[CONTRIBUTION NO. 107 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER CO.]

Chain Transfer in the Polymerization of Styrene. VI. Chain Transfer with Styrene and Benzoyl Peroxide; the Efficiency of Initiation and the Mechanism of Chain Termination[1]

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The rates and degrees of polymerization of styrene have been measured over a wide range of concentrations of benzoyl peroxide at 60°. The contributions to the average degree of polymerization of chain transfer of the polymer radical with the monomer and with the peroxide have been determined. The transfer constant of the monomer is about 6×10^{-5}, comparable to that of ethylbenzene, while the transfer constant of the peroxide, about 0.055, is about six times that of carbon tetrachloride. About 90% of the radicals formed by the spontaneous decomposition of the peroxide start polymer chains. From the rate of decomposition of benzoyl peroxide and the rate of formation of polymer molecules, and from other evidence, it is concluded that essentially all chains end by coupling rather than by disproportionation. The thermal polymerization of styrene leads to about half the rate and degree of polymerization that would be expected from data at low peroxide concentrations. These results may mean that biradicals formed in thermal initiation are unable to attain a statistical distribution and undergo an accelerated termination reaction, possibly leading to very large cyclic molecules. Additional data on the relation between intrinsic viscosity and number average molecular weight of polystyrene lead to the relation: $\bar{M}_n = 167000 \cdot [\eta]^{1.37}$.

Preceding papers from this Laboratory on the effects of carbon tetrachloride[3a,b,d] and hydrocarbon solvents[3a,c] on the polymerization of styrene have not attempted to separate the effects of chain transfer with the monomer and of disproportionation and coupling of radicals. Isolation of these effects is essential to the study of absolute rate constants in polymerization which is presented simultaneously.[4] The present work was originally undertaken to determine, from the rate and degree of polymerization in the presence of benzoyl peroxide, the tendency of styrene monomer to undergo chain transfer with the substituted benzyl radical in polymerizing styrene, but the problems of chain transfer with the initiator, the efficiency of benzoyl peroxide in initiating chains in styrene, and the relative importance of disproportionation and coupling in the termination reaction have proved to be closely related.

Experimental.—The purification of styrene and benzoyl peroxide, preparation of runs in the absence of air, isolation of polymer samples, determination of intrinsic viscosities, and determination of molecular weights by osmotic pressure have been described previously.[3b] Runs 1–10, 11–20, 31–33 and 41–46 were run with different lots of styrene over an interval of 9 months. All polymerizations were carried out at 60° but the concentration of styrene in the pure monomer has been taken as 8.63 moles/l. (the 25° value) instead of 8.35 (60° value). The units used for expressing all rates and rate constants are moles, liters and hours.

The Relation between Intrinsic Viscosity and Number Average Molecular Weight for Unfractionated Polystyrenes.—A relation between number average molecular weight and intrinsic viscosity for unfractionated polystyrenes was desirable because of the greater convenience of the viscosity method for determining molecular weights and because a few polymers had molecular weights too high for satisfactory osmotic pressure determinations. From osmotic pressure measurement on polystyrenes prepared by us (a) in the absence of catalysts and presence of carbon tetrachloride or other solvents or (b) in the absence of solvents and presence of benzoyl peroxide, Ewart, Tingey and Wales[5] obtained the relation[6]

$$\bar{M}_n = 184000[\eta']^{1.277} \qquad \text{(I)}$$

Using only the osmotic data on carbon tetrachloride polymers, together with number average molecular weights from 10,000 to 200,000 by chlorine determinations, the relation

$$\bar{M}_n = 184000\ [\eta']^{1.40} \qquad \text{(II)}$$

was reported,[3b] experiments with other solvents and benzoyl peroxide being omitted for the sake of simplicity. When four experiments with conversions above 12% are omitted, because of possible broadening of molecular weight distribution, then[7]

$$\bar{M}_n = 182000[\eta']^{1.39} \qquad \text{(III)}$$

Table I gives additional osmotic molecular weight–intrinsic viscosity data on polystyrenes made at 60° in the presence of either benzoyl peroxide, butyl bromide, isobutyl chloride or isopropylbenzene at 60 or 100°. In Fig. 1, these data can be compared with the previous osmotic data with carbon tetrachloride polymers[3b] (at conversions less than 12%) which lead to equation (III). Although chain initiation by monoradicals (from peroxides) and termination by coupling (established in the present paper) lead to one molecular weight distribution, while termination by chain transfer leads to another, experimentally there is no significant difference in the intrinsic viscosity–molecular weight relations between polymers initiated thermally in a solvent or by benzoyl peroxide without a solvent. Apparently there is enough transfer in the benzoyl

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[1] Part of the experimental work in this paper was carried out in 1943–1945. The remainder and the preparation for publication were assisted by the Office of Naval Research, under Contract N8onr-544.

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[3] (a) F. R. Mayo, THIS JOURNAL, **65**, 2324 (1943); (b) R. A. Gregg and F. R. Mayo, *ibid.*, **70**, 2373 (1948); (c) R. A. Gregg and F. R. Mayo, *Discussions Faraday Soc.*, **2**, 328 (1947); (d) F. R. Mayo, THIS JOURNAL, **70**, 3689 (1948).

[4] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *ibid.*, **73**, 1700 (1951).

[5] R. H. Ewart and H. C. Tingey, Abstracts of Papers, 111th Meeting American Chemical Society, April, 1947, p. 4Q.

[6] The intrinsic viscosities in this paper (all in benzene solution) are based on concentrations in grams/100 cc. and are therefore equal to intrinsic viscosities based on basal moles/liter divided by 10.4. $[\eta']$ indicates intrinsic viscosities which have not been corrected for kinetic energy.

[7] The effect of omitting the higher conversion experiments is insignificant, particularly since an error has been found in the least squares calculation of Equation (II), which should actually have read: $\bar{M}_n = 182000\ [\eta']^{1.395}$.

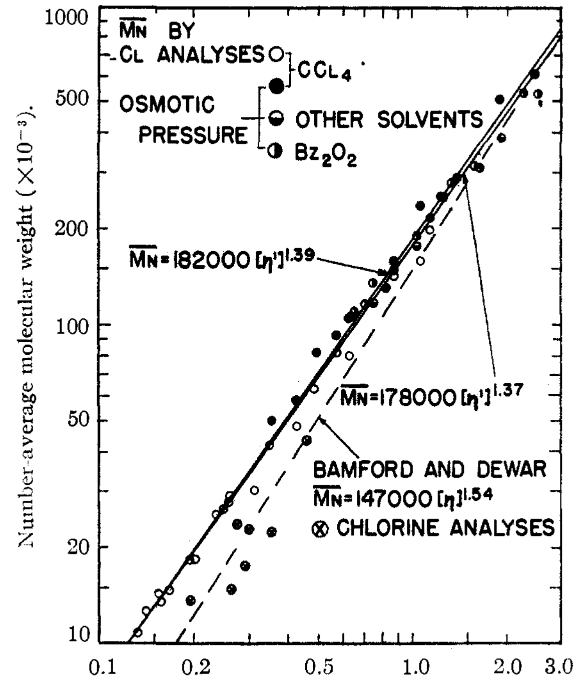

Fig. 1.—Number-average molecular weights of unfractionated polystyrenes as a function of intrinsic viscosity (not corrected for kinetic energy, except for data of Bamford and Dewar[9]).

peroxide series and enough biradical initiation and coupling in the solvent series that the differences are within experimental error; also, the intrinsic viscosity–molecular weight relation for polymer made in the absence of both initiator and solvent is common to both series.

TABLE I

RELATION BETWEEN INTRINSIC VISCOSITY AND NUMBER AVERAGE MOLECULAR WEIGHT

$[Bz_2O_2]_0$, mole/l.	Yield, wt. %	Time, hr.	$[\eta']$[a]	$\bar{M}_n$[b] $\times 10^{-3}$
		Polymerizations at 60°		
0.000619	3.86	8.50	2.51	530
.000870	8.56	18.08	2.27	534
.00248	6.82	8.00	1.59	316
.00248	6.94	8.50	1.60	312
.00413	7.42	7.08	1.33	280
.00907	7.67	5.08	1.03	190
.01322	7.59	4.08	0.878	149
.01767	7.74	3.58	.75	135
.0180	10.8	5.5	.705	116
.0259	8.36	3.25	.655	110
None[c]	12.5	118.2	1.23	254
None[d]	6.8	148	1.94	387
		Polymerizations at 100°		
None[e]	10.3	9.2	1.26	252
None[f]	11.1	13.1	1.03	177
None[g]	12.0	20.2	.757	117.5

[a] Not corrected for kinetic energy; units as in ref. (6). [b] Number average molecular weight by osmotic pressure (Ewart, Tingey and Wales). Contained indicated solvent at following molar solvent: styrene ratios: [c] 3.96 *n*-butyl bromide, [d] 1.10 *i*-butyl chloride, [e] 0.81 *i*-propylbenzene, [f] 1.44 *i*-propylbenzene, [g] 2.87 *i*-propylbenzene.

When all our osmotic and chlorine number average molecular weight data in Fig. 1 are weighted equally, we obtain, by the method of least squares

$$\bar{M}_n = 178000[\eta']^{1.37} \qquad \text{(IV)}$$

$\bar{M}_n$ calculated by Equations (III) and (IV) differs by a maximum of 6% at the highest intrinsic viscosities found, negligibly at the lowest viscosities. Equation (IV) is based on more data, but results have been calculated on both equations to give a measure of the uncertainty involved. Smith[8] has used the same experimental data to estimate molecular weights in a higher range.

Kinetic Energy Corrections.—At the time that the osmotic pressure measurements and chlorine analyses were made, flow times in viscosity determination were such that kinetic energy corrections were uniformly close to 5% and so no correction was made. After the experiments in Table II were nearly complete, it was found that a wider range of flow times had been employed in the latter experiments and that kinetic energy corrections significantly improved the precision of the results. Accordingly, all the intrinsic viscosities in Table II have been corrected for kinetic energy and the molecular weights have been calculated by equations (V) and (VI), which correspond to equations (III) and (IV), respectively, after the intrinsic viscosities have been corrected (increased) by 5%

$$\bar{M}_n = 170000[\eta]^{1.39} \qquad \text{(V)}$$

$$\bar{M}_n = 167000[\eta]^{1.37} \qquad \text{(VI)}$$

Bamford and Dewar[9] have deduced an entirely comparable equation (in the concentration units and form of our equations)

$$\bar{M}_n = 147000[\eta]^{1.54} \qquad \text{(VII)}$$

for carbon tetrachloride-regulated polymers, using only chlorine determinations in the molecular weight range 4800–44000 and a relation between solvent:monomer ratio and intrinsic viscosity of the polymers. They give no details on isolation of their polymers and admit difficulties in chlorine analyses. For a given viscosity, their equation leads to molecular weights 36 to 26% lower than our own in the range where both sets of molecular weight determinations overlap (11000–40000), and to values about the same as ours at $\bar{M}_n$ = 650000. Figure 1 compares equation (VII) with equations (III) and (IV), (V) and (VI) being parallel and lying slightly lower.

The Bamford and Dewar value for the transfer constant of carbon tetrachloride (their k'_3/k_2) at 60°, 0.0136, corresponds to their higher chlorine analyses, and is considerably higher than our value, 0.0092, determined from more consistent data over a wider molecular weight range.[3b,d]

Breitenbach and co-workers[9a] have recently

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[8] W. V. Smith, THIS JOURNAL, **71**, 4077 (1949).

[9] C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (*London*), **192A**, 309, 329 (1948).

[9a] J. W. Breitenbach, A. J. Renner, H. P. Frank and E. Kindl, *Monatsh.*, **81**, 455 (1950). Use of their relation in subsequent parts of the present paper leads to a transfer constant of benzoyl peroxide about 40% of that reported by us, a higher rate for the spontaneous decomposition of benzoyl peroxide in styrene, a lower efficiency of chain initiation, and a greater discrepancy between efficiencies measured by various methods.

TABLE II

POLYMERIZATION OF STYRENE BY BENZOYL PEROXIDE AT 60°

Expt.	Bz_2O_2, mole/l. Initial	Bz_2O_2, mole/l. Average[a]	Yield, wt. %	Time, hr.	$-\Delta[M]/\Delta t$ mole/l./hr.	$(-\Delta[M]/\Delta t)^2$	$[\eta]$[b]	$1/\bar{P}$ ($\times 10^5$) Eq. V	$1/\bar{P}$ ($\times 10^5$) Eq. VI
20	....		9.51	90.0	0.00912	0.0000832	3.83	9.4	9.9
9	....		10.88	120.0	.00782	.0000612	3.49	10.8	11.3
10	....		10.63	120.0	.00754	.0000569	3.53	10.6	11.1
33	....		6.03	72	.00722	.0000521	3.91	9.2	9.6
42	....		6.73	80.75	.00719	.0000517	3.38	11.3	11.8
41	.......[c]		6.54	80.75	.00699	.0000489	3.39	11.2	11.7
24	0.000125	0.000104	10.06	48.25	.0180	.000323	3.56	10.5	11.0
44	.0001265	.000110	7.62	36.0	.0183	.000334	3.20	12.2	12.7
43	.0001265	.000110	7.55	36.0	.0181	.000327	3.14	12.5	13.0
19	.000125	.000110	6.69	32.0	.0181	.000326	3.41	11.1	11.6
8	.0001262	.000112	6.58	30.13	.0189	.000355	3.20	12.2	12.7
7	.0001262	.000112	6.91	30.5	.0196	.000382	3.18	12.3	12.8
6	.0002525	.000224	8.77	30.5	.0248	.000616	2.89	14.0	14.6
5	.0002525	.000224	8.78	30.5	.0249	.000618	2.94	13.7	14.3
45	.000253	.000228	8.06	27.8	.0250	.000625	2.80	14.7	15.3
18	.000500	.000460	7.69	20.25	.0328	.00107	2.67	15.7	16.3
22	.000500	.000461	7.77	20.0	.0335	.00112	2.76	14.9	15.6
3	.000505	.000462	8.55	22.2	.0332	.00110	2.62	16.1	16.7
4	.000505	.000462	8.64	22.2	.0336	.00113	2.64	15.9	16.6
46	.000506	.000466	8.08	20.0	.0349	.001215	2.48	17.4	18.0
2	.001010	.000944	8.64	16.0	.0466	.00217	2.18	20.8	21.5
1	.002526	.00243	7.69	9.0	.0737	.00543	1.69	29.6	30.5
17	.00250	.00240	7.62	9.0	.0731	.00534	1.69	29.6	30.5
16	.00500	.00484	8.17	7.17	.0984	.00967	1.33	41.3	42.4
15	.0100	.00975	8.29	5.0	.143	.0205	1.01	60.5	61.7
14	.0200	.0196	8.81	3.75	.203	.0411	.794	84.4	85.8
13	.0400	.0394	8.40	2.5	.290	.0841	.593	126.5	128.0
12	.0800	.0791	8.20	1.75	.404	.163	.433	196.0	197.0
11	.1600	.1587	7.37	1.08	.587	.345	.321	298.0	297.0

[a] Calculated using the values of k_d and k'_d at the top of Table V. Substantially identical results are obtained using the values at the bottom of the same table, which are based on the same over-all rate of peroxide decomposition at 0.0207 *M*. [b] Corrected for kinetic energy; units as in ref. (6). [c] In this run, the reaction mixture was degassed and distilled *in vacuo* into the reaction tube.

proposed the relation (in our concentration units)

$$\bar{M}_n = 163000[\eta]^{1.25} \qquad \text{(VIII)}$$

for polystyrenes made without initiator or in the presence of peroxides at 20–140°. Their results agree with ours for $[\eta] \simeq 1$, but not for other values of $[\eta]$.

Equations for Rates and Degrees of Polymerization.—The following reactions in the catalyzed and uncatalyzed polymerizations are considered, where M and M· represent styrene and the radical formed from it by addition of a radical. Of the radical pairs (2R·) formed from decomposing benzoyl peroxide (Reaction 2; $R\cdot = C_6H_5\text{-}CO_2\cdot$ or $C_6H_5\cdot + CO_2$), some recombine by a first order reaction because of the cage effect[10] (Reaction 3), and the remainder start polymer chains by addition to styrene (Reaction 4).[11] The fraction of radical pairs starting chains is f

$$f = \frac{k_a[2R\cdot][M]}{k_r[2R\cdot] + k_a[2R\cdot][M]} = \frac{1}{(k_r)/(k_a[M]) + 1}$$

$$2M \xrightarrow{k_i} 2M\cdot \text{(biradical from thermal initiation}^{12}\text{)} \qquad (1)$$

$$Bz_2O_2 \xrightarrow{k_d} 2R\cdot \qquad (2)$$

$$2R\cdot \xrightarrow{k_r} \text{non-radical products} \qquad (3)$$

$$2R\cdot + 2M \xrightarrow{k_a} 2M\cdot \text{ (monoradicals)} \qquad (4)$$

$$\left.\begin{aligned} M\cdot + M &\xrightarrow{k_p} M\cdot \qquad (5) \\ M\cdot + M &\xrightarrow{k_{tr}} \text{polymer} + M\cdot \qquad (6) \end{aligned}\right\} k_{tr}/k_p = C_m$$

$$M\cdot + M\cdot \xrightarrow{k_{td}} 2 \text{ polymer (disproportionation)} \qquad (7)$$

$$M\cdot + M\cdot \xrightarrow{k_{tc}} 1 \text{ polymer (coupling)} \qquad (8)$$

$$M\cdot + Bz_2O_2 \xrightarrow{k_1} \text{polymer} + R\cdot \quad k_I/k_p = C_I \qquad (9)$$

Reactions (6) and (9) represent chain transfer with monomer and initiator, respectively, the corresponding transfer constants[3a] being C_m and C_I. Using the conventional steady state assumption, and assuming that rates of reaction of radicals are independent of their size[3d]

$$[M\cdot] = \left(\frac{k_i[M]^2 + k_d f[Bz_2O_2]}{k_{td} + k_{tc}}\right)^{1/2} \qquad (10)$$

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(10) M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(11) Since the efficiency of chain initiation is above 70%, the peroxide radicals must react readily enough with styrene that their reactions with styrene radicals and peroxide molecules can be neglected. Equation (4) implies that if either R· reacts with styrene to give a styrene radical (second order reaction), then the other R· immediately does likewise.

(12) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, THIS JOURNAL, **71** 497 (1949).

where [M·] is understood to be concentration of free polymer valences including biradicals.[18]

The over-all rate is

$$\frac{-\mathrm{d}[\mathrm{M}]}{\mathrm{d}t} = k_p[\mathrm{M}\cdot][\mathrm{M}] = k_p[\mathrm{M}]\left(\frac{k_i[\mathrm{M}]^2 + k_df[\mathrm{Bz_2O_2}]}{k_{td} + k_{to}}\right)^{1/2} \quad (11)$$

The average degree of polymerization, $\bar{P}$, is

$$\bar{P} = (-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/(\text{half the rate of formation of chain ends}) \quad (12)$$

and

$$1/\bar{P} = \frac{k_{tr}[\mathrm{M}\cdot][\mathrm{M}] + k_I[\mathrm{M}\cdot][\mathrm{Bz_2O_2}] + k_df[\mathrm{Bz_2O_2}] + k_{td}[\mathrm{M}\cdot]^2}{k_p[\mathrm{M}\cdot][\mathrm{M}]} \quad (13)$$

$$\frac{1}{\bar{P}} = C_m + C_I\frac{[\mathrm{Bz_2O_2}]}{[\mathrm{M}]} + \frac{k_df[\mathrm{Bz_2O_2}]}{-\mathrm{d}[\mathrm{M}]/\mathrm{d}t} + \frac{k_{td}(k_i[\mathrm{M}]^2 + k_df[\mathrm{Bz_2O_2}])}{(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)(k_{td} + k_{to})} \quad (14)$$

The last term in (14) is interchangeable with $k_{td}(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)/(k_p{}^2[\mathrm{M}]^2)$.

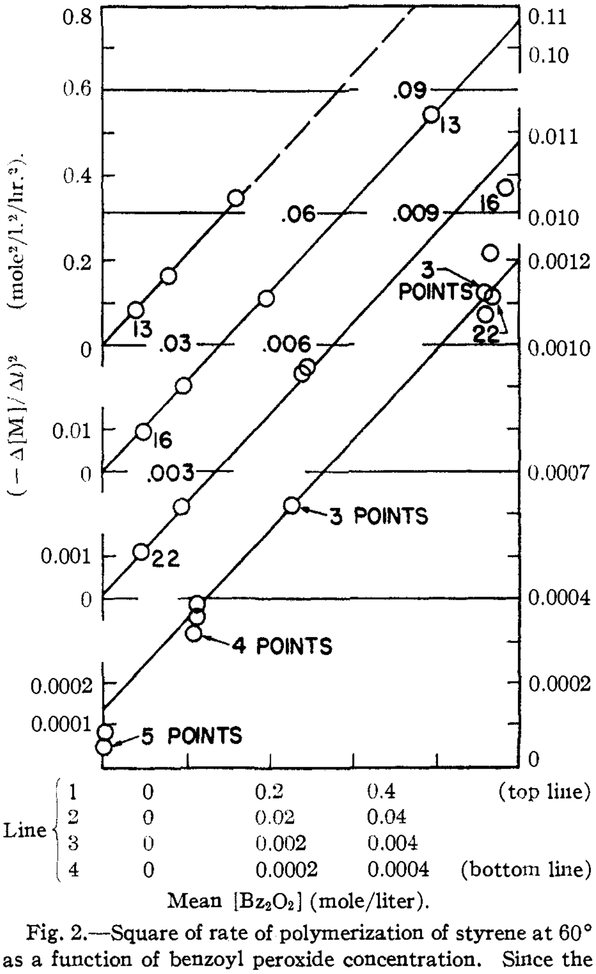

Fig. 2.—Square of rate of polymerization of styrene at 60° as a function of benzoyl peroxide concentration. Since the scale changes by a factor of ten for each line (abscissas indicated at ends of all lines and along two center lines), the last point on each is numbered and reproduced as the first point on the line next above. Each line corresponds to equation (15).

Relation between Catalyst Concentration and Rate of Polymerization.—From equation (11), a plot of $(-\Delta[\mathrm{M}]/\Delta t)^2$ against $[\mathrm{Bz_2O_2}]$ for experiments at the same monomer concentration should be linear. The data in Table II, plotted in Fig. 2, show that this relation applies very well in solvent-free monomer over a thousand-fold range of peroxide concentrations, and leads to the relation

$$(-\Delta[\mathrm{M}]/\Delta t)^2 = 2.13[\mathrm{Bz_2O_2}] + 0.00014 \quad (15)$$

and hence

$$\frac{k_dfk_p{}^2[\mathrm{M}]^2}{k_{td} + k_{tc}} = 2.13 \quad (16)$$

and

$$\frac{k_ik_p{}^2[\mathrm{M}]^4}{k_{td} + k_{tc}} = 0.00014 \quad (16a)$$

The Thermal Polymerization of Styrene.—Of particular interest here are the failures of the experiments with least and no initiator to obey equation (15).[14] Table II points to a thermal rate at 60° of about 0.0072 mole/l./hr., while literature values are 0.0089,[15] 0.0082[16] and 0.0067.[17] Thermal rates of 0.007 and 0.009 mole/l./hr. are 59 and 76% of those predicted by equation (15), $(0.00014)^{1/2}$ and correspond to proportionately lower radical concentrations. A probable cause of low radical concentrations is an accelerated termination reaction, arising from the fact that radicals must be generated in pairs, instead of statistically throughout the reaction mixture.

Thermal polymerization has been assumed to be initiated by biradicals,[18,3a] because this process has a lower energy requirement than any mechanism which is not at least termolecular. For a biradical of 10,000 styrene units, light-scattering measurements[19] give a root mean square distance between the ends of the biradical of ~1050 Å., whereas the average separation of monoradicals required to give the observed thermal rate (from measurements of the propagation constant[4]) would be about 14000 Å. Thus, internal reactions of biradicals are more probable than interradical reactions and should result in an increased rate of destruction of radicals and a lower radical concentration.[20] However, direct union of radicals in biradicals does not seem necessary to account for the unexpectedly low thermal rate: addition of a small proportion of carbon tetrachloride, sufficient to terminate 60–95% of the polymer chains by transfer and to permit separation of most of the original biradicals, gave

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(13) The specific rate constants for initiation and termination, as defined in ref. (4), are multiplied by 2 to give rates of production and consumption of radicals.

(14) Early peroxide experiments, some of which are listed in Table I, gave no indication of a thermal rate and also were not quite as consistent as the more recent experiments in Table II. The experiments in Table I were therefore used only to determine the *relation* between number average molecular weight and intrinsic viscosity, which should not be affected by minor irregularities in rates.

(15) H. Staudinger and W. Frost, *Ber.*, **68**, 2351 (1935).

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

(17) J. W. Breitenbach and W. Thury, *Anz. Akad. Wiss. Wien, Math.-naturw. Klasse*, **83**, 4 (1946); *C. A.*, **43**, 8735 (1949). Both the rates and intrinsic viscosities obtained by these workers at 60° agree with those found by us.

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

(19) P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

(20) The theoretical considerations of R. N. Haward, *Trans. Faraday Soc.*, **46**, 204 (1950), for a molecular weight of 10^6 and $[\mathrm{R}]\cdot = 10^{-9}$ mole/l., give the ratio of intra-biradical to inter-radical termination as 165:1.

no acceleration of the thermal rate.[21] Accordingly, the low thermal rate seems due mostly to the generation of radicals in pairs, and a similar effect might be expected with other monomers at very low initiator concentrations, in the absence of any biradicals.

It will be shown later in this paper that most radical interactions in polymerizing styrene result in coupling rather than disproportionation, that about one transfer reaction with the monomer occurs for every 17000 propagation reactions, and that the average degree of polymerization for thermal polystyrene at 60° is above 9000. Therefore, if chains start entirely with biradicals and end entirely by coupling, a large fraction of the resulting molecules should be closed rings. Interlocking of these should result in gel formation (as pointed out to us by Professor B. H. Zimm), but such gel formation has not been found.[22] This anomaly suggests either an error in our premises or else a very unusual molecular weight distribution in the thermal polymer. We intend to investigate the latter point.

Chain Transfer of Styrene Radicals with Styrene Monomer and with Benzoyl Peroxide.—Equation (14) contains enough unknowns that some simplification is necessary. We shall therefore assume first that all chains end by coupling (equation 8) so that $k_{td} = 0$, and then we shall see how the results are affected if, instead, all chains end by disproportionation (equation 7) so that $k_{tc} = 0$.

If $k_{td} = 0$, equation (14) may be rewritten

$$\frac{\frac{1}{\bar{P}} - C_m}{[Bz_2O_2]} = \frac{C_I}{[M]} + \frac{k_d f}{-d[M]/dt} \qquad (17)$$

Various values of C_m, the transfer constant of the monomer, were tested in order to determine which value would give the best straight line when $(1/\bar{P} - C_m)/[Bz_2O_2]$ was plotted against the reciprocal of the rate, $1/(-d[M]/dt)$. Results were calculated with $\bar{P}$ calculated from both equations (V) and (VI); the first value given, when numerical values appear in the text, is from equation (VI), the second (in parentheses), from equation (V).

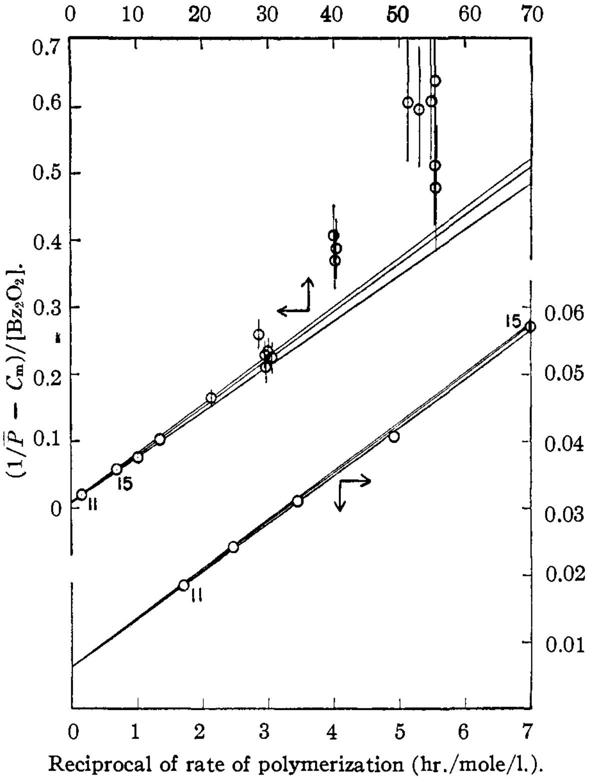

Fig. 3.—Plot of data in Table II according to equations (VI) and (17), to determine rate of initiation and transfer constant of monomer and benzoyl peroxide in the polymerization of styrene at 60°. The center of each circle corresponds to $C_m = 6 \times 10^{-5}$. The upper and lower extremities of the lines through some circles correspond to $C_m = 5$ and 7×10^{-5}, respectively, when these points lie outside the circles.

Inspection of equation (17) shows that the value of the left hand side will be insensitive to C_m at high rates and peroxide concentrations, very sensitive to both C_m and the experimental values of $1/\bar{P}$ at the lowest peroxide concentrations. In fitting various lines to the points, major consideration was given to the experiments on the enlarged scale at the bottom of Fig. 3, only minor consideration to runs where the average peroxide concentration was about 0.0004 mole/l., and no consideration to runs at lower peroxide concentration. The slope and intercept of each line were obtained by a visual fitting to the experimental points, the lines fitting the points closely enough that least squares averaging was not considered necessary. Trials with other values of C_m showed that the experiments at 0.00022 *M* peroxide could *never* be lined up satisfactorily with *all* the experiments at higher peroxide concentration, but since about 23% of the radicals in the low peroxide experiments appear to start as biradicals, the disagreement is not disturbing. Figure 3 illustrates the relation between equation (17) and experiments, using equation (VI) and three values of C_m. The best fits were judged to be those listed in Table III, and for both molecular weight equations, $C_m = 6 \times 10^{-5}$ gave the best fit, with $C_m = 5 \times$

TABLE III

PREFERRED VALUES OF $k_d f$ AND $C_I/[M]$ IN EQUATION (17)

(Polymerization of Styrene by Benzoyl Peroxide at 60°.)

$C_m \times 10^{-5}$	$k_d f$	$C_I/[M]$	
5	0.0074	0.0058	Mol. wt. from eq. (VI)
6	.0072	.0062	
7	.0068	.0070	
5	.0070	.0067	Mol. wt. from eq. (V)
6	.0069	.0068	
7	.0067	.0071	

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[21] Runs with pure styrene and with 2 and 10 volume % of carbon tetrachloride were made in dilatometers at 60° in the complete absence of air according to the technique described elsewhere.[4] Observed rates were 0.00740, 0.00700 and 0.00533 mole/l./hr., respectively, as compared with 0.00740, 0.00710 and 0.00599 calculated for the dilution effect of carbon tetrachloride on an over-all second order reaction. Another run with a different lot of pure styrene gave a rate of 0.00717, showing good agreement with the first blank and the best results in Table II.

[22] A thermal polymerization carried to 96% conversion at 60° gave a polymer which swelled very slowly in benzene without conclusive evidence of gel.

10^{-5} nearly as good and $C_m = 7 \times 10^{-5}$ definitely inferior. We conclude that styrene monomer is about as reactive in chain transfer as ethylbenzene[3c] ($C = 6.7 \times 10^{-5}$). The transfer constant of benzoyl peroxide is then 0.053 (0.059), about six times that of carbon tetrachloride ($C = 0.0092$).[3b]

If $k_{tc} = 0$, equation (14) becomes

$$\frac{1}{\bar{P}} = C_m + C_I\frac{[Bz_2O_2]}{[M]} + \frac{2k_df[Bz_2O_2]}{-d[M]/dt} + \frac{k_i[M]^2}{-d[M]/dt} \quad (18)$$

Making use of the relation from Equations (16) and (16a) that $k_i[M]^2/k_df = 0.00014/2.13$, equation (18) may be put in the form

$$\frac{1/\bar{P} - C_m - 0.0000657k_df/(-d[M]/dt)}{[Bz_2O_2]} = \frac{C_I}{[M]} + \frac{2k_df}{-d[M]/dt} \quad (19)$$

Trial showed that k_df in the left hand term may be taken as half the value determined in Table III for $C_m = 6 \times 10^{-5}$ and with this correction the results in Table IV were obtained by the same process used for Table III. The best fits of most of the points to a straight line were obtained with C_m = 5 or 6 $\times 10^{-5}$ and there was little choice between these values. Comparison of Tables III and IV shows that the mechanism of chain termination has little effect on the value of the transfer constant of benzoyl peroxide or of styrene but that the apparent rate of chain initiation doubles as the termination reaction changes from disproportionation to coupling.

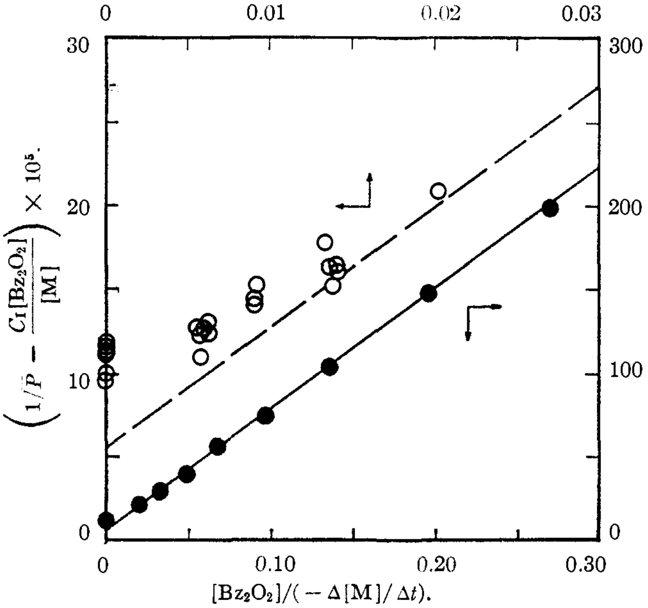

Fig. 4.—Plot of equation (20), taking $C_I/M = 0.0062$ and molecular weights from equation (VI). Open circles are for low-peroxide runs with scale expanded ten times. The broken line near these points is an extrapolation of that through the high-peroxide points.

TABLE IV

PREFERRED VALUES OF k_df AND $C_I/[M]$ IN EQUATION (19)

(Polymerization of Styrene by Benzoyl Peroxide at 60°.)

$C_m \times 10^{-5}$	k_df	$C_I/[M]$	
5	0.0037	0.0058	Mol. wt. from eq. (VI)
6	.00355	.0062	
5	.0035	.0065	Mol. wt. from eq. (V)
6	.00335	.0070	

The following considerations show that the deviations of the low peroxide points in Fig. 3 are consistent with the abnormalities in the thermal polymerization, and also throw some light on the sensitivity of our results to the viscosity-molecular weight relation chosen. If equation (17) is put in the form

$$\frac{1}{\bar{P}} - \frac{C_I[Bz_2O_2]}{[M]} = C_m + \frac{k_df[Bz_2O_2]}{-d[M]/dt} \quad (20)$$

and if $C_I/[M]$ is taken as 0.0062 from Table III, the best fit for the data in Table II, as shown in Fig. 4, is with $C_m = 0.000055$ and with $k_df = 0.00728$, in substantial agreement with Table III. However, the low peroxide points which fell farthest above the lines in Fig. 3 now lie close to the origin, close to the straight line through the other points, and on a smooth curve ending with the point for zero peroxide (which could not be plotted in Fig. 3).[23] Since the peroxide-free runs indicated about half the expected rates in Fig. 2 and about half the expected molecular weights in Fig. 4, the idea that both effects arise from a high termination rate in biradicals is attractive, although the low calculated molecular weights may be due to the effects of large rings on viscosities or to a tendency of the exponent in equations (I)–(VI) to increase[8,19,24] above the range where osmotic molecular weights were measured. In any event, experiments at the two lowest peroxide concentrations exhibit similar effects of intermediate magnitudes. We are therefore justified in neglecting these experiments in Fig. 3 and the accuracy of our values of C_I, C_m and k_df is limited mostly by our molecular weight relations. Tests with equation (20), showed that, as suggested by Tables III and IV, C_m and k_df are insensitive to the molecular weight relation chosen, but that C_I decreased to half its former value when equation (I), corrected for kinetic energy, was substituted for equation (VI).

The only previous values for C_m are those of Bamford and Dewar[9] (their k_3/k_2) at 0 and 25°, and those of Melville and Valentine[25] at 30°. The values of Bamford and Dewar extrapolate to 13.8×10^{-5} at 60°. Since their values depend upon their rate constants for termination by disproportionation (when our data point to coupling), since these constants depend in turn on very high degrees of polymerization at 0 and 25°, well beyond the range in which number-average molecular weights have been measured, and since their molecular weight–viscosity relation is less well established than ours in other ranges, the disagreement is not surprising. In determining C_m (their k_f/k_p) at 30°, Melville and Valentine used benzoyl peroxide concentrations of 0.016

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(23) Plotting the relation (19) in the form $1/P - C_I[Bz_2O_2]/[M] = C_m + 2\,k_df([Bz_2O_2] + 0.000033)/(-d[M]/dt)$ gives results nearly identical with those in Fig. 4 except that k_df is halved and that the zero and low peroxide points now lie farther to the right, about half to two-thirds as far from the broken line.

(24) J. G. Kirkwood and J. Riseman, *J. Chem Phys.*, **16**, 565 (1948).

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

to 0.032 mole/liter, neglected chain transfer with the initiator, and made a long extrapolation, in view of the limited range of their data. That their value, 2.8×10^{-5} at 30°[26] is close to the Bamford and Dewar value, 3.6×10^{-5} at 25°, is not considered significant. The work of Smith[8] on the persulfate-initiated emulsion polymerization of styrene points to a value of $C_m = 2\text{–}6 \times 10^{-5}$ at 60°,[27] but excludes a value as high as that indicated by the work of Bamford and Dewar.

The value of C_I, the transfer constant of benzoyl peroxide with styrene, may be estimated from the work of Nozaki and Bartlett,[28,29] also at 60°. Their expression for the rate of decomposition of benzoyl peroxide in styrene, in our terminology, is

$$-d[Bz_2O_2]/dt = k_d[Bz_2O_2] + k'_d[Bz_2O_2]^{3/2} \quad (21)$$

where k_d (their k_1) is the rate constant for the unimolecular decomposition of peroxide and k'_d (their k_i) is the over-all rate constant for the induced decomposition

$$k'_d = k_I[k_d f/(k_{td} + k_{to})]^{1/2} \quad (22)$$

Since, by Equations (16) and (22)

$$C_I = k_I/k_d = 5.91\, k'_d \quad (23)$$

their results can be compared with ours, as shown in Table V. We consider their over-all rates very satisfactory since we have reproduced them very closely in this Laboratory, with about 0.02 molar solutions of benzoyl peroxide in both styrene and benzene solutions. However, they did not feel able to evaluate k_d and k'_d independently and accurately in the case of styrene, and they chose the ratio of the two, $a(= k_d/k'_d)$, as the value in benzene, 0.386, and then calculated the individual rate constants, as shown first in Table V. Their value of k'_d leads to a value C_I, the transfer constant of benzoyl peroxide, of 0.128, more than twice as large as our values from Equation (17) 0.053 (0.059), appearing last in Table V. Our recalculation of k'_d from their over-all rate data gives a value of C_I somewhat closer to our values but test of the smaller first order rate constant found by them for benzene gives much poorer agreement in C_I. Cohen[30] has measured the rate of decomposition of benzoyl peroxide at different concentrations in 3.46 molar styrene in benzene. As shown in Table V, these data in 40% by volume of styrene, point to a value of k'_d in pure styrene considerably lower than any indicated by Bartlett and Nozaki for either styrene or benzene, but not far from our own, calculated from the transfer constant of benzoyl peroxide. The values of k_d and k'_d, calculated from our values of C_I, show that the spontaneous decomposition of benzoyl peroxide at 60° is 45% faster in styrene than in benzene, and near the average of the other solvents studied by Nozaki and Bartlett. The induced decomposition in styrene is only 55% of the benzene value ($k'_d = 0.0181$), less than in any other solvent studied by these authors; thus the substituted benzyl radical is relatively unreactive, as might be anticipated.

TABLE V

RELATIONS BETWEEN k_d, k'_d, INITIATOR EFFICIENCY AND TERMINATION MECHANISMS[a]

(Polymerization of Styrene by Benzoyl Peroxide at 60°.)

C_I	k'_d	k_d	k_d/k'_d		Chain termination[b]
0.128	0.021[d]	0.0081[d]	**0.386**[c]	0.89(0.85)	C
				.44(.41)	D
.112	.019[e]	**.0088**[e]	.46	.82(.78)	C
				.40(.38)	D
.187	.0316	**.0070**[e]	.221	1.03(.99)	C
				.51(.48)	D
.083	**.014**[f]	**.0081**[f]	.58	.89(.85)	C
				.44(.41)	D
.053[h]	.0090	.0102[g]	1.13	.71	C
				.35	D
(**.059**)[h]	(.0100)	(.0101)[g]	(1.01)	(.68)	C
				(.33)	D

[a] Molecular weights by eq. (VI) (or eq. (V)); boldfaced values in each line are assumed (see footnotes) and other constants in same line are calculated therefrom. All rate constants are in terms of moles, liters and hours. [b] Coupling or disproportionation. [c] Nozaki and Bartlett value for benzene. [d] Calculated by Nozaki and Bartlett for low peroxide concentration. [e] Calculated from Equation (21) and average concentrations from data of Nozaki and Bartlett, using first interval in high $[Bz_2O_2]$ run and 5.5-hour interval (which shows same rate as first interval) in low $[Bz_2O_2]$ run. [f] Equation (21) and the high and low peroxide runs of Cohen at 64° in 40 volume % styrene in benzene lead to $k_d = 0.0156$; $k'_d = 0.0229$. These values were then converted to 60°, using the activation energies for the spontaneous and induced decompositions in benzene of Nozaki and Bartlett, 33,300 and 25,230 cal./mole, respectively. [g] From Equation (21) and low peroxide rate data of Nozaki and Bartlett, as in (*e*). [h] From Tables III and IV, taking $C_m = 6 \times 10^{-5}$.

Efficiency of Initiation.—If we take the limits of k_d in Table V as 0.0070 and 0.0102, we can calculate limits of f, the fraction of radical pairs which start chains, using values of $k_d f$ calculated for $C_m = 6 \times 10^{-5}$ in Tables III and IV. Results are summarized in Table V. If all chains end by coupling, 68–100% of the peroxide molecules which decompose spontaneously start two chains; if all chains end by disproportionation, f is only half as large. Consequently, an independent determination of catalyst efficiency should establish the mechanism of chain termination, and will be considered here.

From the relation between styrene concentration (in toluene) and rate of polymerization at constant concentration of benzoyl peroxide, Schulz and Huse-

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(26) Contrary to the statement of Melville and Valentine, their value of C_m is independent of whether chain termination occurs by disproportionation or coupling.

(27) In Smith's experiments, $1/\overline{P} = C_m +$ half the rate of combination of persulfate/rate of reaction of monomer, so that $C_m =$ (one-half the no. of S atoms per polymer molecule)$/\overline{P}$. His sulfur determinations yield values of C_m from zero up to $4\text{–}5 \times 10^{-5}$ at 50–70°. In the highest intrinsic viscosity polymer (10.6) obtained by him at 50°. $1/\overline{P} \sim C_m$. His estimate of the molecular weight, 8.2×10^6, was made using a correction of the Kirkwood–Riseman[24] or Debye–Bueche[19] type and leads to $C_m = 1.3 \times 10^{-5}$ at 50°. However, the work of T. G. Fox and P. J. Flory (*J. Phys. Colloid Chem.*, **53**, 197 (1949)) indicates that a linear relation for log $[\eta]$ *vs.* log M is satisfactory and from Equation (IV) (not corrected for kinetic energy), $C_m = 2.8 \times 10^{-5}$, also at 50°.

(28) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

(29) Chain transfer of styrene with benzoyl peroxide at 22° has been established qualitatively by J. W. Breitenbach and G. Bremer, *Monatsh.*, **80**, 107 (1949).

(30) S. Cohen, THIS JOURNAL, **67**, 17 (1945).

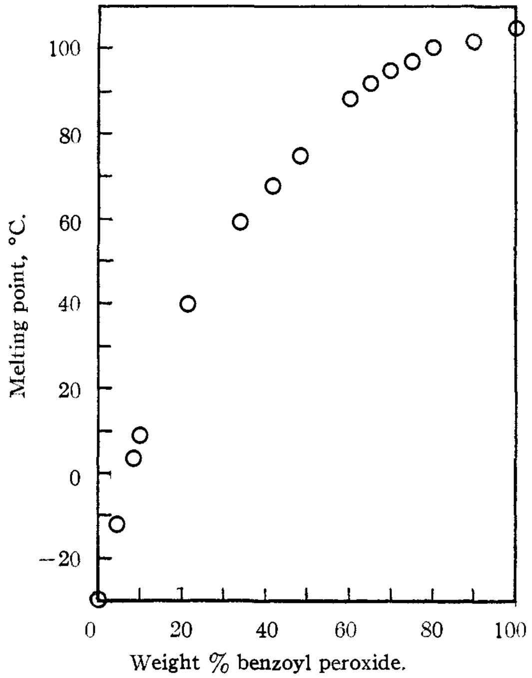

Fig. 5.—Melting point (final disappearance of crystals) of styrene–benzoyl peroxide mixtures, in capillary tubes (60% or more peroxide), or in test-tubes.

mann[31] and Josefowitz and Mark[32] have concluded that styrene and benzoyl peroxide react reversibly to form a 1:1 complex, with equilibrium constants increasing from about 0.2 to 0.36 between 25° and 50°. However, as shown in Fig. 5, melting points of styrene–benzoyl peroxide mixtures give no evidence of complex formation. The completely fused 1:1 mixture (69.94% peroxide) started to crystallize at 90° and was not completely frozen until −29.5° was reached.[33] Accordingly, the suggestion of Matheson[9] that the equilibrium constants of the above workers be interpreted as k_a/k_r seems preferable and without objections.

In order to obtain a direct measure of initiator efficiency at 60° in a solvent less susceptible than toluene to free radical attack, the rates of polymerization of styrene–benzene mixtures containing 0.004 mole/l. of benzoyl peroxide were measured. The cells were filled and the dilatometric rates measured as described elsewhere,[4] and in addition the rates were also determined by isolation of polymer after 10% reaction.[34] Results are summarized in Table VI. According to theory, neglecting the thermal rate at the peroxide concentration used

$$\frac{[\mathrm{M}]^3}{(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)^2} = \frac{k_{tc} + k_{td}}{(k_a/k_r)k_p{}^2k_d[\mathrm{Bz_2O_2}]} + \frac{(k_{tc} + k_{td})[\mathrm{M}]}{k_p{}^2k_d[\mathrm{Bz_2O_2}]} \tag{24}$$

and a plot of $[\mathrm{M}]^3/(-d[\mathrm{M}]/\mathrm{d}t)^2$ against [M], as in Fig. 6 gives $k_a/k_r = 1.18$, and the efficiency, f, is then calculated to be 0.908 in pure styrene.[35] However, the definition of f from the cage effect assumes that k_d is independent of the solvent: monomer ratio, and Table V shows that k_d in styrene may be as much as 40–45% higher than in benzene. Therefore the calculation of f was repeated, assuming that k_d is proportional to $1 + 0.0486$ [M] as [M] varies from zero to 8.63, by plotting $(1 + 0.0486[\mathrm{M}])\ [\mathrm{M}]^3/(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t)^2$ against [M]. As shown in Fig. 6, k_a/k_r then becomes 2.47 and f, about 0.95. Thus the calculated initiator efficiency is not very sensitive to a moderate shift in k_d as the medium changes, and we cannot be sure that k_d changes at all in these mixtures.

TABLE VI

RATE OF POLYMERIZATION OF STYRENE–BENZENE MIXTURES WITH 0.004 M BENZOYL PEROXIDE AT 60°

[M]	$(-\mathrm{d}[\mathrm{M}]/\mathrm{d}t) \times 10^5$ (moles/l./sec.)[a]	g. polymer isolated cc. contraction
8.35[b]	2.55	4.811
5.845	1.734	4.764
3.339	0.930	4.730
0.835	.1855	4.384
.418	.0838	4.505

[a] By isolation of polymer. [b] Pure styrene; 8.63, 25° value, used elsewhere in this paper.

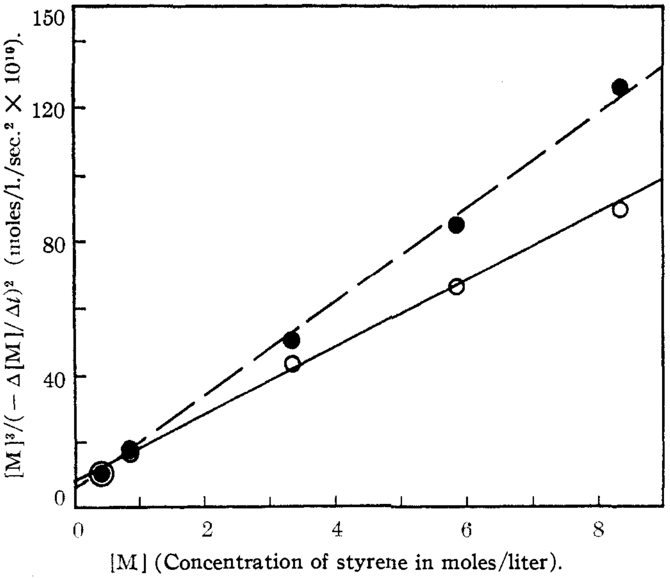

Fig. 6.—Determination of initiator efficiency by equation (24): ○, $[\mathrm{M}]^3/(-\Delta[\mathrm{M}]/\Delta t)^2$ *vs.* [M]; ●, $(1 + 0.0486[\mathrm{M}])\ [\mathrm{M}]^3/(-\Delta[\mathrm{M}]/\Delta t)^2$ *vs.* [M].

The rate data of Schulz and Husemann at 27° and 50°, lead to an efficiency calculated to be 0.71 at 60° if k_d is constant, 0.82 if it increases with

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[31] G. V. Schulz and E. Husemann, *Z. physik. Chem.*, **39B**, 246 (1938).

[32] D. Josefowitz and H. Mark, *Polymer Bulletin*, **1**, 140 (1945).

[33] These esperiments were carried out by Mr. D. M. Alderman, now deceased, in 1943.

[34] Each reaction mixture was washed with benzene into a flask containing 5 mg. of chloranil, and then the solvent and styrene were pumped off using the frozen benzene technique. The final weight of polymer was corrected for the initiator and inhibitor. A small correction was also made for initiator decomposition assuming one CO_2 liberated per molecule decomposed.

[35] Dr. C. H. Bamford has pointed out to us that if appreciable reaction occurs between adjacent 2-benzoxy-1-phenylethyl and benzoxy radicals at the cage, it is not possible to determine f by our method. However, the high efficiencies indicated by the inhibitor method suggest that such reactions are not important.

styrene concentration. The rate data of Josefowitz and Mark at 25° and 47.5° similarly lead to efficiencies of 0.76 and 0.86, respectively.

Further evidence of initiator efficiency comes from other work[4] in which the induction period caused by a known amount of inhibitor was measured and where $k_p^2/(k_{td} + k_{tc})$ was found to be 2.74. Combining this value with equation (16) gives $k_d f = 0.0104$. This value lends support to the highest values of k_d in Table V and points also to an efficiency close to 100%.

The Mechanism of Chain Termination.—All of these efficiency estimates are good evidence that most, if not all, chain termination in styrene at 60° occurs by coupling. If the efficiency of initiation, f, is taken as 0.90, then only in the event that our values of C_I are only half as large as they should be can any disproportionation occur. If disproportionation is to occur, then k_d, the rate of spontaneous decomposition, must be as small or smaller than in benzene, or the efficiency must be smaller than any of our estimates, or both.

Many attempts have been made to determine the number of catalyst residues per polystyrene molecule and thus the relative importance of disproportionation and coupling, but many of these[36] researches suffer from at least one of the following defects: neglect of appreciable chain transfer with the catalyst, high proportion of solvent, high conversion of monomer, high reaction temperature with neglect of thermal reaction, or inconsistent results.[37] Two rather recent papers seem free from these defects and the results point clearly to termination by coupling. M. G. Evans[38] has polymerized styrene in water with ferrous ion and hydrogen peroxide. The molecular weights of polymer fractions were determined by osmotic pressure measurements and hydroxyl determinations on the same fractions indicated somewhat more than two hydroxyl groups per molecule. Smith,[8] in this Laboratory, has investigated the emulsion polymerization of styrene at 39–90° initiated by potassium persulfate with radioactive sulfur. The results also indicate the presence of about two persulfate groups per polymer molecule when the molecular weight is governed by chain initiation.

Kharasch, McBay and Urry[39] have decomposed acetyl peroxide in several alkylbenzenes and have obtained bibenzyl derivatives from coupling of radicals, with no evidence of disproportionation of substituted benzyl radicals. Similar results were obtained with di-*t*-butyl peroxide.[40]

In view of the above results, the conclusion of Banford and Dewar[9] and of Melville and Valentine[25] that chain termination in styrene polymerization occurs only by disproportionation seems unjustified. The former authors draw this conclusion from the results of Price and Tate,[36] whose best experiments employed 20 weight % of tribromobenzoyl peroxide on the styrene and a 20% solution of styrene in benzene, and who found close to one peroxide fragment per molecule. Melville and Valentine have rejected the evidence that small substituted benzyl radicals couple exclusively in the liquid phase on the grounds that other small radicals disproportionate and that even substituted benzyl radicals disproportionate in the vapor phase (at 800°).[41] Their arguments from molecular weights of biradical-initiated polymers have been answered in an earlier section of this paper or in the accompanying paper.[4]

Relative Importance of Chain Terminating Steps.—Figure 7 shows how various termination mechanisms contribute to the over-all molecular weight of styrene polymerized at various concentrations of benzoyl peroxide at 60°. All radicals are taken to interact by coupling; C_m is taken as 6×10^{-5} and C_I as 0.056. $(1/P) \times 10^5$ is the number of polymer molecules (*i. e.*, pairs of chain endings) per hundred thousand styrene units. Although the contribution of chain transfer with the monomer is constant, the proportion of chain endings due to transfer with the peroxide increases steadily with the peroxide concentration.

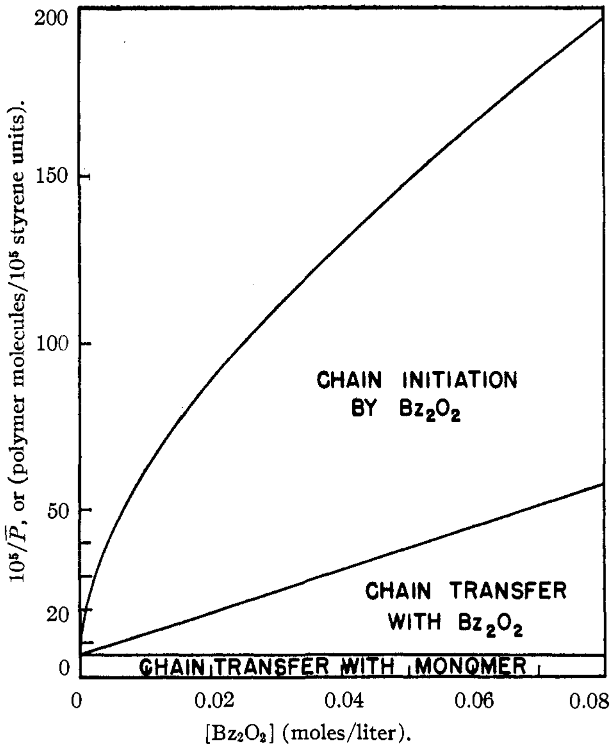

Fig. 7.—Source of chain ends in the polymerization of styrene at 60° as a function of benzoyl peroxide concentration.

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(36) W. Kern and H. Kammerer, *J. prakt. Chem.*, **161**, 81 (1942); C. C. Price, R. W. Kell and E. Krebs, THIS JOURNAL, **64**, 1103 (1942); C. C. Price and D. A. Durham, *ibid.*, **64**, 2508 (1942); C. C. Price and B. E. Tate, *ibid.*, **65**, 517 (1943), A. T. Blomquist, J. R. Johnson and H. J. Sykes, *ibid.*, **65**, 2446 (1943); H. F. Pfann, D. J. Salley and H. Mark, *ibid.*, **66**, 983 (1944); J. W. Breitenbach and H. Schneider, *Ber.*, **76B**, 1088 (1943).

(37) Although Breitenbach and Schneider concluded that their polymer from styrene and *o*-bromobenzoyl peroxide contained one peroxide residue per polymer molecule, molecular weights from our equation VI and their intrinsic viscosities correspond to two residues per molecule.

(38) M. G. Evans, *J. Chem. Soc.*, 266 (1947).

(39) M. S. Kharasch, H. C. McBay and W. H. Urry, *J. Org. Chem.*, **10**, 401 (1945).

(40) W. H. Urry, private communication.

(41) M. Szwarc, *J. Chem. Phys.*, **16**, 128 (1948).

Acknowledgment.—Drs. W. V. Smith, R. H. Ewart and Ellen B. Bevilacqua of this Laboratory have materially assisted the authors through discussions, suggestions and assistance in calculations.

SCHENECTADY, N. Y. RECEIVED JULY 10, 1950

[CONTRIBUTION NO. 108 FROM THE GENERAL LABORATORIES OF THE UNITED STATES RUBBER COMPANY]

Rate Constants in Free Radical Polymerization. III. Styrene[1]

BY MAX S. MATHESON,[2] E. E. AUER, ELLEN B. BEVILACQUA[3] AND E. J. HART[2]

By use of the rotating sector technique, the average lifetimes of growing polystyrene radicals in the photosensitized polymerization of the liquid monomer have been determined at 10, 30 and 50°. Rates of initiation have also been determined by three methods which agree closely: (1) from variation of polymer molecular weight with rate of polymerization, (2) from the rate of decomposition of the initiator, 2-azobisisobutyronitrile, and (3) from the rate of consumption of the inhibitor, 2,2-diphenyl-1-picrylhydrazyl. Comparison of the three methods gives strong evidence that termination occurs mostly by coupling of radicals. From the above experiments, the propagation rate constant, k_p, is found to be $2.16 \times 10^7 e^{-7760/RT}$, and the termination rate constant, $2k_t$, to be $2.59 \times 10^9 e^{-2370/RT}$. The propagation constant is in fair agreement with literature values, but the termination constant is 20-fold that reported by Bamford and Dewar. Reasons are given why our result is to be preferred. At 60° the propagation constant for styrene is one-half that for methyl methacrylate and one-twentieth that for vinyl acetate, while the termination constant for styrene is four times that for methyl methacrylate and one-half that for vinyl acetate. In the initial stages of polymerization the rate constants are found to be independent of radical length. At 40% conversion the termination constant decreases somewhat, but the decrease is less than that found in methyl methacrylate.

Introduction

In the first two papers of this series the application of the rotating sector technique to the measurement of the polymerization rate constants of methyl methacrylate[4] and vinyl acetate[5] was described. In this paper, application of this method to styrene polymerization is reported and discussed. The rate constants obtained are compared with those of Bamford and Dewar,[6] who investigated this monomer with their viscosity method, with those of Melville and Valentine[7] obtained also by the rotating sector method, and with the propagation rate constant found by Smith[8] for the emulsion polymerization of styrene.

Experimental

Purification of Materials.—Dow styrene was distilled under nitrogen through a 50-plate column to give a product, n^{20}D 1.5465, b.p. 44.5° at 18 mm. The product was then recrystallized five times under dry nitrogen with an overall yield of 50%. The recrystallized material was stored in evacuated glass tubes in the dark at −25°. Since biacetyl gave such a low photosensitized rate of polymerization, 2-azobispropane was used as a sensitizer in the styrene experiments. The resulting rate was about twice the rate with biacetyl for equal absorbed intensities at 3660 Å. The 2-azobispropane was synthesized by the method of Lochte, Noyes and Bailey.[9] From the fractionated material a middle cut was retained, b.p. 89.5–90.5 (762 mm.), n^{20}D 1.3903; (lit.,[9] b.p. 88.5° (750 mm.), n^{23}D 1.3890). The α-azobisisobutyronitrile, obtained from the Naugatuck Chemical Division of this company, was recrystallized three times from redistilled C.P. toluene. The ultraviolet absorption curves for 2-azobispropane and α-azo-bis-isobutyronitrile as measured by Mr. M. D. Allen of this Laboratory are given in Fig. 1. A sample of 2,2-diphenyl-1-picrylhydrazyl generously sent by Professor P. D. Bartlett was used without further purification.

Apparatus and Procedure.—The experimental apparatus and procedure were essentially those described in refs. (4) and (5). Irradiations were all at 3660 Å. as in ref. (4). The cells were filled as for methyl methacrylate and vinyl acetate, 2-azobispropane being distilled (and α-azo-bis-isobutyronitrile being weighed) into the reaction cells. The main experimental differences were due to the fact that the polymerization of styrene by light is much slower than that of methyl methacrylate or vinyl acetate, while the thermal polymerization (in the dark) is much faster than with the other monomers. Because of the low rates of photopolymerization, the cells used at 10° and at 30° in sector experiments were surmounted with 1 mm. capillaries instead of 2 mm., except for those reactions photosensitized by α-azo-bis-isobutyronitrile. For accurate results rates had to be measured over a longer period. Further, because of the high thermal or dark rates of polymerization, accurate measurements on the dark rate were necessary. Because the dark rate increased more rapidly with temperature than did the light rate, experiments could not be made at temperatures much above 50° with the available light intensities using 2-azobispropane as a sensitizer. In the experiments at 10° some difficulty was experienced with erratic measurements of rates. This was due to the low rate of polymerization and to the fact that the water in the Dewar surrounding the top of the cell capillary was warmer than the bath and was not stirred by convection. A few degrees change in room temperature was found to affect the temperature of the capillary and the apparent rates. This difficulty was corrected in the vinyl acetate work by providing continuous circulation of water through the Dewar. Except as otherwise noted, no experiment was carried beyond 5–10% conversion.

Densities.—Since the rates were followed dilatometrically, the densities of monomer and polymer must be known as a function of temperature. Further, since monomer and polymer volumes may not be additive in solution,[10] the apparent density of polystyrene in styrene must be determined in the proper concentration range. The polystyrene sample for density experiments was prepared as follows: 200 cc. of styrene plus 0.2 cc. of biacetyl was irradiated *in vacuo* to form a hard polymer. This polymer was cut in strips of 2 mm. square cross section and then heated 20 hours at 120° under continuous evacuation with an oil diffusion pump. Spectroscopic analysis showed less than

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[1] In this paper half of the experiments and all of the preparation for publication were carried out with the assistance of the Office of Naval Research under Contract N8onr-544.

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