Radical Vinyl Polymerization. Reactions of Benzoyl Peroxide during Bulk Polymerization of Styrene with Labeled Initiator†

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ABSTRACT: Styrene was polymerized in bulk at 30 to 80 °C by initiation with ^{14}C-labeled benzoyl peroxide. The rate of polymerization and the rate of incorporation of end groups were measured dilatometrically and by tracer technique, respectively. At constant temperature, but varying initiator concentration, a set of equations was developed for these rates and solved by a Gauss–Newton procedure. From this procedure, (a) the term for rate of production of primary radicals ($2fk_{d,1}$), (b) the constants for secondary as well as induced decomposition of the initiator, (c) the transfer to the initiator, (d) the different initiation rates, and (e) the primary radical termination were determined. By the simultaneous determination of the constants their interdependence was taken into account. The temperature dependence of the secondary initiation ($k_{d,2}$), in contrast to literature data, shows a positive activation energy.

A complicated reaction is kinetically accessible if the different reaction steps can be adequately described in terms of the rate constants and concentrations of different reacting species present in the reaction assembly. In radical polymerization involving a monomer and initiator, this is very often a considerable problem in view of the large number of major and minor reactions.

In radical polymerization with initiator at fixed temperature usually the overall rate of propagation is measured as a function of the concentrations of monomer [M] and initiatior [I]. The result is a quotient of the rate constants for decomposition, propagation, and termination.

$$2fk_d k_p^2/k_t$$

Separate determinations of the effective initiator radicals lead to $2fk_d$ and thus to the ratio k_p^2/k_t.

The observation of the other rate constants as for instance primary radical termination, higher type of initiator decomposition, or transfer is usually done by evaluation of the constant of interest only, setting the other to zero.

A better method would be, e.g., to determine first the constant or ratio for primary radical termination and use this to measure, e.g., the initiations by secondary decomposition of the initiator. In this case there should be an influence of $k_{d,2}$ on $2fk_d k_p^2/k_t$ and $k_{prt}/k_{i,1}k_p$ which hitherto has been neglected.

In this paper a different method of evaluation is applied. With a labeled initiator, in addition to the overall rate of propagation, the rate of incorporation of the initiator into the polymeric chains could be measured. With fixed [M] (bulk polymerization) and T, but seven different initiator concentrations [I], a set of equations for the determination of the different rate constants is available, which is solved numerically by a Gauss–Newton procedure. By this technique, the influence of the different rate constants upon each other is taken into account.

(I) The System Styrene–Benzoyl Peroxide

The polymerization of styrene with benzoyl peroxide (BPO) in the temperature range from 30 to 80 °C is the object of this work. The BPO used is carbonyl labeled with ^{14}C; corresponding tests with ring-labeled BPO are planned.

Styrene with BPO has very often been studied for its polymerization behavior. With labeled BPO, two investigations of the constants for secondary initiation are available from Bevington and Toole,[1,2] who measured two types of initiation at 60 and 80 °C in benzene solution. The evaluation concerned only the secondary decomposition; other effects such as primary radical termination, transfer, etc., were neglected.

It seemed worth while to study the styrene–BPO system again with the following purposes: (1) measurements over a wider temperature range to gain better insight into the temperature dependencies, (2) polymerization in bulk instead of solution, which means one parameter less, [M] = constant, and avoids complications possibly resulting from the solvent influence on the reaction constants, and (3) application of a new evaluation method which takes into account the interdependence of the different rate constants. To our knowledge the number of constants evaluated here is higher than in any other paper on the styrene–BPO system.

Since for BPO the term $2fk_d$ is not known with adequate accuracy, it had to be determined with the other constants: secondary and induced decomposition, primary radical termination, transfer to the initiator, and the individual steps of initiation. In order to handle a limited number of constants, the ratio k_p^2/k_t was assumed to be known in the first attempt to evaluate polymerization reaction kinetics in this manner.

(II) Kinetic Relationships

In connection with the bulk polymerization of styrene, two types of reactions may be distinguished: those mainly connected with the monomer, and others mainly connected with the initiator. The principal purpose of the present work is to examine the kinetic behavior of the initiator benzoyl peroxide.

Under conventional conditions, as is the case in this work, propagation is the main reaction. The consumption of monomer [M] occurs almost exclusively by addition of monomer units to polymer radicals, the concentration of which is [P·]. This is done with a rate of propagation expressed by

$$R_p = k_p[\mathrm{M}][\mathrm{P}\cdot] \quad (1)$$

Usually the conditions are chosen to give kinetic chain lengths ν_0 between $10^2 \leq \nu_0 \leq 10^4$. Then each step of initiation is followed by 10^2 to 10^4 steps of propagation.

The comparatively infrequent nonpropagation steps determine the molecular weight and the molecular weight distribution of the polymer produced and are thus of considerable importance. Special attention is attached to the reactions of termination between two polymer radicals, having the rate[3,4]

$$R_t = k_t[\mathrm{P}\cdot]^2 \quad (2)$$

and of chain transfer to monomer[5,6] with the rate

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† Dedicated to Dr. M. L. Huggins on the occasion of his 80th birthday

$$R_{\mathrm{tr,M}} = k_{\mathrm{tr,M}}[\mathrm{M}][\mathrm{P}\cdot] \tag{3}$$

At the same time, the initiator-specific reactions are of great importance. The initiator radical $[\mathrm{R_i}\cdot]$ starts the polymerization according to

$$R_{\mathrm{i}} = k_{\mathrm{i}}[\mathrm{M}][\mathrm{R_i}\cdot] \tag{4}$$

and, on the other hand, is able to deactivate a polymer radical by a step[7,8] called primary radical termination

$$R_{\mathrm{prt}} = k_{\mathrm{prt}}[\mathrm{P}\cdot][\mathrm{R_i}\cdot] \tag{5}$$

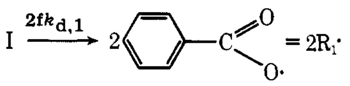
There are many initiators which undergo additional reactions; among them is BPO with unusually many reactions, the behavior of which is not yet fully understood. The transfer constant, commonly considered to be 10^{-2} to 10^{-1}, is surprisingly high.[9] Further, the resulting benzoyl radical partially undergoes secondary decomposition to produce phenyl radicals.[10] The phenyl radicals are likewise able to start kinetic chains and to terminate them.

Because of the versatility of the BPO reactions, it is necessary to apply tracer techniques in order to follow the minor reactions with sufficient accuracy.[1] The benzoyl radical at the initiation reaction and at the primary radical termination also produces benzoate groups, which can be hydrolyzed and thus determined.[11]

It seems useful to review briefly the reactions of interest:

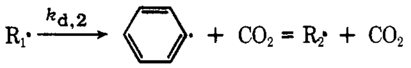
(1) **Rate Constants.** Benzoyl peroxide is one of the most often applied initiators. It shows a broad array of reaction possibilities and has been the object of many experimental investigations.[12] Different steps of formation of radicals have to be taken into account.

Decomposition.



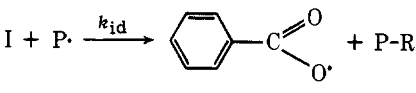
(6a)

primary decomposition



(6b)

secondary decomposition



(6c)

induced decomposition

Initiation.

$$\mathrm{R_1}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{i,1}}} \mathrm{R_1{-}M}\cdot \tag{7a}$$

primary initiation

$$\mathrm{R_2}\cdot + \mathrm{M} \xrightarrow{k_{\mathrm{i,2}}} \mathrm{R_2{-}M}\cdot \tag{7b}$$

secondary initiation

If the ester end groups are eliminated by hydrolysis some $^{14}\mathrm{C}$ activity remains in the polymer. The rest of the remaining activity in the polymer chain, with a rate proportional to R_{p} and [I], corresponds to an initiator transfer with H exchange. This behavior is to be expected only with a reaction which will be named tertiary initiation and described later.

Transfer. In addition to the induced decomposition, eq 6c, we have a transfer with H exchange (end group labeled twice)

$$\mathrm{I} + \mathrm{P}\cdot \xrightarrow{k_{\mathrm{tr,I}}} \mathrm{P} + \mathrm{I}\cdot \tag{8}$$

Since transfer to the monomer is not covered by our experiments, $k_{\mathrm{tr,M}}$ is omitted here.

Termination. Chain termination occurs by one of three reactions:

$$\mathrm{P_n}\cdot + \mathrm{P_m}\cdot \xrightarrow{k_{\mathrm{t}}} \mathrm{P_n} + \mathrm{P_m} \text{ or } \mathrm{P_{n+m}} \tag{9a}$$

polymer radical termination

$$\mathrm{R_1}\cdot + \mathrm{P}\cdot \xrightarrow{k_{\mathrm{prt,1}}} \mathrm{R_1{-}P} \tag{9b}$$

primary radical 1 termination

$$\mathrm{R_2}\cdot + \mathrm{P}\cdot \xrightarrow{k_{\mathrm{prt,2}}} \mathrm{R_2{-}P} \tag{9c}$$

primary radical 2 termination

It is our aim to evaluate the rate constants or ratios of rate constants. For this purpose, three sets of data are accessible: measurements of R_{p} itself, measurements of R_{p} and R_{E} where R_{E} is the rate of incorporation of labeled initiator parts, and measurements of R_{p} and $R_{\mathrm{E,u}}$, with $R_{\mathrm{E,u}}$ the rate of incorporation of the unhydrolyzed parts of the initiator. Thus a sufficient accuracy, at best, could be expected for six constants. Under these conditions, it is reasonable to put

$$k_{\mathrm{prt,2}}[\mathrm{P}\cdot][\mathrm{R_2}\cdot] = 0 \tag{10a}$$

where it follows that

$$k_{\mathrm{i,2}}[\mathrm{R_2}\cdot][\mathrm{M}] = k_{\mathrm{d,2}}[\mathrm{R_1}\cdot] \tag{10b}$$

Indeed, the rate of primary radical termination by $\mathrm{R_2}\cdot$ is negligible for our experiments which will be discussed further in detail.

(2) **Equations for Radicals and Rates of Polymerization as well as Rates of Incorporation of Labeled Initiator.** Free-radical polymerization kinetics give the following equations for primary radicals:

$$\begin{aligned} \mathrm{d}[\mathrm{R_1}\cdot]/\mathrm{d}t &= 2fk_{\mathrm{d,1}}[\mathrm{I}] + k_{\mathrm{id}}[\mathrm{P}\cdot][\mathrm{I}] \\ &= -k_{\mathrm{i}}[\mathrm{M}][\mathrm{R_1}\cdot] - k_{\mathrm{d,2}}[\mathrm{R_1}\cdot] - k_{\mathrm{prt,1}}[\mathrm{P}\cdot][\mathrm{R_1}\cdot] \end{aligned}$$

and for polymer radicals

$$\begin{aligned} \mathrm{d}[\mathrm{P}\cdot]/\mathrm{d}t &= k_{\mathrm{i}}[\mathrm{M}][\mathrm{R_1}\cdot] + k_{\mathrm{d,2}}[\mathrm{R_1}\cdot] \\ &= -k_{\mathrm{t}}[\mathrm{P}\cdot]^2 - k_{\mathrm{id}}[\mathrm{P}\cdot][\mathrm{I}] - k_{\mathrm{prt,1}}[\mathrm{P}\cdot][\mathrm{R_1}\cdot] \end{aligned}$$

Assuming stationary state conditions, $[\mathrm{R_1}\cdot]$ becomes

$$[\mathrm{R_1}\cdot] = \frac{2fk_{\mathrm{d,1}}[\mathrm{I}] + k_{\mathrm{id}}[\mathrm{I}][\mathrm{P}\cdot]}{k_{\mathrm{i}}[\mathrm{M}] + k_{\mathrm{d,2}} + k_{\mathrm{prt,1}}[\mathrm{P}\cdot]} \tag{11a}$$

and the polymer radical concentration becomes

$$k_{\mathrm{t}}[\mathrm{P}\cdot]^2 = 2fk_{\mathrm{d,1}}[\mathrm{I}] - 2k_{\mathrm{prt,1}}[\mathrm{P}\cdot][\mathrm{R_1}\cdot] \tag{11b}$$

$[\mathrm{P}\cdot]$ is taken from eq 1, thus applying the common long-chain approximation.

R_{p} is determined from the volume contraction of the polymerizing system. As was shown recently,[13] it is more reliable to determine $\beta = R_{\mathrm{p}}/[\mathrm{M}]_0$ from

$$\ln \frac{[\mathrm{M}]_0}{[\mathrm{M}]} = \beta \frac{2}{k_{\mathrm{d,1}}} \left[1 - \exp\left(-\frac{k_{\mathrm{d,1}}}{2} t \right) \right]$$

as an average instead of using the initial slope versus time. The change of $[\mathrm{M}]_0/[\mathrm{M}]$ gives more accurate values, even if $k_{\mathrm{d,1}}$ is not exactly known.

The abbreviation

$$F_{\mathrm{prt}} = k_{\mathrm{prt,1}}/(k_{\mathrm{i,1}}[\mathrm{M}] + k_{\mathrm{d,2}})k_{\mathrm{p}}$$

describes a parameter for the primary radical termination depending on [M], where [M] is, of course, a constant for bulk polymerization. With F_{prt} and $C_{\mathrm{id}} = k_{\mathrm{id}}/k_{\mathrm{p}}$, eq 11b becomes

Table I
Rate Constants as a Function of Temperature

t, °C	$2fk_{d,1}$	$(k_{id}/k_p) \times 10^2$	$k_{prt,1}/k_{i,1}k_p$	$(k_{tr,I}/k_p) \times 10^3$
30	7.84×10^{-8}	2.83	4.05×10^6	−0.9
40	2.99×10^{-7}	3.56	9.25×10^5	−0.9
50	1.15×10^{-6}	4.51	2.33×10^5	1.6
60	4.47×10^{-6}	5.80	6.41×10^4	1.5
80	5.06×10^{-5}	7.12	5.70×10^3	5.1

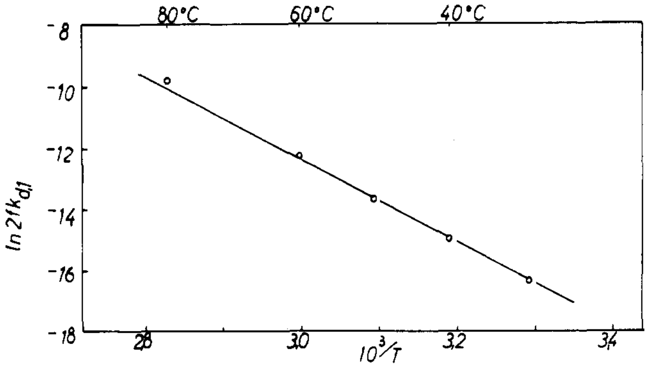


Figure 1. Arrhenius plot of ln $2fk_{d,1}$ as obtained with $k_p{}^2/k_t$ from ref 14.

$$\frac{k_t}{k_p{}^2}\frac{R_p{}^2}{[I][M]^2} = 2fk_{d,1} - 2\left[2fk_{d,1} + C_{id}\frac{R_p}{[M]}\right]\frac{F_{prt}\,(R_p/[M])}{1 + F_{prt}\,(R_p/[M])} \quad (11c)$$

The ^{14}C content is measured as

$$n_E = \frac{\text{counting rate for polymer}}{\text{counting rate for initiator}}$$

and the rate of incorporation into the chain by

$$R_E = n_E R_p$$

Experimentally n_E was determined by liquid scintillation counting with an external standard. The efficiency of the system used (Packard Model 3377) was 70%; the background was 20 cpm. The counting rates were selected between 10^5 and 10^3 cpm for samples before and after hydrolysis, respectively.

BPO was purified chromatographically and by repeated precipitation with methanol from chloroform solution. All traces of initiator were removed from polymer before counting, as was finally proved by GPC fractionation.

The rate of incorporation of ^{14}C into the polymer is given by

$$R_E = k_i[M][R_1\cdot] + k_{prt,1}[P\cdot][R_1\cdot] + (k_{i,d} + 2k_{tr,I})[I][P\cdot]$$

or with eq 11a

$$\frac{R_E}{[I]} = 2fk_{d,1} + 2C_I\frac{R_p}{[M]} - \left[\frac{k_{d,2}}{k_{d,2} + k_i[M]}\right]\frac{2fk_{d,1} + C_{I,d}\,(R_p/[M])}{1 + F_{prt}(R_p/[M])} \quad (12a)$$

$k_{d,2}/(k_{d,2} + k_{i,1}[M])$ corresponds to $(1 - x)$ from Bevington[1,2] and C_I is the relative transfer constant to the initiator obtained from a Mayo plot.

All the polymers with labeled end groups were hydrolyzed. Contrary to expectation, there remained a slight radioactivity. The rate of incorporation ($R_{E,u}$) of remaining ^{14}C after hydrolysis is:

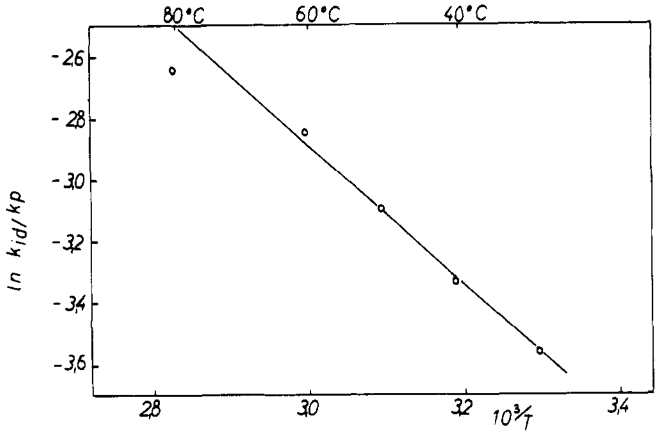


Figure 2. Arrhenius plot for induced decomposition k_{id}/k_p covering only the hydrolyzable initiator parts.

$$R_{E,u} = k_{i,3}[M][R_1\cdot] + 2k_{tr,I}[I][P\cdot]$$

$$\frac{R_{E,u}}{[I]} = \left[\frac{k_{i,3}[M]}{k_{d,2} + k_i[M]}\right]\frac{2fk_{d,1} + C_{i,d}\,(R_p/[M])}{1 + F_{prt}(R_p/[M])} + C_{tr,I}\frac{R_p}{[M]} \quad (12b)$$

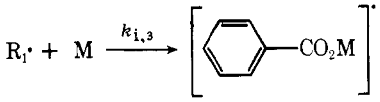
Here it is necessary to split C_I into two terms:

$$c_I = C_{id} + C_{tr,I}$$

and similarly

$$k_i = k_{i,1} + k_{i,3}$$

It was necessary to introduce a third initiation reaction. With the first initiation type, ^{14}C-labeled polymers with ester end groups are formed. The second initiation yields polymers with phenyl end groups, which are unlabeled. The third initiation type results in labeled end groups. This reaction is presently expressed by the following equation



since the site of the active center is not yet known.

(III) Discussion

The aim of this work is a joint evaluation of the relations for the overall rate of propagation, eq. 11c, and for the rates of incorporation of the labeled initiator, eq. 12a and 12b. From eq. 11c the term $2fk_{d,1}k_p{}^2/k_t$ can be determined and from eq. 12a and 12b the term $2fk_{d,1}$. For the joint evaluation of eq 11c, 12a, and 12b (or eq A1a, A1b, and A1c in the Appendix) it is necessary to know the ratio $k_p{}^2/k_t$.

For this purpose, the ratio was taken from

$$(k_p{}^2/k_t) = 13.52 - 57.77[\text{kJ mol}^{-1}]/RT \quad (13)$$

as was recently reported,[14] from our own work using AIBN in connection with the tracer technique. Equation 13 probably is more reliable than the older relations of Henrici-Olivé/and Olivé[5] or Tobolsky and Offenbach,[15] who used the experimental rather inaccurate number average degree of polymerization P_n in determining the numerical values.

In order to obtain the term $2fk_{d,1}$ eq 11c is used, which for $R_p{}^2/[I][M]^2 = 0$ gives $2fk_{d,1}k_p{}^2/k_t$. Thus the extrapolation of the experimental results minus eq 13 determines

$$\ln\,(2fk_{d,1}) = \ln\,(2fk_{d,1}k_p{}^2/k_t)_{extr} - \ln\,(k_p{}^2/k_t)_{eq\,13}$$

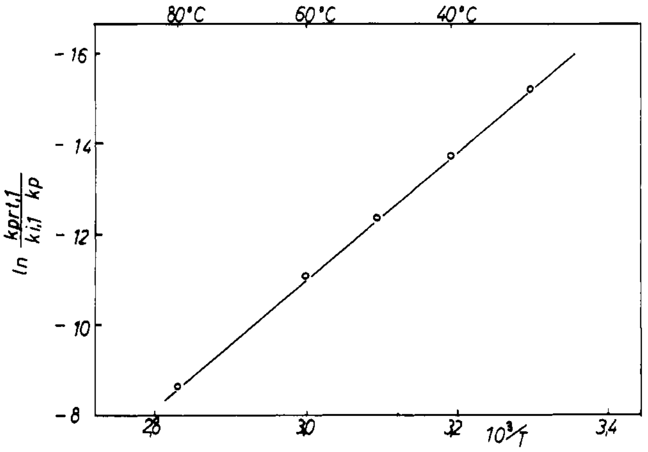


Figure 3. Arrhenius plot for primary radical termination $k_{\mathrm{prt},1}/(k_{\mathrm{i},1}k_{\mathrm{p}})$.

The values of $2fk_{\mathrm{d},1}$ for the different temperatures are summarized in Table I and plotted in Figure 1. This Arrhenius plot results in the relation

$$\ln(2fk_{\mathrm{d},1}) = 26.39 - 107.6[\mathrm{k\ mol^{-1}}]/RT \qquad (14a)$$

Application of the relation of Henrici-Olivé and Olivé[5] instead of our eq 13 would result in an activation energy of 97.1 kJ mol^{-1}; application of the Tobolsky–Offenbach relation[15] gives 101.9 kJ mol^{-1} for the same energy.

Since eq. 14a involves consideration of a whole set of newly determined constants, it should not be directly comparable to literature data. Moreover, the activation energy of $2fk_{\mathrm{d},1}$ is lower than that of the decomposition of benzoyl peroxide in benzene and in the absence of styrene. For the latter case, from data of Barnett and Vaughan,[16] the relation

$$\ln(k_{\mathrm{d}}') = 36.68 - 137.48[\mathrm{kJ\ mol^{-1}}]/RT \qquad (15)$$

may be deduced. The k_{d}' covers a complicated reaction, discussed already by Bartlett and Nozaki.[17] Also the $2fk_{\mathrm{d},1}$ values reported by Tobolsky and Baysal[18] have a lower activation energy, 122.89 [kJ mol^{-1}], then eq 15.

Since the complicated reaction schemes are quite different with and without styrene it is not possible to determine the initiator efficiency f and, therefore, usually the efficiency is declared $f \approx 1$.

The relative constants of induced decomposition of the initiator $k_{\mathrm{id}}/k_{\mathrm{p}}$ are summarized in Table I as well. They concern a very important reaction. The temperature dependence according to Figure 2 is given by

$$\ln(k_{\mathrm{id}}/k_{\mathrm{p}}) = 4.11 - 19.27[\mathrm{kJ\ mol^{-1}}]/RT \qquad (16)$$

or with k_{p} taken from a recent paper[14]

$$\ln(k_{\mathrm{id}}) = 21.86 - 52.84[\mathrm{kJ\ mol^{-1}}]/RT \qquad (16a)$$

The absolute value of $k_{\mathrm{id}}/k_{\mathrm{p}}$ in the temperature range between 30 and 80 °C according to eq 16 is between 10^{-2} and 10^{-1}. For 60 °C we have $k_{\mathrm{id}}/k_{\mathrm{p}} = 5.8 \times 10^{-2}$, while Mayo[19] reported 5.5×10^{-2} and Johnson and Tobolsky[20] 7.5×10^{-2}. The agreement may be called very good considering the different methods of determination, here by radioactive labeling and in the other investigations via the number average degree of polymerization P_{n}. Higher values of $k_{\mathrm{id}}/k_{\mathrm{p}}$ have been reported only by Breitenbach and Schindler,[21] working also with P_{n}.

It is important to take induced decomposition into account as a source of production of primary radicals. At the highest initiator concentrations its contribution is about 21% of the overall production of primary radicals and shows a small temperature dependence only.

Table II
Contributions of the Three Initiation Rates R_{i} in Percent

T, °C	$R_{\mathrm{i},2}/R_{\mathrm{i}}$	$R_{\mathrm{i},1}/R_{\mathrm{i}}$	$R_{\mathrm{i},3}/R_{\mathrm{i}}$
30	40	58	2
40	29	69	2
50	22	77	1
60	16	83	1
80	(1)[a]	(98)	(0.5)

[a] The values of 80 °C are given in parentheses only, since experimental inaccuracy seems to have produced a too low $R_{\mathrm{i},2}/R_{\mathrm{i}}$.

The rate laws for induced decomposition,

$$R_{\mathrm{id}} = k_{\mathrm{id}}[\mathrm{P}\cdot][\mathrm{I}] \qquad (17)$$

and primary radical terminations from eq 9b resemble each other since $[\mathrm{R_I}\cdot]$ is approximately proportional to [I]. With induced decomposition a new primary radical appears which comes from a polymer radical. This makes no significant contribution to the overall rate of propagation, but produces noticeable a reduction in the degree of polymerization. The regular primary radical termination involves the termination of a polymer radical and results in a lower overall rate of propagation. It is possible to determine the contribution of the two reactions separately by conventional kinetics, but the experimental error with the tracer technique should be less.

The overall rate of propagation affects the ratio of

$$\frac{k_{\mathrm{prt},1}}{k_{\mathrm{p}}(k_{\mathrm{i},1} + k_{\mathrm{i},2}/[\mathrm{M}] + k_{1,3})}$$

Only in the case of the same temperature dependencies for the three initiation types could other than an "effective" Arrhenius relation be given. Thus it is reasonable to calculate the ratio for the single initiation constants, of which $k_{\mathrm{i},1}$ is the most important, and this is given in Table I. From these values the Arrhenium relation

$$\ln(k_{\mathrm{prt},1}/k_{\mathrm{i},1}k_{\mathrm{p}}) = -31.58 + 88.65[\mathrm{kJ\ mol^{-1}}]/RT \qquad (18)$$

is obtained; compare Figure 3.

The corresponding relation for azoisobutyronitrile is[14]

$$\ln(k_{\mathrm{prt}}/k_{\mathrm{i}}k_{\mathrm{p}}) = -14.00 + 67.67[\mathrm{kJ\ mol^{-1}}]/RT \qquad (19)$$

A comparison between eq 18 and 19 supports the contention that a benzoyl radical needs an appreciably higher activation energy for initiation.

The transfer constants, also summarized in Table I, show an increase with temperature. The negative values at 30 and 40 °C fall well within the error limits which are at least $\pm 2 \times 10^{-3}$. It appears that no serious error is introduced in the kinetic treatment if this process is neglected.

Of course, there is a dependence of the constants evaluated on the value assumed for the ratio $k_{\mathrm{p}}^2/k_{\mathrm{t}}$. To test this effect, higher values than those resulting from eq 13 were also used. In this case, the initiation constants can become negative, but the shortcoming is minimized in further calculations. As an example, eq 13 at 40 °C gives $k_{\mathrm{p}}^2/k_{\mathrm{t}} = 1.672 \times 10^{-4}$, while from Tobolsky's relation[15] $k_{\mathrm{p}}^2/k_{\mathrm{t}} = 3.521 \times 10^{-4}$ results. The corresponding ratios for primary radical termination were $k_{\mathrm{prt},1}/(k_{\mathrm{i},1}k_{\mathrm{p}}) = 6.37 \times 10^5$ (5.96×10^5) and for induced decomposition $k_{\mathrm{id}}/k_{\mathrm{p}} = 3.56 \times 10^{-2}$ (4.37×10^{-2}), with the values based on Tobolsky in parentheses.

It remains for us to discuss the different initiation steps observed in the experiments described here. The contributions of the individual initiation rates to the overall initiation rate, as calculated with $k_{\mathrm{p}}^2/k_{\mathrm{t}}$ from eq 13, are summarized in Table II. If $k_{\mathrm{p}}^2/k_{\mathrm{t}}$ from ref 5 or 15 is taken instead from eq 13, then

Table III
Comparison of the Measured Values of $R_p/[M]_0$, $n_ER_p/[I]_0$, and $n_{E,u}R_p/[I]_0$ with those Calculated with the Constants in Tables I and II

Time $10^{-4}t$, s	Concn $10^3[I]_0$, mol L^{-1}	Measures values			Calcd with constants of Tables I and II		
		$10^7R_p/[M]_0$, s^{-1}	$10^8n_ER_p/[I]_0$, s^{-1}	$10^9n_{E,u}R_p/[I]_0$, s^{-1}	$10^7R_p/[M]_0$, s^{-1}	$10^8n_ER_p/[I]_0$, s^{-1}	$10^9n_{E,u}R_p/[I]_0$, s^{-1}
$T = 30$ °C							
11.62	96.820	6.522	7.702	1.070	6.263	8.035	1.056
11.52	63,837	5.391	7.085	1.031	5.305	7.521	1.134
12.30	34.654	4.300	6.757	1.325	4.100	6.876	1.233
12.99	23.014	3.375	6.333	1.133	3.424	6.515	1.288
18.18	15.217	2.820	6.115	1.329	2.841	6.204	1.335
25.65	4.184	1.555	5.517	1.433	1.553	5.518	1.438
34.70	1.220	0.883	5.457	1.955	0.856	5.148	1.493
$T = 40$ °C							
4.02	95.829	19.01	32.15	4.176	18.38	33.47	4.674
5.76	63.184	15.36	30.09	4.562	15.44	31.49	4.884
6.00	34.299	11.15	28.58	5.493	11.82	29.05	5.140
7.02	22.778	9.65	27.29	5.180	9.82	27.71	5.280
7.02	15.061	7.61	26.99	6.065	8.11	26.57	5.398
10.38	4.141	4.46	23.95	5.729	4.39	24.09	5.652
11.64	1.207	2.57	22.68	5.643	2.41	22.77	5.786
$T = 50$ °C							
1.49	94.839	54.75	132.2	13.11	52.50	135.9	16.54
1.49	62.531	44.30	125.6	13.68	43.81	128.3	15.04
1.95	33.945	33.55	117.9	13.06	33.28	119.0	13.22
2.14	22.543	27.41	113.9	12.32	27.55	114.0	12.23
2.32	14.906	23.03	109.6	12.13	22.69	109.7	11.39
3.19	4.098	12.22	99.8	9.36	12.20	100.5	9.57
4.44	1.194	6.80	111.3	8.66	6.67	95.7	8.61
$T = 60$ °C							
0.80	93.849	140.4	534.7	56.56	145.6	541.3	57.41
0.53	61.878	120.2	501.5	43.19	120.9	513.2	53.32
0.67	33.590	89.5	478.8	49.47	91.3	479.7	48.39
0.85	22.308	72.4	454.9	47.11	75.4	461.6	45.72
0.95	14.750	61.0	447.1	43.48	61.93	446.3	43.47
1.53	4.055	33.2	415.4	59.15	33.2	413.8	38.64
1.91	1.182	18.1	413.3	35.23	18.09	396.7	36.10
$T = 80$ °C							
0.80	88.200	853.8	6675	698.9	896.0	6318	676.0
0.10	60.572	768.5	6223	570.5	751.8	6106	599.8
0.11	32.882	577.7	5947	514.9	562.7	5828	499.9
0.13	21.837	465.8	5715	440.5	462.2	5680	446.8
0.17	14.439	371.3	5776	416.5	378.3	5556	402.4
0.26	3.970	201.2	5412	313.8	201.0	5295	308.6
0.34	1.157	108.6	5266	246.6	109.2	5160	260.0

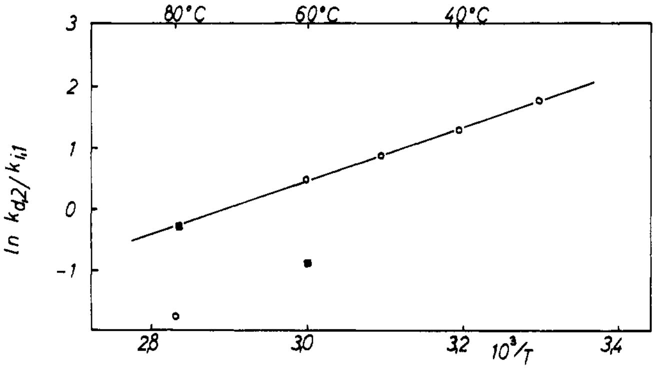


Figure 4. Arrhenius plot of the ratio of the constants for secondary decomposition and primary initiation $k_{d,2}/k_{i,1}$: (■) k_1/k_2 from Bevington,[2] (○) this work.

negative initiation constants occur, which, of course, are physically unreasonable. In Table II the ratio of special interest is

$$\frac{R_{i,2}}{R_i} = \frac{k_{d,2}}{(k_{i,1} + k_{i,3})[M] + k_{d,2}} \tag{20}$$

Quantitative evaluation of the second initiation step has been reported by Bevington and Toole.[1,2] Working with styrene and BPO in benzene they showed that in dilute solution most of the benzoyl radicals develop carbon dioxide before undergoing other reactions. In these experiments effects of induced decomposition are partially included as may be seen from eq 11c.

The two values found were[1,2] $k_1/k_2 = 0.4$ at 60 °C and $k_1/k_2 = 0.7$ at 80 °C. Their constants k_1 and k_2 correspond to the constants of this work as $k_1 = k_{d,2}$; $k_2 = k_{i,1} + k_{i,3}$ or

$$\frac{R_{i,2}}{R_i} = \frac{k_1}{k_2[M] + k_1} = \left(1 + \frac{k_2}{k_1}[M]\right)^{-1}$$

which results (in percent as in Table II) for 60 °C and $[M] = 8.35$ in $R_{i,2}/R_i = 4.6\%$ and for 80 °C in $R_{i,2}/R_i = 8.0\%$ with $[M] = 8.17$, respectively.

In Figure 4 the two values of Bevington and Toole[1,2] are plotted as a function of inverse temperature. In order to place the $R_{i,2}/R_i$ of Table II in this graph, the following equation is used

$$\frac{k_1}{k_2} = \frac{k_{d,2}}{k_{i,1}} = \frac{[M]R_{i,2}/R_i}{1 - R_{i,2}/R_i} \tag{20a}$$

From the eight points in Figure 4 the relation

$$\ln (k_{d,2}/k_{i,1}) = -13.30 + 38.0[\text{kJ mol}^{-1}]/RT \qquad (21)$$

results.

It has to be kept in mind that the primary radical termination by phenyl radicals has been neglected. The error will be largest at 30 °C, when 40% of the secondary initiation takes place, and will almost disappear at 80 °C. Even at 30 °C the error is not expected to exceed 6%. The type of third initiation, resulting from the unhydrolyzed part of the initiator fragments, does not contribute more than 2%.

For $R_{i,3}/R_{i,1} = k_{i,3}/k_{i,1}$ the Arrhenius relation is

$$\ln (k_{i,3}/k_{i,1}) = -18.39 + 37.78[\text{kJ mol}^{-1}]/RT \qquad (22)$$

The accuracy of the determination of $k_{i,3}/k_{i,1}$ is well beyond the experimental error limits. Speculating, one could say $k_{d,2}$ and $k_{i,3}$ belong to correlated reactions and perhaps are characterized by similar activation energies. Nevertheless, it could be imagined that the reaction of the benzoyl radical with the monomer results in an oxazolyl radical which then initiates the carboxyl group. This type of initiation contributes to the unhydrolyzable part of the activity distinctly more than transfer to the initiator.

(IV) Conclusion

Applying dilatometric measurements of R_p in connection with a tracer technique to the initiated radical polymerization of styrene in bulk with benzoyl peroxide as initiator, a simultaneous evaluation of the constants for primary radical termination, for secondary and induced decomposition, for transfer to the initiator, and for the different types of initiation was reported. The method involved a simultaneous calculation of the different constants by numerical least-squares method using measurements with different initiator concentrations. This evaluation technique takes into account the interdependence of the single constants and thus demands less presuppositions then others. It seems worth while to develop it further.

Appendix

When evaluating the rate measurements alone, eq 11c necessitates further approximations; compare, e.g., ref 22. Here no such procedure is required. At each temperature seven different initiator concentrations are measured. Thus seven sets of data for the three relations 11c, 12a, and 12b are available. The six quantities in question have to be fixed in such a manner as to simultaneously minimize the error for the three equations.

For brevity, the following expressions are introduced:

$$X_1 = 2fk_{d,1};\ X_2 = \frac{k_{prt,1}}{k_i k_p[M]_0};\ X_3 = \frac{k_{id}}{k_p}$$

$$X_4 = \frac{k_{i,1}}{k_{i,1} + (k_{d,2}/[M])};\ X_5 = \frac{k_{i,3}}{k_{i,1} + (k_{d,2}/[M])};\ X_6 = \frac{k_{tr,I}}{k_p}$$

Equations 11c, 12a, and 12b can be rewritten as

$$[1 + X_2\beta]\left[\frac{k_t\beta^2}{k_p{}^2[I]}\right] = X_1 - [X_1 + 2X_3\beta]X_2\beta \qquad (A1a)$$

$$[1 + X_2\beta]\left[\frac{n_{E-E,u}\beta[M]}{[I]}\right] = X_3\beta + [X_1 + 2X_3\beta]X_2\beta - X_4[X_1 + X_3\beta] \qquad (A1b)$$

$$[1 + X_2\beta]\left[\frac{n_{E,v}\beta[M]}{[I]}\right] = X_5[X_1 + X_3\beta] + X_6\beta[1 + X_2\beta] \qquad (A1c)$$

Adding eq A1a and A1b yields

$$(1 + X_2\beta)\left[\frac{k_t\beta^2}{k_p{}^2[I]} + \frac{n_{E-E,u}\beta[M]}{[I]}\right] = [1 - X_4][X_1 + X_3\beta] \qquad (A2)$$

Using $Y_i = Y_{i,1} + Y_{i,2}$ for the left-hand-side term in square brackets and applying the least-squares method, it follows that

$$\sum_i \beta_i Y_i{}^2 = X_1[1 - X_4] \sum_i \beta_i Y_i + X_3[1 - X_4] \sum_i \beta_i{}^2 Y_i - X_2 \sum_i \beta_i{}^2 Y_i{}^2 \qquad (A3a)$$

$$\sum_i \beta_i Y_i = X_1[1 - X_4] \sum_i \beta_i + X_3[1 - X_4] \sum_i \beta_i{}^2 - X_2 \sum_i \beta_i{}^2 Y_i \qquad (A3b)$$

$$\sum_i Y_i = X_1[1 - X_4] \sum_i \beta_i{}^0 + X_3[1 - X_4] \sum_i \beta_i - X_2 \sum_i \beta_i Y_i \qquad (A3c)$$

This set of three linear equations is solvable elementarily and the solutions are

$$X_2;\ (1 - X_4)X_1;\ (1 - X_4)X_3$$

These can be used for a new system of three equations containing only known quantities on the lhs.

$$\left[\frac{1 + X_2\beta_i}{1 - X_2\beta_i}\right]Y_{1,i} = X_1 - 2X_3\left[\frac{X_2\beta_i{}^2}{1 - X_2\beta_i}\right] \qquad (A4a)$$

$$\left[\frac{(1 - X_4)[X_1 + X_3\beta_i]}{1 - X_2\beta_i}\right] - \left[\frac{1 + X_2\beta_i}{1 - X_2\beta_i}\right]Y_{2,i} = X_1 - 2X_3\left[\frac{X_2\beta_i{}^2}{1 - X_2\beta_i}\right] \qquad (A4b)$$

$$[1 + X_2\beta_i]Y_i = X_1X_5 + X_3X_5\beta_i + X_6\beta_i[1 + X_2\beta_i] \qquad (A4c)$$

In eq A4a and A4b the essential terms X_1 and X_3 are linear, and for the three equations a quasilinear Newton calculus is possible.

The quality of the results of this numerical calculation is tested with the observed constants as summarized in Tables I and II. These are inserted into eq 11c, which is of the third power in the overall rate of propagation R_p. R_p is computed and then used to determine n_E and $n_{E,u}$ from eq 12a and 12b, respectively.

The measured and computed $R_p/[M]_0$, $n_E R_p/[I]_0$, and $n_{E,u}R_p/[I]_0$ are compared in Table III. The reproduction of the measured values by the calculated ones seems to be quite acceptable.

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