}{P_n} = C_m + \frac{C_I R_p^2}{B_I[\mathrm{M}]} + AR_p \qquad (4)$$

Data for $1/p_n$ *versus* R_p for each of the catalysts studied was obtained by varying the initial catalyst concentration and measuring the corresponding intrinsic viscosity and rate. In practice the intrinsic viscosities were measured at about 10% conversion. The intrinsic viscosities were converted to P_n by means of equation II of reference (2).

$$P_n = 1770[\eta]^{1.40} \qquad (5)$$

Plots of $1/p_n$ *versus* R_p for polymerization of pure styrene at 60° catalyzed by Bz_2O_2 and Azo are shown in Fig. 1 and the same type of plot is shown in Fig. 2 for *t*-BPH and CHP. As is seen from these figures, the $1/P_n$ *versus* R_p plot is a straight line for Azo and is a curved line for the other catalysts.

From equation (4) it is clear that the necessary and sufficient condition that the $1/P_n$ *versus* R_p plot should be a straight line is that $C_I = 0$. If the second term on the right hand side is not zero, it will contribute a term proportional to R_p^2.

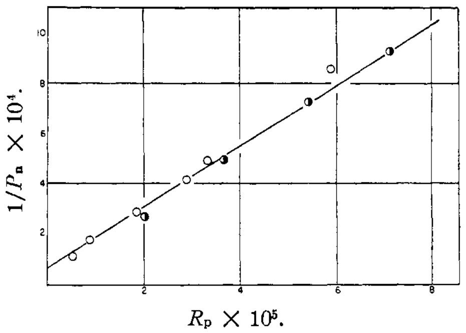

Fig. 1.—$1/P_n$ *versus* R_p for polymerization of pure styrene at 60° catalyzed by Bz_2O_2 and AzO: ◑, Azo; ○, Bz_2O_2.

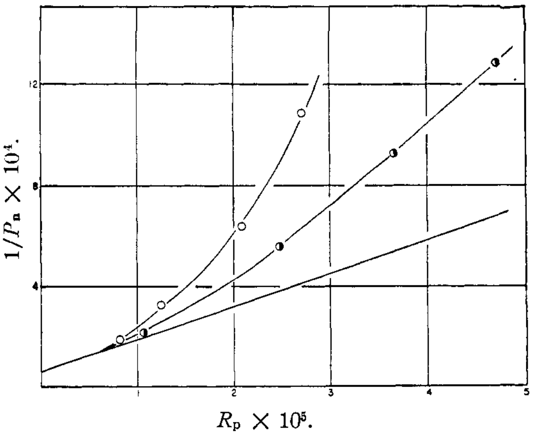

Fig. 2.—$1/P_n$ *versus* R_p for polymerization of pure styrene at 60° catalyzed by *t*-BPH and CHP: ○, *t*-BPH; ◑, CHP; —, monoradical line determined by equation (7).

We conclude that inasmuch as the $1/P_n$ *versus* R_p plot is a straight line for Azo, the chain transfer constant C_I for this catalyst is zero to within the limits of our experimental accuracy. This is not unexpected since this catalyst decomposes at nearly the same rate in all solvents and shows no induced decomposition. The absence of induced decomposition implies that there can be no radical transfer of a growing polymer chain with the catalyst, because the latter would almost certainly bring about induced decomposition.

The resulting equation obtained from equation (1) when $C_I = 0$ is

$$\frac{1}{P_n} = C_m + AR_p \qquad (6)$$

We have termed this straight line the monoradical line inasmuch as it depicts the highest molecular weight that can be achieved in bulk polymerization of styrene at 60° by use of monoradical initiation.

The straight line fitting the data for 2-azo-bis-isobutyronitrile is

$$\frac{1}{P_n} = 6 \times 10^{-5} + 12.3R_p \qquad (7)$$

By comparing (2), (6) and (7) we obtain

$$C_m = 6 \times 10^{-5};\ A = \frac{2k_{td} + k_{tc}}{k_p^2[\mathrm{M}]^2} = 12.3 \qquad (8)$$

The value of C_m obtained in this way agrees exactly with that obtained in reference (2), which places the value of C_m between 5×10^{-5} and 7×10^{-5}. From the values of the absolute rate constants of Matheson, *et al.*,[6] who assumed that $k_{td} = 0$ and found that $k_{tc} = 3.6 \times 10^7$, $k_p = 176$, one calculates $A = 16.6$, which agrees fairly closely with our value of 12.3.

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(5) H. W. Melville and L. Valentine, *Trans. Faraday Soc.*, **46**, 210 (1950).

(6) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **73**, 1700 (1951).

One can recast equation (I) in the form

$$\frac{1}{P_n} - AR_p = \frac{1}{P_n} - 12.3\ R_p = C_I\frac{[\text{Cat}]}{[\text{M}]} + C_m \quad (9)$$

For the three catalysts showing chain transfer a plot of $(1/P_n - 12.3R_p)$ *versus* [Cat]/[M] should give a straight line whose slope is C_I, the chain transfer constant to catalyst. This has been shown for Bz_2O_2 in Fig. 3 and for *t*-BPH and CHP in Fig. 4. For the benzoyl peroxide line in Fig. 3 we have used the data of Mayo, *et al.*,[2] as well as our own data. It is clear from these figures that the points do fall on straight lines, from the slopes of which one can calculate the following chain transfer constants

$C_I = 0.048$ benzoyl peroxide
$C_I = 0.063$ cumene hydroperoxide
$C_I = 0.035$ *t*-butyl hydroperoxide

Our value of C_I for benzoyl peroxide of 0.048 agrees quite closely with the previously reported value of 0.055.[2]

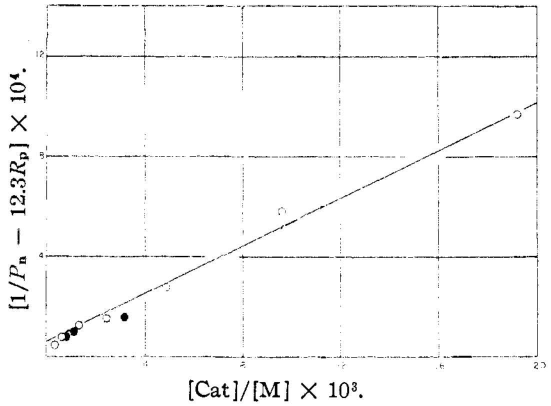

Fig. 3.—$[1/P_n - 12.3R_p]$ *versus* [Cat]/[M] for Bz_2O_2: ●, our data; O, data from reference (2).

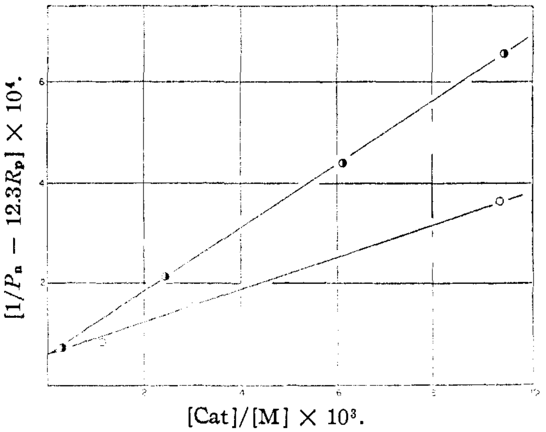

Fig. 4.—$[1/P_n - 12.3R_p]$ *versus* [Cat]/[M] for *t*-BPH and CHP: O, *t*-BPH; ◑, CHP.

It should be noted that although the chain transfer constant for benzoyl peroxide lies between the values for the two hydroperoxides, the plot of $1/P_n$ *versus* R_p shows much less deviation from the monoradical line for Bz_2O_2 than for *t*-BHP or CHP. This can easily be seen from Figs. 1 and 2, and in fact it is also clear from Fig. 1 that the $1/P_n$ *versus* R_p line for BzO_2 shows inappreciable deviation from the monoradical line until values of R_p exceeding 5×10^{-5} mole liters^{-1} seconds^{-1}. The reason is apparent from equation (4) inasmuch as the value of B_I for Bz_2O_2 is much larger than for *t*-BPH or CHP. For a given value of R_p, the contribution of the second term on the right hand side of equation (5), representing deviation from the monoradical line, is greater for the hydroperoxides than for Bz_2O_2, even though the values of C_I are all comparable. We are indebted to Drs. Mayo and Matheson for discussion concerning this question.

We might also point out that the value of B_I is very large for the Azo catalyst. Its chain transfer constant, although nearly zero, must be finite. It this were so, the $1/P_n$ *versus* R_p curve for Azo would deviate from a straight line at sufficiently high values of R_p. However, one would have to use such large values of R_p that the accuracy of the experiments would be in doubt.

Rates of Polymerization *versus* Catalyst Concentrations.—The relation between R_p and catalyst concentration for bulk polymerization was already indicated in equation (3).

$$R_p^2 = B_I[\text{Cat}] \quad (3)$$

Figure 5 shows a plot of R_p *versus* $[\text{Cat}]^{1/2}$ for Azo and Bz_2O_2. The plots are straight lines in all cases. The values of B_I are

$$\begin{aligned} B_I &= 5.19 \times 10^{-7} \text{ mole liter}^{-1}\text{ sec.}^{-2} && \text{Azo} \\ B_I &= 1.21 \times 10^{-7} \text{ mole liter}^{-1}\text{ sec.}^{-2} && Bz_2O_2 \\ B_I &= 4.06 \times 10^{-9} \text{ mole liter}^{-1}\text{ sec.}^{-2} && t\text{-BHP} \\ B_I &= 2.49 \times 10^{-8} \text{ mole liter}^{-1}\text{ sec.}^{-2} && \text{CHP} \end{aligned} \quad (10)$$

Our values for rate of Bz_2O_2 catalyzed polymerization agree very closely with those of Mayo, *et al.*[2] When their rates are expressed in our units (moles liter^{-1} sec.$^{-1}$) the equation they give relating R_p and $[Bz_2O_2]$ is $R_p^2 = 1.64 \times 10^{-7} [Bz_2O_2] + 1.08 \times 10^{-11}$. The constant term appearing in their equation is due to the rate of thermal polymerization, which we have neglected in our approximation.

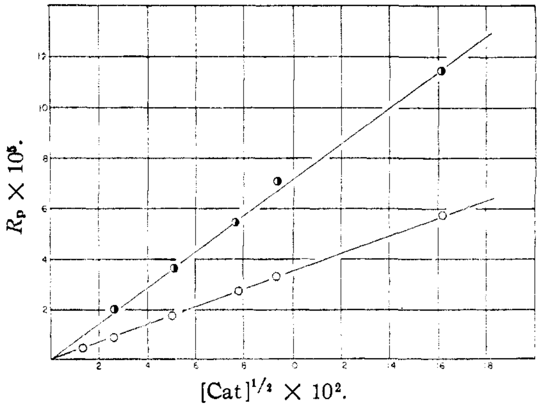

Fig. 5.—R_p *versus* $[\text{Cat}]^{1/2}$ for Bz_2O_2 and Azo: ◑, Azo; O, Bz_2O_2.

Rate of Initiation of Polymer Chains.—The rate of initiation of monoradical polymer chains, which we shall denote by R_i, is a quantity which must be distinguished from the rate at which the catalyst breaks into radicals, inasmuch as not all the primary radicals from the catalyst may start polymer chains. The quantity R_i is easily evaluated from the steady state condition on the polymer radicals.[6]

$$R_i = \frac{2(k_{tc} + k_{td})}{k_p^2[\text{M}]} R_p^2 \quad (11)$$

Equation (11) can be transformed by use of equation (2) defining the quantity A and equation (8) which gives the numerical value of A.

$$R_i = \frac{2}{1+x} AR_p^2 = \frac{24.6R_p^2}{1+x} \quad (12)$$

where

$$x = k_{td}/(k_{td} + k_{tc}) \quad (13)$$

The quantity x therefore varies between zero and unity and represents the fractional part of the termination process due to disproportionation.

From equation (2) it is clear that provided the quantity x is known, R_i can be calculated from data on R_p and P_n only. This is so because we have shown that A can be evaluated from these data only. By substituting equation (3) for R_p^2 in equation (12), and using the values B_I in equations (10) we obtain the following relations between R_i and the concentrations of the various catalysts.

$$R_i = \frac{2AB_I[\text{Cat}]}{1 + x}$$

$$R_i = \frac{1.28 \times 10^{-5}}{1 + x}\,[\text{Azo}]$$

$$R_i = \frac{2.96 \times 10^{-6}}{1 + x}\,[\text{Bz}_2\text{O}_2] \qquad (14)$$

$$R_i = \frac{9.96 \times 10^{-8}}{1 + x}\,[t\text{-BHP}]$$

$$R_i = \frac{6.12 \times 10^{-7}}{1 + x}\,[\text{CHP}]$$

Catalyst Decomposition Rates and Catalyst Efficiency.—The catalyst 2-azo-bis-isobutyronitrile undergoes a first order decomposition at very nearly the same rate in all solvents. It is believed that the rate of decomposition of this catalyst is equal to its rate of primary cleavage into a radical pair.[7,8] For benzoyl peroxide, on the other hand, the total rate of decomposition in a solvent is equal to the sum of its spontaneous cleavage rate (first order) plus another term representing radical induced decomposition of the catalyst which is often three-halves order but may also be of a different order.[9,10]

$$-\frac{\text{d}[\text{Cat}]}{\text{d}t} = k_\text{d}[\text{Cat}] + k_\text{d}'[\text{Cat}]^y \qquad (15)$$

where k_d is the specific rate constant for spontaneous cleavage, k_d' the specific rate constant for induced decomposition, and y the order of the induced decomposition. For Azo the second term vanishes. Inasmuch as the induced decomposition reaction produces no free radicals, the rate at which monoradical catalyst fragments are being produced by the catalyst is $2\ k_d$ [Cat].

The catalyst efficiency is properly defined as[2]

$$f = R_i/2k_\text{d}[\text{Cat}] \qquad (16)$$

By substituting equation (14) in equation (16) we obtain

$$f(1 + x) = AB_I/k_\text{d} \qquad (17)$$

In Table I values of k_d for Azo and Bz_2O_2 as given by various workers are shown. Also these values of k_d have been divided by AB_I obtained from equations (8) and (10) in order to obtain the quantity $f(1 + x)$. It is seen that by the method outlined here the catalyst efficiency cannot be calculated independently of a knowledge of x defined in equation (13).

The values of $f(1 + x)$ in Table I range from 0.63 to 0.83. If all termination occurred by combination of radicals, x would be zero and the catalyst efficiencies shown in Table I would range from 66 to 83%. The efficiencies would be half as large if all termination were by disproportionation (*i.e.*, $x = 1$). It seems to us more likely that two different catalysts would have nearly the same efficiency if the efficiencies were nearly 100% rather than nearly 50%, and thus we think that the data in Table I speak in favor of termination by combination. The most elegant way of obtaining x is by end-group analysis, and recent tracer studies along this line[11] confirm the conclusion that $x = 0$ (*i.e.*, $k_{td} = 0$). Mayo, *et al.*,[2] give a method for calculating chain efficiency and x independently of each other, and this and other confirmatory evidence that they cite also lead them to conclude that $k_{td} = 0$.

TABLE I

SPONTANEOUS DECOMPOSITION AND CATALYST EFFICIENCY AT 60°

Catalyst	k_d (seconds^{-1}) $\times 10^{-6}$	Reference	AB_I $\times 10^{-6}$	$f(1 + x)$
Azo	9.15	7	6.3	0.69
Azo	7.6	8	6.3	.83
Bz_2O_2	2.25	9	1.48	.66
		concd. peroxide solutions		
Bz_2O_2	2.25	0	2.02	.90
		dilute peroxide solutions		
Bz_2O_2	2.83	2	2.02	.71

Chain Transfer to Catalyst and Induced Decomposition.—In reference (2) (equations 22 and 23 and Table V) a rather remarkable calculation is carried out by which the rate of induced decomposition is calculated from the value of C_I or *vice versa*. This calculation is based on Mayo's assumption that the polystyryl radicals alone cause the induced decomposition of the benzoyl peroxide, and that combination or disproportionation of these radicals is the chain-terminating step for induced decomposition. This is opposed to the Nozaki–Bartlett concept[9] for induced decomposition in solvents where the rate of induced decomposition is small. According to these workers the induced decomposition is due to the attack of $C_6H_5COO.$(or $C_6H_5.$) radicals on the peroxide, and the chain termination step for induced decomposition is the recombination of benzoate radicals or phenyl radicals.

The following arguments speak in favor of the Mayo mechanism: (a) the excellent agreement obtained for C_I calculated from peroxide decomposition data using Mayo's hypothesis[2] and the actual values of C_I obtained by analysis of polymerization data; (b) the very great inhibition exerted by styrene on the induced decomposition of benzoyl peroxide.[9] This shows that the polystyryl radical is indeed rather inactive toward benzoyl peroxide, but it also shows that styrene is very reactive toward $C_6H_5COO\cdot$ or $C_6H_5\cdot$ so that few of these radicals will persist long enough to induce Bz_2O_2 decomposition. (c) The high

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(7) F. M. Lewis and M. S. Matheson, THIS JOURNAL, **71**, 747 (1949).

(8) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

(9) K. Nozaki and P. D. Bartlett, *ibid.*, **68**, 2377 (1946).

(10) C. Gardner Swain, W. T. Stockmayer and J. T. Clarke, *ibid.*, **72**, 5426 (1950).

(11) L. M. Arnett and J. M. Peterson, April, 1951, Meeting of the A.C.S.

efficiency of initiation for Bz_2O_2 polymerization of styrene calculated in reference (2) and in this paper also shows that $C_6H_5COO\cdot$ radicals and $C_6H_5\cdot$ radicals are rapidly converted to polystyryl radicals in styrene.

In spite of the arguments presented in the preceding paragraph it is our opinion that the relative amount of induced decomposition caused by $C_6H_5COO\cdot$ and $C_6H_5\cdot$ radicals as compared to polystyryl radicals (or other polymer radicals) warrants further quantitative study. If the $C_6H_5COO\cdot$ radicals were alone responsible for induced decomposition (which may yet be found to be the case in some vinyl polymerizations), an induced decomposition of the catalyst might exist in the complete absence of chain transfer to catalyst.

Kinetics of Diradical Initiation.—If the initiation step for vinyl polymerization were the formation of a diradical which could add monomer on both ends, the equations for $1/P_n$ *versus* R_p developed in the previous sections would have to be modified. Such diradical initiation has been variously postulated for the thermal and photoinitiation of vinyl polymerizations and the validity of these postulates will be discussed in the concluding sections of this paper. Diradical initiation may in principle be obtained by using suitable ring peroxides or ring azo compounds, or even (although less cleanly) with polymeric peroxides.[12] We shall discuss below the conditions that would obtain when diradical initiation is achieved.

(a) In the case of diradical initiation considering chain transfer to monomer, termination both by combination and disproportionation, but neglecting ring formation, one obtains the following equation relating $1/P_n$ and R_p.[3,4]

$$\frac{1}{P_n} = C_m + \frac{k_{td}}{k_p^2[M]^2} R_p = C_m + \frac{x}{1+x} AR_p = 6 \times 10^{-5} + \frac{x}{1+x} 12.3R_p \quad (18)$$

Melville and Watson[13] have deduced a similar expression for $1/P_n$ wherein only termination by disproportionation is considered. If k_{tc} is set equal to zero in our kinetic expressions,[3] they become identical with those of Melville and Watson. In equation (18) no term for chain transfer to catalyst is included because in this paper we shall evaluate the applicability of equation (18) to thermal and photoinitiation only.

(b) In the case of diradical initiation one also has the possibility that a diradical will terminate by coupling of the radical ends of the same chain to produce rings.[2,14] Very little is known about this situation from either the experimental or theoretical point of view, although Haward[14] has made some interesting calculations showing that ring formation is favored if the diradical concentration is low and if the degree of polymerization is small. We have not presented the general equations which would account for ring formation, transfer, combination and disproportionation since it is difficult to make definitive kinetic assumptions concerning ring formation.

Ring formation would be evidenced experimentally by a profound change in the distribution of molecular sizes and also by a marked change in the relationship between P_n (determined osmometrically) and $[\eta]$.

Photo-initiated Polymerization.—The photo-initiated polymerizations of styrene under various light intensities were carried out at 60° as described in the section on experimental procedure. Using tubes of 10, 8 and 4 mm. diameter, it was found that the values of R_p and $[\eta]$ were independent of tube diameter. This showed that the reaction was proceeding homogeneously throughout the tube.

By variation of the light intensity one can control the rate of initiation and hence the value of R_p. In this way it was possible under the conditions used to obtain photo-rates up to eight times the thermal rate. Values of P_n for a given photo rate were evaluated from intrinsic viscosities and equation (5).

Inasmuch as the theoretical equations refer to a true number average degree of polymerization, and the molecular weight distribution might be quite different for photo-initiated polymers and for polymers initiated by monoradical producing catalysts it was thought advisable to check equation (5) for photopolymers by an osmometric measurement. The osmotic pressure value of P_n obtained for the photopolymer produced by the strongest light intensity was 4240 as compared with a value of 4450 obtained from its intrinsic viscosity and equation (5). The difference is within the limits of error of the osmometric method. The result indicates that the molecular weight distribution obtained in photopolymerization is the same as that obtained in catalytically prepared polystyrene. It is also negative evidence for the existence of diradical initiation in photopolymerization, since Bamford and Dewar[15] have already shown theoretically that the $P_n \sim [\eta]$ relation is significantly different for diradical and monoradical initiation.

Further negative evidence regarding the existence of diradical initiation in the photopolymerizations carried out here is obtained by examination of the $1/P_n$ *versus* R_p plot. This plot for photopolymerization is shown in Fig. 6 where it has been compared to the data for Bz_2O_2 and Azo. The data for the Azo catalyst define the monoradical line, (equation (7)), which is drawn as a solid line in the figure. The dotted lines represent the limiting forms of equation (18) where $x = 0$ and $x = 1$ (corresponding to $k_{td} - 0$ and $k_{tc} = 0$, respectively). If diradical initiation is actually occurring, and ring formation is negligible, the line defined by $1/P_n$ *versus* R_p would be some place between the two dotted lines shown in Fig. 6, probably near the horizontal line since x is probably nearly zero.

The experimental data for photopolymers actually lies very close to the monoradical line. We would regard it as quite a striking coincidence if

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after equation (19) were properly corrected to account for ring formation, it would give the monoradical line. We therefore conclude that photopolymerizations carried out under our conditions proceed *via* chains growing in one direction only. This result is not completely surprising since the energy of incident light quanta in the wave length region used is sufficient to cleave the styrene molecule as has already been pointed out by Flory.[16] A phenyl and a vinyl radical might be formed, or a hydrogen atom and an α-styryl radical. It is also possible that the irradiation may cause a transfer of a hydrogen atom from one styrene molecule to another. Such processes would obviously lead to monoradicals growing in one direction.

Thermal Polymerization.—In the case of the thermal polymerization of styrene the datum for $1/P_n$ *versus* R_p lies very close to intercept determined by C_m (see Fig. 6). It is therefore difficult to decide whether this point lies on the monoradical or diradical line. The observed P_n is actually somewhat smaller than would be expected on the basis of the monoradical line (equation (7)). This may result from ring formation which would alter the relation between P_n and $[\eta]$ and between $1/P_n$ and R_p, or it may be due to the fact that at extremely low radical concentration the formation of radicals in pairs (even if monoradicals are produced) would accelerate the termination reaction.[2] Finally, it may be that the value of P_n is not really known with great accuracy for thermal polymers.

A recalculation of the specific rate of initiation for the thermal polymerization, assuming the rate expression for initiation to be $k_i[M]^2$ gives $k_i = 2.15 \times 10^4 \exp(-24{,}400/RT)$.[17,18]

Experimental

Materials.—The monostyrene was purified by repeated washings with 10% sodium hydroxide followed by water washings. After drying over calcium chloride, the styrene was fractionally distilled at reduced pressure and the middle fraction used within two days. Benzoyl peroxide from Cadet Chemical Company was recrystallized twice from chloroform and petroleum ether and assayed a minimum of 98% on iodometric analysis. The 2-azo-bis-isobutyronitrile was furnished by Dr. C. G. Overberger and was recrystallized twice from ether to give a melting point of 104°. The *t*-butyl hydroperoxide was supplied by the Novadel Agene Company and gave an assay of 90.2%. The cumene hydroperoxide was supplied by the Hercules Powder Corporation and purified according to their procedure as reported by Fordham and Williams.[19] Iodometric analysis showed the material to have a purity of 98.5%.

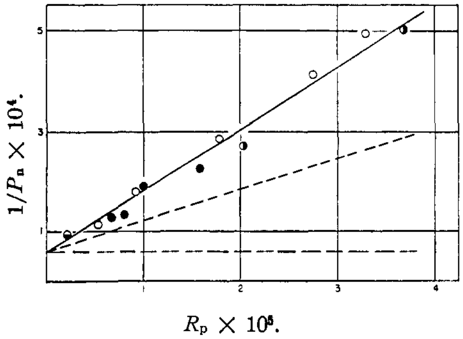

Fig. 6.—$1/P_n$ *versus* R_p for photopolymerization, thermal polymerization and catalyzed polymerization of styrene at 60°: ◒, thermal run; ●, photo runs; ○, Bz_2O_2; ◑, Azo. Solid line represents monoradical line (equation (7)). Dotted lines represent diradical line (equation (19)) for limiting conditions $x = 0$ and $x = 1$.

Procedure.—All catalyst–styrene systems were placed in glass ampoules, cooled, and sealed under a vacuum of 10^{-4} mm. The charged ampoules were then transferred to a 60 ± 0.05° thermostat. After the proper reaction time, the tubes were removed and immediately placed in a Dry Ice–acetone mixture. When opened, the ampoule contents were diluted with toluene containing a small quantity of hydroquinone. The polymer was then precipitated with methanol, filtered, washed, and then dried *in vacuo* to constant weight. In all experiments the monomer conversion was less than 15%.

For the photo runs, the purified styrene was placed in thin Pyrex tubes and sealed under a vacuum of 10^{-4} mm. using two G.E. R-S sun lamps as the light source. The emission spectra of these lamps is principally the discrete mercury line spectrum superimposed on a weak continuous background. The bulbs have a corex glass envelope that transmits radiation of about 290 mμ or longer wave length. After proper exposure, the tubes were removed and treated in the same way as the catalyst–styrene systems. Intrinsic viscosity determinations, rate measurements and calculation of P_n were made according to the methods of reference (2).

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