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APPLICATION OF A CALORIMETRIC METHOD IN RADIATION-INDUCED POLYMERIZATIONS—I

DETERMINATION OF PROPAGATION AND TERMINATION RATE CONSTANTS FOR METHYL METHACRYLATE

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Abstract—A calorimetric method, in which a thermistor was the temperature sensitive element, has been adapted for following the non-stationary states of the polymerization of methyl methacrylate, induced by γ-rays.

A polymerization rate dependence on (dose rate)$^{\frac{1}{2}}$ has been found over the approximate range from 0·2 to 20 rad/sec and at temperatures between −25° and 55°.

Values of the ratio of the propagation to termination rate constants have been determined in this range of temperatures by following the initial and final non-stationary states, immediately after the irradiation is abruptly started or reduced.

Using values of the initiation rates, determined by means of the DPPH inhibition method, the individual values of the rate constants have been obtained. They obey closely the Arrhenius law over the range of temperature investigated.

INTRODUCTION

IN FREE-RADICAL polymerizations, if the simplified kinetic scheme holds, the steady-state rate R_p is given by:

$$R_p = \frac{k_p}{k_t^{\frac{1}{2}}} (M)\, R_i^{\frac{1}{2}} \tag{1}$$

where: k_p and k_t are the rate constants for chain propagation and chain termination, respectively

(M) is the monomer concentration and

R_i is the initiation rate.

The individual values of k_p and k_t can be deduced by measuring R_p and R_i, and knowing the ratio k_p/k_t. The latter can be determined by following the initial or final non-stationary states, whenever the free-radical production is abruptly started or interrupted.$^{(1)}$

A number of examples have been reported, where polymerization is initiated by u.v. rays, mostly in the presence of a photosensitizer.

An experimental technique commonly adopted for following the polymerization kinetics in the non-stationary state is based on recording rapidly by means of thermocouples$^{(2-4)}$ or thermistors$^{(5-7)}$ the temperature rise (ΔT) due to the heat of polymerization according to:

$$\Delta T = -\frac{\Delta H}{C_M}\left[\frac{-\Delta(M)}{(M)}\right] \tag{2}$$

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where: $\Delta(M)/(M)$ is the fraction of the monomer converted to polymer,

ΔH is the molar enthalpy change of polymerization and
C_M is the monomer molar thermal capacity.

Adiabatic conditions are ensured by the fact that the reactions have to be followed only for very short times and the temperature-sensitive element is situated at the centre of the reacting system. The method of earlier workers$^{(2-6)}$ is based on the equation:

$$\frac{-\Delta(M)}{(M)} = k_p/k_t \ln\left(\cosh \frac{t}{\tau}\right) \tag{3a}$$

which gives $-\Delta(M)/(M)$ as a function of time (t) from the initial instant of polymerization, τ being the average lifetime of the chain radicals. When t exceeds 3τ, the non-steady state ends and the curve (3a) approximates closely to the straight line:

$$\frac{-\Delta(M)}{(M)} = k_p/k_t \left(\frac{t}{\tau} - \ln 2\right) \tag{3b}$$

which intersects the time-axis at $\tau \ln 2$ and the slope of which is $k_p/k_t\tau$, a term equal to $R_p/(M)$ when equation (1) holds.

The method of later workers$^{(7)}$ is based on an equation obtained for the non-stationary state resulting from a sudden decrease in the rate of free radical production:

$$\Delta\left[\frac{-\Delta(M)}{(M)}\right] = -\frac{k_p}{k_t} \ln\left[1 - \frac{(M\cdot)_i - (M\cdot)_f}{(M\cdot)_i + (M\cdot)_f}\right] \tag{4}$$

where $\Delta[-\Delta(M)/(M)]$ is the fractional conversion increment occurring during the decrease in the polymer radical concentration from the initial steady-state concentration $(M\cdot)_i$ to the final steady-state concentration $(M\cdot)_f$ and to be attributed to the fraction of polymer radicals exceeding $(M\cdot)_f$.

In this work, both methods of determining k_p/k_t have been applied to the polymerization of methyl methacrylate induced by ^{60}Co γ-rays, using a thermistor as a temperature-sensitive element.

EXPERIMENTAL

Materials

Methyl methacrylate (kindly supplied by Montecatini Edison S.p.A.) was repeatedly washed with 10 per cent solutions of $Na_2S_2O_3$, NaOH and with distilled water, dried over anhydrous Na_2SO_4 and fractionally distilled under 100 mmHg of N_2 at 47°. The middle fraction was collected, re-distilled, transferred to the high-vacuum line and degassed. After pre-polymerization by γ-rays, carried out until the monomer became viscous, it was distilled under vacuum into the reaction vessel. After this treatment, no induction period was observed.

1,1′-diphenyl-2-picrylhydrazyl (DPPH), as high purity crystals for e.p.r., was a Fluka product and used as received.

Chloroform was a C.Erba R.P. product and purified by a twofold fractional distillation.

Apparatus

The reaction cell and the arrangement for control of temperature and exposure to γ-rays are shown in Figs. 1 and 2 respectively. The temperature changes during irradiation are determined by measuring the corresponding resistance changes of the thermistor, using a Wheatstone bridge in which the produced off-balance voltages, suitably amplified, are fed to a galvanometer equipped with a pen recorder, whose drum was made to move at speeds of up to 18 mm/sec by applying external synchronous motors. The apparatus has already been described in detail elsewhere.$^{(8)}$

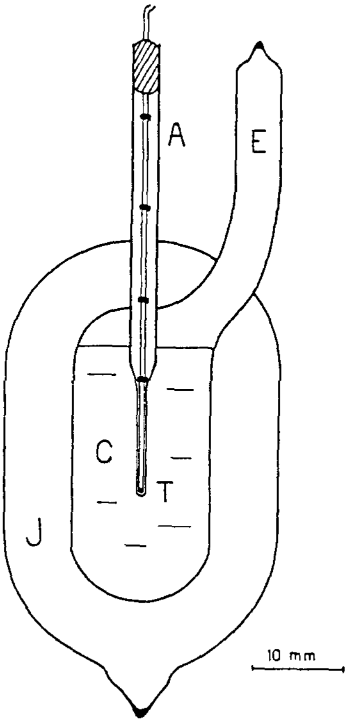

FIG. 1. Pyrex glass apparatus for following polymerizations calorimetrically. C = 6 ml capacity cell; T = bead type thermistor; A = sheath for the thermistor and cables; E = side tube; J = jacket.

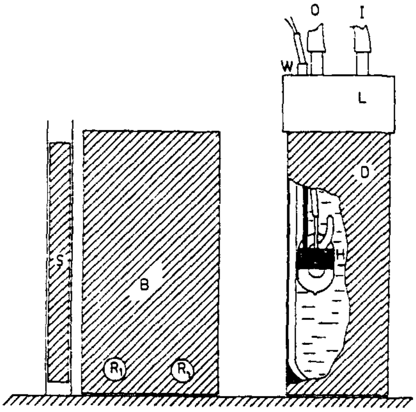

FIG. 2. Arrangement for starting radiation-induced polymerizations abruptly. S = ^{60}Co source; B = lead brick; R_1 and R_2 = steel bars; D = Dewar; H = brass holder; L = teflon lid; I and O = inlet and outlet of thermostat fluid (water or methanol); W = hole for thermistor wires.

The irradiations were made at nearly a dozen dose rates, which were obtained by placing the reaction cell at different distances from a 1000 Curie ^{60}Co source, and have been determined by means of the Fricke solution irradiated in the reaction cell, using G(Fe^{3+}) = 15·6.

The interposition of a lead brick, as indicated in Fig. 2, prevented the reaction cell from being exposed to a varying radiation intensity during the time required for the ^{60}Co source to be fully extracted. The lead brick was made to slide horizontally on two steel bars, so that the irradiation could be started abruptly.

By a compressed air operated machine (Waircom API, Milan), which was electrically controlled, the lead brick (22 cm high, 15·5 cm long and with a thickness variable up to 12 cm) was either interposed between the source and the cell or removed so quickly that the latter became fully shielded or fully unshielded in less than 0·02 sec. At the moment of shielding or of unshielding the cell, the lead brick actuated a solenoid by which a pen mark was made on the recording paper.

PROCEDURE

When a substance is irradiated for the time t, the following relation can be applied:

$$I_M t = C_M \, \Delta T + \Delta U \tag{5}$$

where: I_M is the dose rate of energy absorbed by a mole of substance;

ΔT is the temperature increment in adiabatic conditions after the irradiation time t;

ΔU is the energy change produced in a mole of substance by the composition changes which occurred in the irradiation time t.

If ΔU is negligible in comparison with $I_M t$, the temperature increment ΔT is practically given by $I_M t/C_M$. This was the case with liquids in which the radiation-induced changes of composition occurred only to a very small extent,$^{(8)}$ and should be approximately verified in inhibited monomers. Actually slightly higher ΔT values were found with inhibited methyl methacrylate, probably due to incompletely suppressed polymerization.

When inhibitor-free monomers are irradiated, a contribution to the temperature increment, due to the energy change ΔU resulting from polymerization, must be taken into account. Since this is defined by Eqn. (2), the total temperature increment is approximately given by:

$$\Delta T \simeq \frac{I_M t}{C_M} - \frac{\Delta H}{C_M}\left[\frac{-\Delta(M)}{(M)}\right]. \tag{6}$$

Although the energy absorption contribution is rigorously equal to $I_M t/C_M$ only if no composition changes occur, the differences arising in case of polymerization should not be such to affect appreciably Eqn. (6), especially when $I_M t/C_M$ is only a comparatively small fraction of the total temperature increment.

To apply the procedure based on Eqn. (3a), substitution of (3a) in (6) is made, obtaining:

$$\Delta T \simeq \frac{I_M t}{C_M} - \frac{\Delta H}{C_M}\frac{k_p}{k_t}\ln\left[\cosh\frac{t}{\tau}\right] \tag{7a}$$

which gives ΔT as a function of time t from the start of irradiation.

When t exceeds 3τ, the non-stationary state ends, and the curve (7a) approximates closely to the straight line:

$$\Delta T \simeq \left[\frac{I_M}{C_M} - \frac{\Delta H}{C_M}\frac{k_p}{k_\tau}\right] t + \frac{\Delta H}{C_M}\frac{k_p}{k_t}\ln 2. \tag{7b}$$

From the slope, which can be referred to as the stationary-state rate of temperature increase $(\mathrm{d}T/\mathrm{d}t)_s$, $R_p/(M)$ can be obtained knowing I_M, C_M and ΔH.

The intercept x on the time-axis is readily recognized to be:

$$x = \tau \ln 2 \left[1 - \frac{I_M/C_M}{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_s}\right]. \tag{8a}$$

An example of a run is shown in Fig. 3 where the galvanometric deflection, proportional to the rise in temperature of the monomer at the thermistor position, is recorded. Line AB gives the thermal drift and the points B and E correspond to the pen marks B′ and E′ made at the instants the cell becomes unshielded and shielded, respectively. Between B and E, the curve initially is accelerating and, from D onwards, becomes a straight line in agreement with the fact that (7a) approximates (7b) after a certain time. The slope of DE gives $(\mathrm{d}T/\mathrm{d}t)_s$; x, as defined by (8a), can be obtained from the segment BC, allowance being made for the measuring circuit response lag c.

Let x' denote the segment BC; then:

$$x' = c + \frac{k_p \ln 2}{k_t} \left[1 - \frac{I_M/C_M}{\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_s}\right] \bigg/ \frac{R_p}{(M)}. \tag{8b}$$

Carrying out experiments at different dose rates and plotting x' against

$$\left[1 - \frac{I_M/C_M}{(\mathrm{d}T/\mathrm{d}t)_s}\right] \bigg/ [R_p/(M)],$$

a straight line is to be expected which cuts the x' axis at a time equal to c and from whose slope k_p/k_t can be obtained, provided the response lag is of the same order of magnitude or less than the free-radical life-times being measured.

In order to apply Eqn. (3a) rigorously, the free-radical concentration in the system at the moment when the shield is removed, $(M\cdot)_b$, should be negligible in comparison with the steady-state free-radical concentration attainable with the shield removed, $(M\cdot)_s$.

The maximum value to which the ratio $(M\cdot)_b/(M\cdot)_s$ may reach is given by the ratio of the steady-state polymerization rate with shield in place to the steady rate with the shield removed.

With the radiation shielding employed in this work, this ratio could not be considered truly negligible. However, to attain the stationary state with inserted shield, a rather long time was required, owing to the long free-radical life-time. Therefore the value $(M\cdot)_b$ could be made sufficiently small by reducing to a minimum the irradiation time with interposed shield after extraction of the source.

To apply the procedure based on Eqn. (4), experiments were carried out in the same way as above, but attention was paid to the final part of the curve DEFG of Fig. 3, which had to be considerably prolonged at the expense of the initial part. For this purpose, before the removal of the shield, the Wheatstone bridge was unbalanced in such a way that the recording of the galvanometer deflection started from the point D onwards.

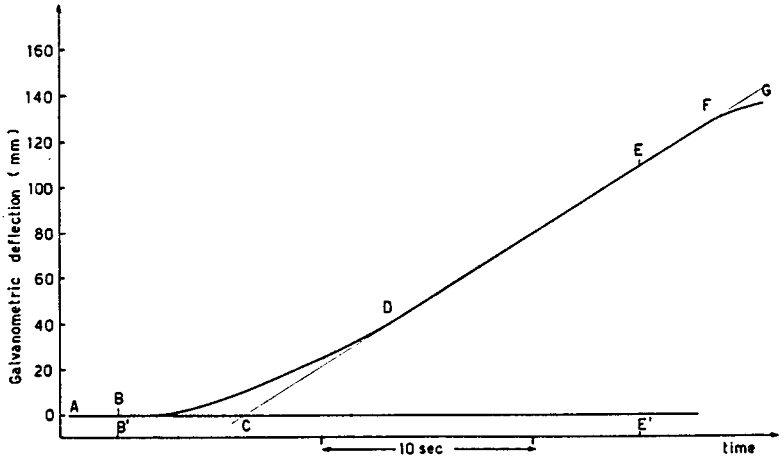

FIG. 3. Recorder curve of methyl methacrylate polymerization at 5·1° and 2·04 rad/sec, measurement sensitivity = 1·293 × 10^{-4}°C/mm).

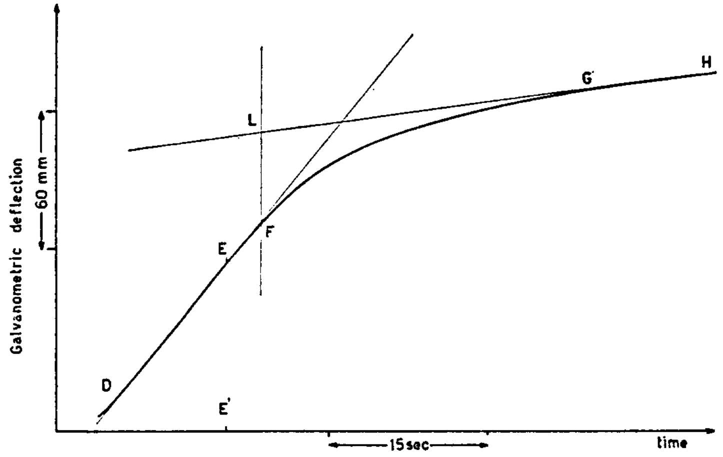

FIG. 4. Recorder curve of methyl methacrylate polymerization at 5·0° and at 2·04 rad/sec, measurement sensitivity = 1·293 × 10^{-4}°C/mm).

An example is shown in Fig. 4. From the slope of line DE, the steady-state fractional conversion rate with removed shield $[R_p/(M)]_i$ is obtained, as before. At the instant E, the reaction cell becomes shielded by a lead brick with a thickness such that the radiation intensity reduced to about 1/100 of the previous value. Thus, after the circuit response lag *c* and precisely from point F onwards, the slope appears to decrease continuously in accordance with the sudden reduction of the term I_M/C_M and the progressive decay of the free-radical concentration from the steady value $(M\cdot)_i$ without the shield in place to the steady value $(M\cdot)_f$ with the shield in place. From point G onwards, $(M\cdot)_f$ is attained, and the slope remains constant as long as the adiabatic conditions prevail; from it, the steady-state fractional conversion rate with interposed shield, $[R_p/(M)]_f$, can be deduced.

The segment FL gives the temperature increment $\Delta(\Delta T)$ attributable to the polymerization fractional conversion increment

$$\Delta\left[\frac{-\Delta(M)}{(M)}\right],$$

as defined by Eqn. (4), thus:

$$\Delta(\Delta T) \simeq \frac{\Delta H}{C_M}\cdot\frac{k_p}{k_t}\ln\left[1-\frac{(M\cdot)_i-(M\cdot)_f}{(M\cdot)_i+(M\cdot)_f}\right] \tag{9}$$

by which k_p/k_t can be readily obtained from the experimental data, since the logarithmic term is evidently equal to

$$\ln\left[1-\frac{(R_p)_i-(R_p)_f}{(R_p)_i+(R_p)_f}\right].$$

Determination of the rate of initiation of polymerization (R_i) was made by the use of DPPH as inhibitor, which is assumed to react with small polymer radicals with 1 : 1 stoichiometry, thus:

$$R_i = \frac{[\mathrm{DPPH}]}{t_i}, \tag{10}$$

where t_i is the induction period.

For measuring the induction period, a given amount of a standard solution of DPPH in chloroform was introduced into the cell and, after evaporation of the solvent, the monomer was added as usual. The increase of temperature occurring during radiation was recorded at a low amplification factor of the measuring circuit, and at a low speed of the recorder drum. The consumption of DPPH was revealed by a rising of the galvanometric deflection from a negligible value to very high values with a slope at first continuously increasing and then continuously decreasing. The end of the induction period could be taken either at the inflection point, where the maximum rate of polymerization could be assumed, or at the point of intersection with the time axis obtained by prolonging the almost linear part of the curve, where the polymerization was not yet occurring at a substantial rate.

TABLE 1. VALUES OF DENSITY, MOLAR THERMAL CAPACITY (C_M) AND HEAT OF POLYMERIZATION (ΔH) AT VARIOUS TEMPERATURES FOR METHYL METHACRYLATE

Temperature (°C)	Density (g/ml)	C_M (cal/°C, mole)	ΔH (kcal/mole)
−24	0·991	41·6	−13·00
−15·0	0·981	42·2	−13·20
−5·0	0·971	43·1	−13·35
5·0	0·960	44·0	−13·50
15·5	0·948	44·8	−13·65
25·0	0·937	45·8	−13·80
34·0	0·927	46·7	−14·00
43·3	0·915	47·7	−14·20
52·2	0·902	48·4	−14·35

The molar heats of methyl methacrylate at the various experimental temperatures (Table 1) were either literature data(9, 10) or values obtained from them by means of interpolation and extrapolation.

The molar enthalpy change (ΔH) for converting liquid methyl methacrylate into polymer dissolved in a large amount of monomer at 25° was taken as $-13 \cdot 80$ kcal/mole ($-13 \cdot 8 \pm 0 \cdot 2$ at $26 \cdot 9°$).(11) Since the temperature coefficient is very small, the values at other experimental temperatures could be calculated satisfactorily by means of the monomer specific heats from Table 1 together with the polymer specific heats reported in the literature.(9, 12, 13)

Literature values of monomer densities were also used to calculate monomer concentrations.(14)

RESULTS

With every new batch of monomer, a number of runs were carried out, some of them as a test for reproducibility. Every batch was used for conversions less than 1 per cent to obtain polymerization rates in a polymer-free system. In agreement with the results of North *et al.*,(15) a decrease in polymerization rates with conversion was found in batches of monomer polymerized up to 5–8 per cent conversions by successive short irradiation runs, carried out at 5·1° using either a dose rate of 6·40 rad/sec throughout or different dose rates. However, as to be expected when the polymer mol. wt. is rather low,(15) the decrease was rather slight in the above conditions.

Polymerization runs, relative to the method based on Eqn. (3a), were made for the whole series of dose rates at intervals of 10° in the range −25° to 55°. The reproducibility of $(\mathrm{d}T/\mathrm{d}t)_s$ values was found to be within 5–7 per cent, except at the low temperatures and dose rates. The results at 5·1° are reported in Table 2. Column 4 indicates the smallness of the energy absorption contribution to the total rate of temperature rise.

The values of R_p obtained at all the temperatures are displayed in Fig. 5, in which $\log_{10} R_p$ is plotted vs. $\log_{10}$ (dose rate). The experimental points lie on straight lines, with slopes equal to $0 \cdot 50 \pm 0 \cdot 01$.

The temperature dependence of the ratio $k_p/k_t^{\frac{1}{2}}$ can be readily established by plotting $\log_{10} R_p/M$ vs. (absolute temperature)$^{-1}$ at constant R_i. Choosing the latter as the value corresponding to the rate of energy absorption 3/d rad/sec, denoting d as the monomer density, the straight line of Fig. 6 is obtained. From the slope, the activation energy is 3·9 kcal/mole.

In order to determine the value of $k_p/k_t^{\frac{1}{2}}$ at 5·0°, the inhibition method measurements of R_i have been performed at two greatly different dose rates. In Fig. 7 each concentration of DPPH is plotted against the two inhibition times obtained by the two ways of choosing the end points. Both the alignment of the resulting points and the agreement between the two different choices support the reliability of the adopted procedure. Table 3 shows the two values of R_i, together with the values of $k_p/k_t^{\frac{1}{2}}$ and the free-radical yield G_R deduced from them. The R_p values are derived from the data of Fig. 5.

Taking the average of the two values in Table 3 for $k_p/k_t^{\frac{1}{2}}$ at 5·0°, the ratio $k_p/k_t^{\frac{1}{2}}$ at any other temperature within the investigated range is given by:

$$\log_{10} (k_p/k_t^{\frac{1}{2}}) = 1 \cdot 46 - 846/T. \qquad (11)$$

TABLE 2. POLYMERIZATION OF METHYL METHACRYLATE AT 5·1° AND AT THE DOSE RATES UTILIZED THROUGHOUT THIS WORK; DATA OBTAINED BY MEANS OF THE METHOD BASED ON EQN. (3a)

Dose rate (rad/sec)	$\left(\frac{dT}{dt}\right)_s \times 10^3$ (°C/sec)	$I_M/C_M \times 10^3$ (°C/sec)	$\frac{I_M/C_M}{(dT/dt)_s}$	$\left[\left(\frac{dT}{dt}\right)_s - \frac{I_M}{C_M}\right] \times 10^3$ (°C/sec)	$[R_p/(M)] \times 10^6$ sec^{-1}	$R_p \times 10^6$ (moles/l.sec)	$\left[1 - \frac{I_M/C_M}{(dT/dt)_s}\right] / \frac{R_p}{(M)}$ $\times 10^{-4}$(sec)	x' (sec)
22·3	2·70	0·121	0·045	2·58	8·40	80·6	—	—
11·1	1·90	0·060	0·032	1·84	5·99	57·4	—	—
7·52	1·49	0·041	0·028	1·45	4·72	45·3	20·6	4·6
4·97	1·27	0·027	0·021	1·24	4·04	38·7	24·2	4·8
3·27	0·967	0·018	0·019	0·949	3·09	29·6	31·7	5·2
2·04	0·749	0·011	0·015	0·738	2·40	23·0	41·0	6·0
1·21	0·615	0·007	0·011	0·608	1·98	19·0	49·9	6·4
0·624	0·465	0·003	0·006	0·462	1·50	14·4	66·2	7·2
0·359	0·321	0·002	0·005	0·319	1·04	9·97	95·2	8·7
0·228	0·279	0·001	0·004	0·278	0·906	8·69	109·9	10·0

The values of x' were not determined at the highest dose rates, because in those cases the shielding brick arrangement could not be utilized.

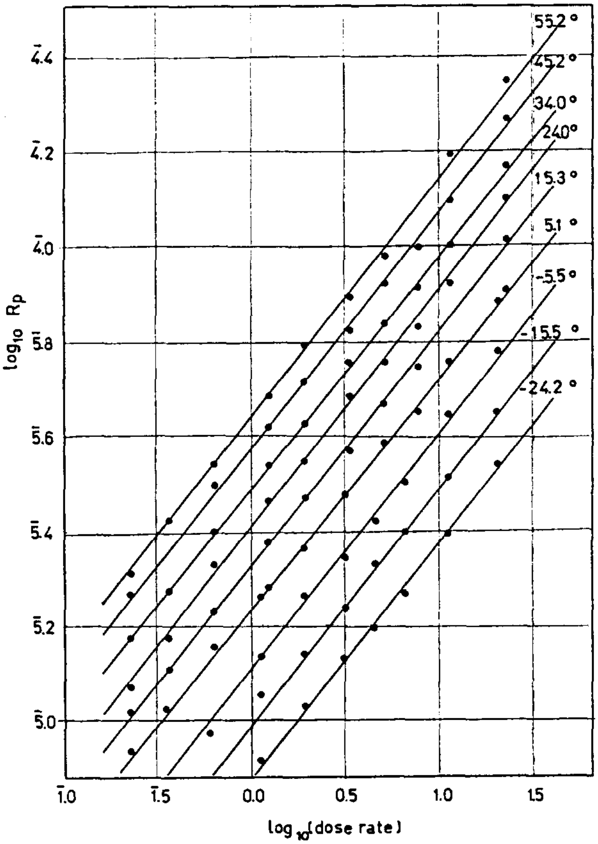

FIG. 5. Dose rate dependence of polymerization rate for bulk methyl methacrylate. The temperature of polymerization is shown on each curve.

TABLE 3. DATA FOR THE POLYMERIZATION OF METHYL METHACRYLATE AT 5·0° AT TWO DOSE RATES. INITIATION RATES (R_i) OBTAINED BY INHIBITION METHOD

Dose rate (rad/sec)	$R_i \times 10^8$ (moles/l.sec)	$R_p \times 10^6$ (moles/l.sec)	$\frac{k_p}{k_t^{\frac{1}{2}}} \times 10^2$	G_R
10·04	4·90	54·4	2·56	4·9
1·75	0·82	23·0	2·64	4·7

The ratios k_p/k_t according the method based on Eqn. (3a) were obtained from the values of x', taken simultaneously with the values of $(dT/dt)_s$ from the recorded curves. It must be mentioned however, that, unlike $(dT/dt)_s$, the values of x' were found reproducible only within 20–30 per cent and sometimes, especially at the low temperatures, the reproducibility was even poorer.

The results at 5·1° are reported in Table 2.

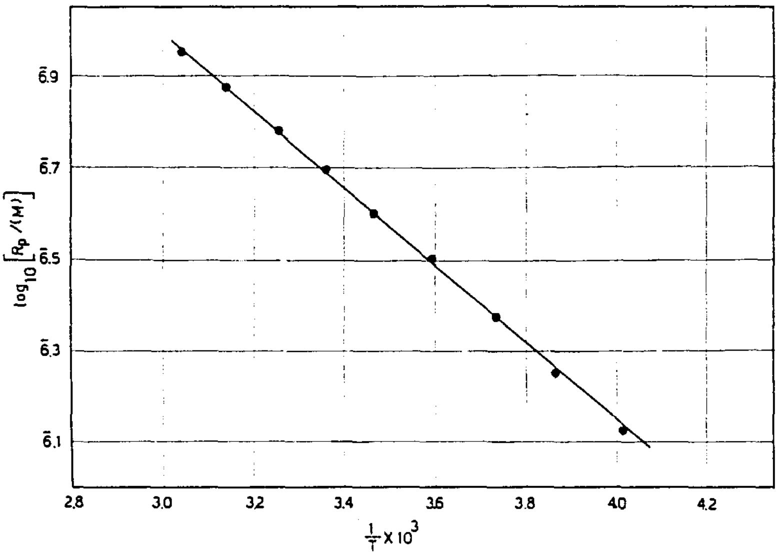

FIG. 6. Arrhenius plot of the fractional conversion rates of methyl methacrylate polymerization taken from Fig. 5 at dose rate of 3/d rad/sec, where d is the monomer density at each temperature.

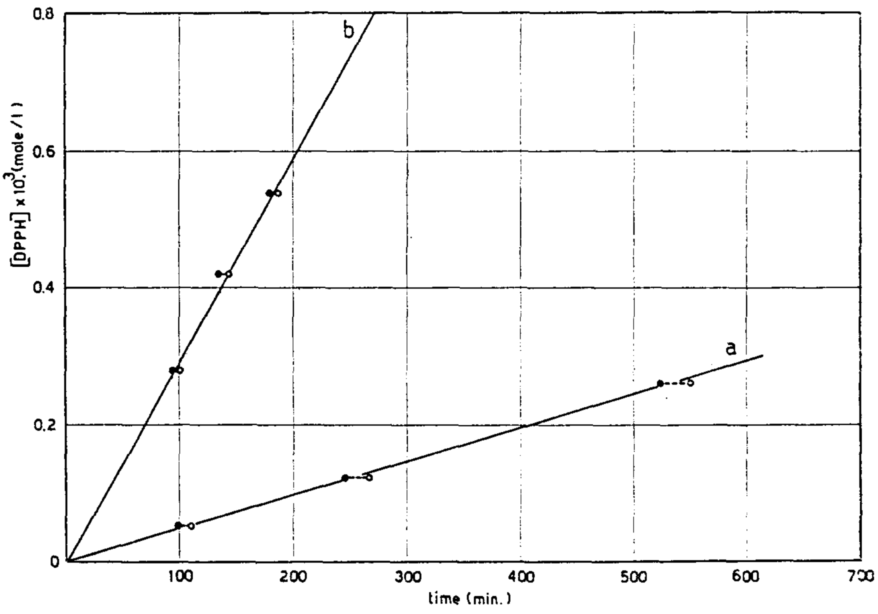

FIG. 7. Determination of rate of initiation for the bulk polymerization of methyl methacrylate at 5·0° at the dose rates: (a) 1·8 and (b) 10·1 rad/sec. DPPH concentrations are plotted against induction times, taken from: (●) the inflection point of the galvanometric deflection/time curves, (○) the intercept with the time axis by extension of the curve linear portions.

The diagrams obtained by plotting x' against

$$\left[1 - \frac{I_M/C_M}{(\mathrm{d}T/\mathrm{d}t)_s}\right] \Big/ \frac{R_p}{(M)}$$

are shown in Fig. 8 for some of the investigated temperatures. Though the points appear to be scattered, fairly good straight lines can be drawn and both the instrument lag and the ratios k_p/k_t can be determined. The values of k_p/k_t thus derived are reported in Table 4.

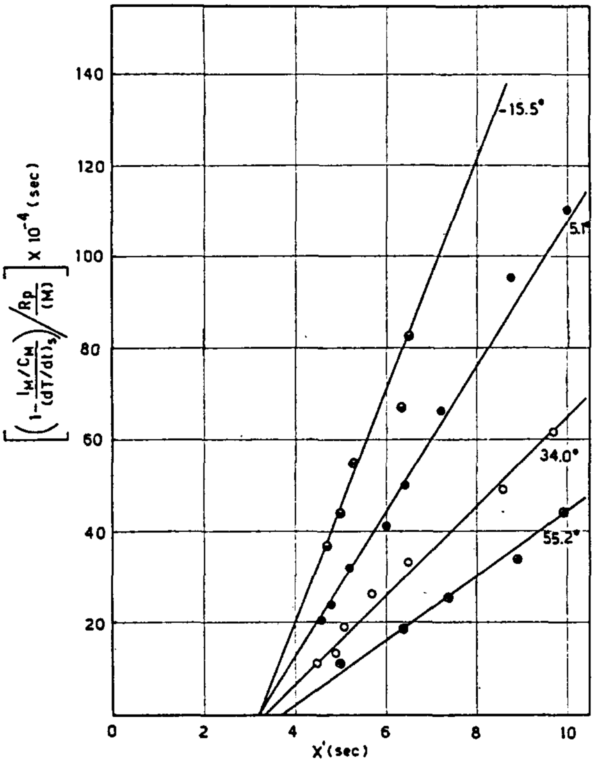

FIG. 8. The variation of the rate with radical life time for the bulk polymerization of methyl methacrylate. The temperature of polymerization is indicated on each curve.

The same table also contains the average values of k_p/k_t obtained by the method based on Eqn. (4); the reproducibility was found to be within 8 per cent also at low temperatures.

The point F in Fig. 4, which was determined from point E by taking the instrument lag equal to that found under the same conditions with the other method, was always nearly coincident with the point of divergence between the recorder curve and its slope. Always the steady-state polymerization rates with the shield in place were checked by means of runs carried out entirely with the interposed shield, where obviously the requirement of adiabatic conditions could be better fulfilled.

Table 4 shows that there is satisfactory agreement between the two series of ratios k_p/k_t. This also can be seen in Fig. 9, where the values of $\log_{10} k_p/k_t$ are plotted against

TABLE 4. RATIO BETWEEN THE PROPAGATION AND TERMINATION RATE CONSTANTS (k_p/k_t) IN THE POLYMERIZATION OF METHYL METHACRYLATE. DATA OBTAINED AT A NUMBER OF TEMPERATURES BY (a) METHOD BASED ON EQN. (3a); (b) METHOD BASED ON EQN. (4)

					(a)				
Temp. °C	55·2	45·2	34·0	24·8	15·3	5·1	−5·5	−15·5	−24·7
$k_p/k_t \times 10^6$ Eqn. (3a)	20·1	16·7	14·4	12·5	11·0	9·25	6·0	5·8	8·1
					(b)				
Temp. °C	56·3	45·3	34·8	24·8	14·8	5·8	−5·5	−14·5	−24·2
$k_p/k_t \times 10^6$ Eqn. (4)	18·6	15·5	14·4	12·0	11·1	9·7	8·37	7·15	6·58

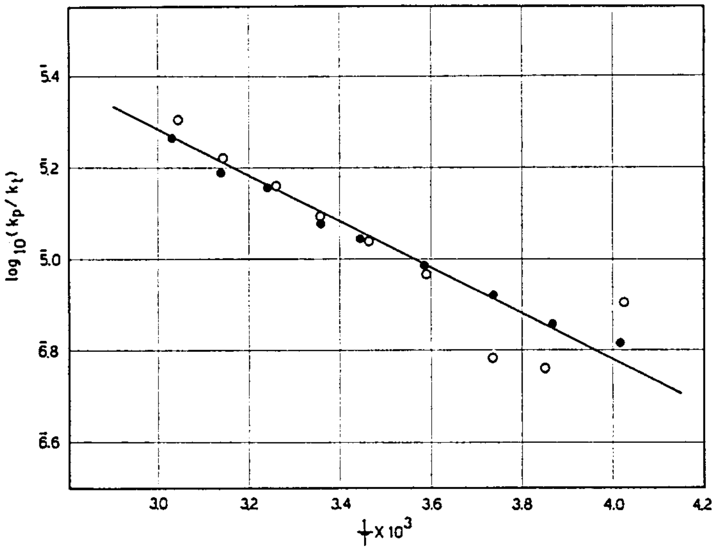

FIG. 9. Arrhenius plot of the ratio of the propagation to termination rate constants for methyl methacrylate polymerization: (○) method based on Eqn. (3a); (●) method based on Eqn. (4).

(absolute temperatures)$^{-1}$. Apart from the poorly reproducible data obtained with the method based on Eqn. (3a) at low temperatures, all the other points are not widely scattered from the straight line. Because of the better reproducibility, in drawing the line, greater importance has been attached to the measurements carried out with the method based on Eqn. (4).

From Fig. 9 it can be deduced:

$$\log_{10} \frac{k_p}{k_t} = -3{\cdot}20 - \frac{504}{T}. \tag{12}$$

From Eqns. (11) and (12) the individual values of the rate constant are given by:

$$\log_{10} k_p = 6{\cdot}12 - \frac{1188}{T} \text{ or } k_p = 1{\cdot}3 \times 10^6 \, \mathrm{e}^{-5450/RT} \tag{13}$$

$$\log_{10} k_t = 9{\cdot}32 - \frac{684}{T} \text{ or } k_t = 2{\cdot}1 \times 10^9 \, \mathrm{e}^{-3150/RT}. \tag{14}$$

Measurements for polymerization rate were also made at 25·0° with methyl methacrylate diluted with chloroform. The procedure was the same as in bulk polymerization, with I_M, C_M and density replaced by the sums of the contributions of the components of the mixture.

The results obtained with three solutions are summarized in Fig. 10. It can be seen that in all cases $\log_{10} R_p$ is a linear function of $\log_{10}$ (dose rate) as in the bulk polymerization, only the slope shows a slight tendency to decrease with dilution from the value of 0·5; slopes of 0·48, 0·46 and 0·44 are found for the solutions with monomer to solvent ratios of 1:1, 1:5 and 1:14, respectively.

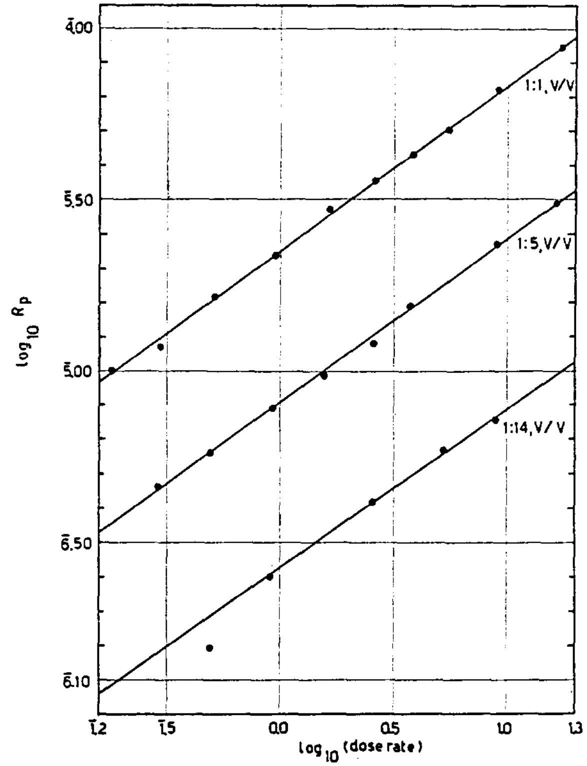

Fig. 10. Dose rate dependence of rate of polymerization at 25·0 for methyl methacrylate dissolved in chloroform. The monomer to solvent volume ratios are shown.

DISCUSSION

For the validity of the calorimetric method for following polymerizations induced by γ-rays, reference should be made to what has been said in the case of the photopolymerizations followed calorimetrically(2–4) and with a thermistor as the sensitive element.(5–7) Furthermore, it should be mentioned that the rates of absorption of γ-ray energy measured by calorimetry in liquids undergoing no chemical changes, are in good agreement with those determined by the Fricke dosimeter.(8)

Actually, in the cited experiments at 5·1° up to 5–8 per cent conversion either with a constant dose rate of 6·40 rad/sec or with different dose rates, in which at intervals the polymerization rates were controlled, the conversions calculated from the polymerization rates were somewhat lower than those obtained by weighing the polymer produced. However, these discrepancies should not be considered to invalidate the calorimetric data, the test being rather crude.

In order to compare the rates of polymerization obtained in this work with existing literature data, use can be made of the $\log_{10}/\log_{10}$ diagram in which the polymerization rates from previous studies, normalized at 20°, have been reported as a function of dose rate by Chapiro.(16) It can be verified that, within the range of the dose rates investigated in this work, the straight line which is interpolated at 20° from the data of Fig. 5, agrees at high dose rates but lies below Chapiro's curve at lower dose rates, where our values of R_p amount to about 2/3 of the literature values. In view of the differences in experimental conditions, the disagreement can be regarded as tolerable.

An essential discrepancy, however, can be seen between the dose rate dependence found in this work and that reported in the literature. While for the latter the slope of the plot $\log_{10} R_p/\log_{10}$ (dose rate) is 0·5 only at low dose rates and decreases at high dose rates, in this case the slope is 0·5 over the whole range investigated. Consequently, also the assumption of a decreased efficiency of chain initiation at relatively high dose rate, advanced to explain the previous data, should be rejected if the present results are reliable.

In order to investigate this point further, the dose rate dependence of polymerization rate has been measured with methyl methacrylate dissolved in chloroform. In this way, decreasing with dilution the monomer efficiency in scavenging primary radicals, the reaction in which primary radicals disappear by mutual interaction should become increasingly competitive at a constant or increasing dose rate and so of radical production. For the latter condition to be fulfilled, it is sufficient to operate at constant dose rate, in view of the radiolysis behaviours of methyl methacrylate and chloroform. If the dose rate is so chosen that competition between the two reactions occurs to some extent even in bulk, a substantial decrease in chain initiation efficiency is to be expected at the reduced monomer concentrations of the solutions.(16) But this seems not to be the case for the whole range of dose rates here investigated, since the square root relationship continues to hold satisfactorily down to very low concentrations, even though a tendency to curve cannot be ruled out in the plots $\log_{10} R_p/\log_{10}$ (dose rate) of Fig. 10, as indicated by the decrease of the slope below 0·5.

For all these results, with which also the G_R values found at the two different dose rates by means of the inhibition method are consistent, Eqn. (1) can be considered to hold in these experimental conditions and consequently the methods based on Eqns. (3a) and (4) should be applicable for the determination of the ratio k_p/k_t.

From the results of these determinations, it appears that the two methods, though relative to the pre-effect in one case and the post-effect in the other case, do not concern conditions characterized by different rate constants also at the lower temperatures, in contrast to what has been observed by other workers.(17)

In the comparison with the k_p/k_t data listed in Ref. 18, to which a few others can be added,(6, 15, 17, 19, 20) the values of Table 4 are found to agree fairly well with most of them and quite well with the k_p/k_t values, (multiplied by 10^6): 7·8 (5°), 10·9 (30°), 16·1 (50°) and 20·6 (60°) by Matheson *et al.*;(14) 9·8 (15°), and 13·6 (30°) by Bengough *et al.* (2a); 11·0 (25°) by Chinmayanandam *et al.*;(21) 14·0 (30°) and 19·0

(50°) by Fujii *et al.*;(22) 13·0 (20°) by Fujii *et al.*;(6) 14·3 (30°) by North *et al.*;(15, 19) 12·1 (30°) by Yokota *et al.*(20)

As to the temperature dependence of k_p/k_t and of $k_p/k_t^{\frac{1}{2}}$, it can be inferred from Fig. 9 and especially from Fig. 6 that there is no marked deviation from the Arrhenius law as would be expected by a marked change with temperature of the relative importances of combination and disproportionation in the chain termination step,(23) the activation energies for the two reactions being different. The results are better accounted for by a chain termination step in which either disproportionation prevails over combination for the whole temperature range(17, 24, 25) or the diffusion together of two reactive macromolecular centres is rate-determining.(15, 17, 19, 20)

In the light of recent data,(15, 17, 19, 20, 26, 27) the latter interpretation should be favoured, though it does not strictly require the validity of Arrhenius law for k_t. A steady change in the apparent termination activation energy observed over the temperature range from −23° to 40° has been explained by the similar change of activation energy for viscous flow of polymer solutions,(27) while a discontinuity in activation energy for termination, on passing from high to low temperatures, has been correlated with a transition from a random flexible coil to a random rigid coil.(17, 28)

In the derivation of Eqns. (13) and (14) for the rate constants for propagation and termination, determinations of rates of initiation are involved; the various available methods have been discussed.(25) The inhibition method with DPPH is likely to give higher values than other methods and consequently lower values of $k_p/k_t^{\frac{1}{2}}$ and, for fixed k_p/k_t values, lower values of both k_p and k_t; this point should be taken into account when rate constants from different sources are compared.

In the comparison with the published data on k_p and k_t, obviously confined to those derived by utilizing the above cited ratios k_p/k_t in order to avoid fortuitous coincidences, the values calculated from Eqns. (13) and (14) are found to agree satisfactorily with those reported in Table 5. The rate constants from Ref. 14 can be seen to be very close to the corresponding values of this work; there is some difference in their temperature dependence. This is in line with the different activation energies determined experimentally: 4·89 instead of 3·9 kcal/mole for $k_p/k_t^{\frac{1}{2}}$ and 3·47 instead of 2·3 kcal/mole for k_p/k_t.

TABLE 5. RATE CONSTANTS FROM DIFFERENT SOURCES FOR THE PROPAGATION (k_p) AND TERMINATION (k_t) REACTIONS IN THE POLYMERIZATION OF METHYL METHACRYLATE

	k_p (l/mol sec)					k_t 10^{-6} (l/mol sec)				
Temp.		Reference					Reference			
(°C)	this work	(14)	(23)	(15)	(20)	this work	(14)	(23)	(15)	(20)
5	71	60				7·2	8·2			
30	162	143	251	229	141	11·5	12·2	21	16·0	11·6
40	214		322			13·8		22		
50	275	295	410			15·8	16·7	24		
60	355	367	515			18·6	18·7	25		

With the data of Ref. 23, for which use has been made of the k_p/k_t values of Ref. 14 and of revised values of $k_p/k_t^{\frac{1}{2}}$, the agreement is not so good. Assuming the revised data as more reliable,(29) an explanation for the fact that the derived k_p and k_t are approximately 1·5 times as great as those of this work, is to be found in the difference between the methods used to determine R_i.

To this respect, it should be noted that the activation energy of 3·9 kcal/mole found here for $k_p/k_t^{\frac{1}{2}}$ is close to the value of 4·16 of Ref. 23.

As to the other data in Table 5, relative to only a single temperature, the rate constants from Ref. 15 are not claimed to be very accurate and those from Ref. 20 are very close to the results of this work, in accord with the fact that the DPPH inhibition method has been utilized in both cases.

Regarding the average G_R value of 4·8 for methyl methacrylate here obtained, a comparison with existing data is not easy and very meaningful since the published values are so widely scattered; however it is not very dissimilar from those found by other authors using DPPH.(16) Therefore it seems justifiable to consider the calorimetric method as suitable for determining the individual rate constants for the propagation and termination reactions in free-radical polymerization induced by γ-radiation.

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Résumé—Pour suivre l'état non-stationnaire de la polymérisation du méthacrylate de méthyle induite par le rayonnement γ, on a mis au point une méthode calorimétrique dans laquelle l'élément sensible à la température est une thermistance.

On a trouvé que la vitesse de polymérisation variait en (intensité)$^{\frac{1}{2}}$ pour un domaine d'environ 0,2 à 20 rad/sec et à des températures comprises entre −25 et 55°.

Les valeurs du rapport des constantes de vitesse de propagation et de terminaison ont été déterminées dans ce domaine de température à partir de la mesure des états non-stationnaires initial et final qui se produisent immédiatement après que l'irradiation soit brusquement commencée ou reduite.

En utilisant les valeurs des vitesses d'amorçage, déterminées par la méthode d'inhibition au DPPH, on a obtenu les valeurs de chacune des constantes de vitesse. Elles obéissent étroitement à la loi d'Arrhénius dans le domaine de température considéré.

Sommario—Si e' adattato un metodo calorimetrico, basato sull'impiego di un termistore, per seguire gli stati non stazionari nella polimerizzazione del metilmetacrilato, indotta da raggi γ.

Si e' trovato che la velocita' di polimerizzazione dipende dalla radice quadrata della velocita' di dose nell'intervallo che va circa da 0,2 a 20 rad/sec e per temperature comprese fra −25° e 55°.

A queste temperature si sono determinati i rapporti fra le costanti di velocita' di propagazione e quelle di terminazione seguendo, immediatamente dopo il brusco inizio o riduzione dell'irraggiamento, i risultanti stati non stazionari iniziali e finali.

Usando i valori delle velocita' di inizio determinati per mezzo del metodo d'inibizione con il difenilpricrilidrazile, i singoli valori delle costanti di velocita' sono stati ottenuti. Essi obbediscono con buona approssimazione alla legge di Arrhenius nell'intervallo di temperatura esaminato.

Zusammenfassung—Eine calorimetrische Methode mit einem Thermistor als temperaturempfindlichem Element wurde ausgearbeitet, um die nicht stationären Zustände der durch γ-Bestrahlung induzierten Polymerisation von Methylmethacrylat zu verfolgen.

Eine Abhängigkeit der Polymerisationsgeschwindigkeit mit Intensität$^{\frac{1}{2}}$ wurde über einen Bereich von etwa 0·2 bis 20 rad/sec und bei Temperaturen zwischen −25° und 55° gefunden.

Die Werte für das Verhältnis der Geschwindigkeitskonstanten von Wachstum und von Kettenabbruch wurden in diesem Temperaturbereich bestimmt durch Verfolgung der nicht-stationären Zustände zu Beginn und am Ende, unmittelbar nachdem die Bestrahlung abrupt gestartet oder gestoppt wird.

Mit Hilfe der Werte für die Startgeschwindigkeiten bestimmt nach der DPPH Inhibierungsmethode wurden die einzelnen Werte für die Geschwindigkeitskonstanten erhalten. Sie gehorchen nahezu der Arrhenius-Gleichung in dem untersuchten Temperaturbereich.