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PROPAGATION AND SIZE-DEPENDENT CHAIN TERMINATION RATE PARAMETERS IN THE POLYMERIZATION OF ACRYLATES IN AQUEOUS SOLUTION AS STUDIED BY PULSE RADIOLYSIS

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ABSTRACT

The radiation polymerizations of ethyl acrylate (EA) and hydroxyethyl acrylate (HEA) monomers in aqueous solutions were studied. For pulse radiolytic experiments, optical detection was used to measure the concentration of intermediates. The absorption spectra taken after a 2.6-μs pulse in N_2O-saturated acidic solution of EA and HEA are shown to have maxima at 300 nm. It was proved by comparative measurements that these maxima belong to α-carboxy alkyl radicals. At a low acrylate concentration (below 1 mmol$\cdot$dm^{-3}) and a relatively high dose/pulse value (above 30 yY), the decay of the transient signal occurs close to second-order kinetics. Average values of the termination rate parameters were calculated from aftereffect measurements. A computer program based on numerical integration was applied in order to estimate the individual rate parameters.

INTRODUCTION

Kinetic methods based on aftereffect experiments are often applied to study the polymerization kinetics of vinyl monomers [1]. These methods are based on fast initiation (e.g., by a short pulse of light) of the chemical reaction and then following the fate of the intermediates by such techniques as ESR, light absorption, and conductivity. Pulse radiolysis makes use of energy absorbed from accelerated electrons, and the intermediates are observed in the majority of cases by kinetic spectroscopic methods [2-6].

Here we report on our investigations carried out on ethyl acrylate (EA) and hydroxy-ethyl acrylate (HEA) model compounds in dilute aqueous solutions using pulse radiolytic and continuous ^{60}Co gamma radiolytic experiments. Water radiolysis produces intermediates of hydrated electrons (e_{aq}^-), hydroxyl radicals, and hydrogen atoms with radiation chemical yields (G value) of 2.7, 2.7, and 0.55 intermediate/100 eV energy absorbed, respectively [7]. In a former study [8] we found that EA and HEA react with e_{aq}^- with rate parameters of 4.4×10^9 and 7.5×10^9 $\text{mol}^{-1}\cdot\text{dm}^3\cdot\text{s}^{-1}$ and with OH with 7.3×10^9 and 1.1×10^{10} $\text{mol}^{-1}\cdot\text{dm}^3\cdot\text{s}^{-1}$. The solubility of EA in water is very limited, only 6 $\text{mmol}\cdot\text{dm}^{-3}$ at 25°C. However, HEA is very soluble in water.

EXPERIMENTAL

HEA was purchased from Scientific Polymer Products, and the inhibitor was removed by using the chromatographic column supplied. EA, ethyl 2-chloropropionate, and *tert*-butanol were Fluka products and were purified by distillation before use. The aqueous solutions were prepared in triply distilled water.

Pulse radiolysis using optical detection was performed with the 4 MeV LINAC of the Institute [9]: pulse-lengths were 80 ns or 2.6 μs and the dose/pulse values were 10–20 or 30–100 Gy, respectively. The doses were determined by KSCN dosimetry taking $\epsilon_{480\text{nm}}$ for the $(\text{SCN})_2^-$ ion as 7600 $\text{mol}^{-1}\cdot\text{dm}^3\cdot\text{cm}^{-1}$ [10]. The absorbances were calculated from the oscilloscope traces and were converted to $G\epsilon$ by dividing the absorbances by the dose and multiplying by a conversion factor of 9.65 $\times 10^6$ Gy $(100\ \text{eV})^{-1}\cdot\text{mol}^{-1}\cdot\text{dm}^3\cdot\text{cm}^{-1}$. The $G\epsilon$ values are proportional to the concentration of intermediate.

Continuous irradiations were performed using the ^{60}Co gamma source of the Institute. The solutions were irradiated in sealed 1 cm, Suprasil quartz cuvettes, and the dose was determined by alcoholic chlorobenzene dosimetry. The evaluation of irradiated samples was carried out by means of a Varian DMS 80 spectrophotometer, and here also the absorbances were converted to $G\epsilon$ values. In steady-state irradiations the $G\epsilon$ values are proportional to the formation rate of the light-absorbing species.

The solutions were deaerated by helium or nitrogen bubbling. The time necessary to minimize the oxygen content of the solution was determined experimentally. The presence of oxygen in the solution results in peroxy-type intermediates with very long lifetimes. In order to avoid the disturbing effect of the remaining oxygen, the first measurement after deaeration was not taken into account. (One pulse was enough to consume the remaining oxygen.) Nitrous oxide saturation was carried out by the bubbling technique. The pH of the solutions was set by $HClO_4$, phosphate buffers, and NaOH.

All measurements were carried out at room temperature.

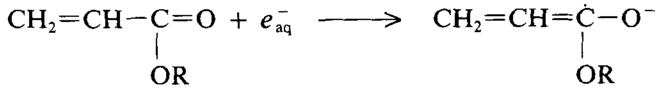
Reaction of OH Radical with EA and HEA

The experiments were carried out in N_2O-saturated solutions ($[N_2O] = 0.025$ $\text{mol}\cdot\text{dm}^{-3}$) in order to convert the hydrated electrons into OH radicals by the reaction [7]

$$N_2O + e_{aq}^- \xrightarrow{+H_2O} N_2 + OH + OH^-,$$

$$k_1 = 8.7 \times 10^9\ mol^{-} \cdot dm^3 \cdot s^{-1} \qquad (1)$$

Since the competing reactions of e_{aq}^- with acrylates



$$CH_2{=}CH{-}\underset{\substack{|\\ OR}}{C}{=}O + e_{aq}^- \longrightarrow CH_2{=}CH{=}\underset{\substack{|\\ OR}}{\dot{C}}{-}O^- \qquad (2)$$

have comparable rate parameters, a nearly complete transformation of e_{aq}^- into OH ($\geq 97\%$) occurs only at low (≤ 1 mmol$\cdot$dm^{-3}) acrylate concentrations: the *G*-value of the OH radicals in such solutions is 5.4. At low concentrations the reaction of intermediates of water radiolysis with acrylate molecules takes place to about 90% through reaction of OH and to 10% through H atoms. (In our former study [8] the e_{aq}^- adduct was shown to decay by second-order processes or by a pseudofirst-order process of protonation at the β-carbon atom, thus producing an α-carboxy alkyl radical.)

The absorption spectra taken after the 2.6-μs pulse in N_2O-saturated acidic solutions of EA and HEA are shown in Figs. 1 and 2, Curve A; typical time-absorbance curves are shown in Fig. 3. These spectra differ considerably from that of the electron adduct (B) taken in an N_2-saturated solution also containing 0.5 mol$\cdot$dm^{-3} *tert*-butanol in order to convert the OH radicals into *tert*-butanol radicals that do not give appreciable light absorption above 260 nm [7]. However, Spectra A in Figs. 1 and 2 are similar to Spectrum D of Fig. 1 that was taken in an

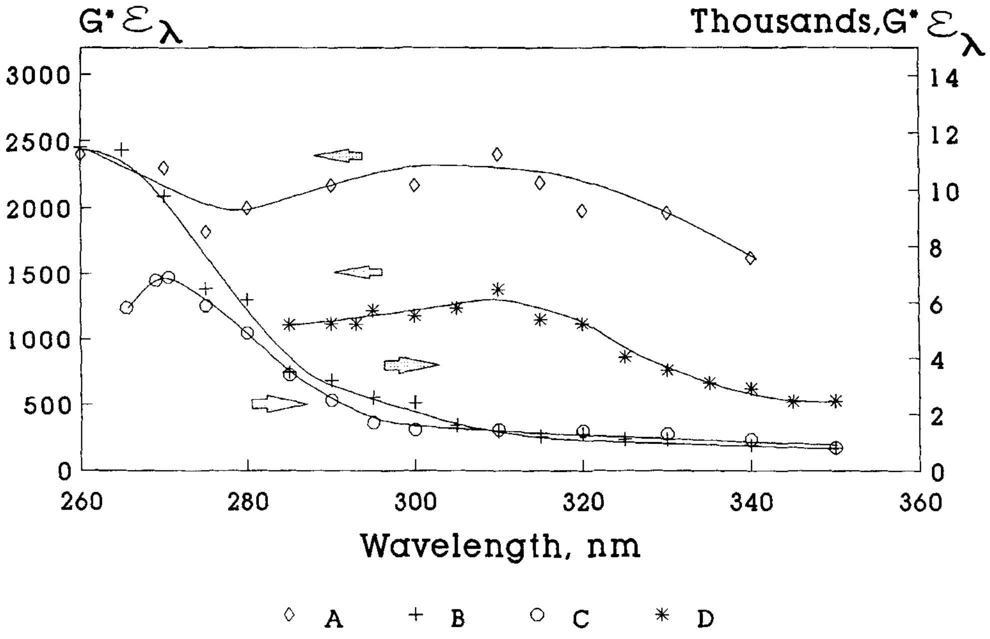


FIG. 1. OH (A) and e_{aq}^- (B) adduct spectrum in EA solutions just after the pulse at pH 5.1 and OH adduct spectrum at pH 9.1 160 μs after the pulse (C). D is the spectrum taken in 1 mmol$\cdot$dm^{-3} 2-chloropropionate ethyl ester solution just after the pulse.

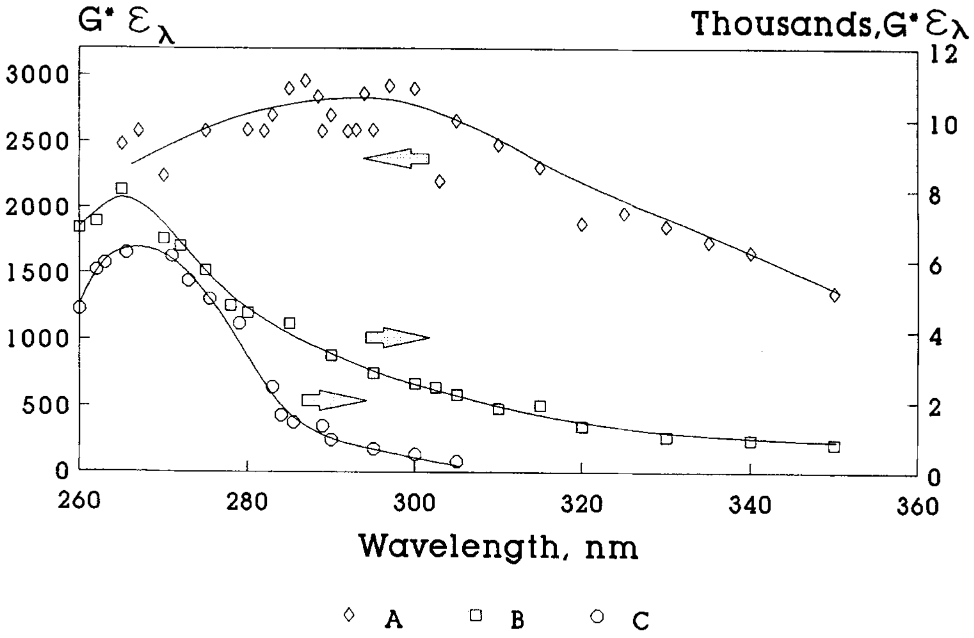


FIG. 2. OH (A) and e_{aq}^- (B) adduct spectrum in HEA solutions just after the pulse at pH 5.1 and OH adduct spectrum at pH 9.1 160 μs after the pulse (C).

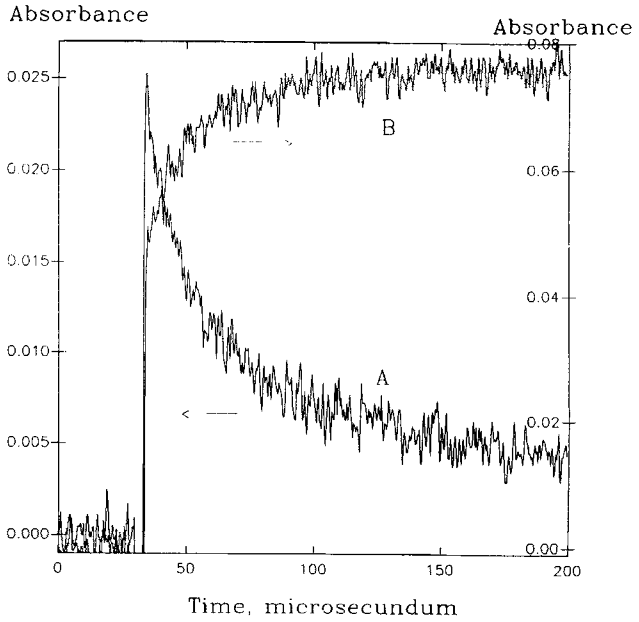
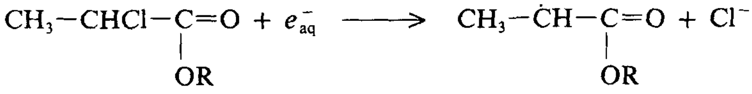


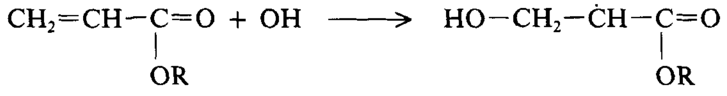
FIG. 3. Typical absorbance-time curves taken in N_2O-saturated 1 mmol·dm^{-3} HEA solution. (A) pH 4.6, λ = 310 nm. (B) pH 9.1, λ = 268 nm.

N_2-saturated solution containing 1 mmol·dm^{-3} 2-chloropropionate ethyl ester and 0.5 mol·dm^{-3} *tert*-butanol where α-carboxy alkyl radicals are produced in the reaction with e_{aq}^-:



$$\mathrm{CH_3{-}CHCl{-}\underset{\displaystyle OR}{\underset{|}{C}}{=}O} + e_{aq}^- \longrightarrow \mathrm{CH_3{-}\dot{C}H{-}\underset{\displaystyle OR}{\underset{|}{C}}{=}O} + \mathrm{Cl^-} \qquad (3)$$

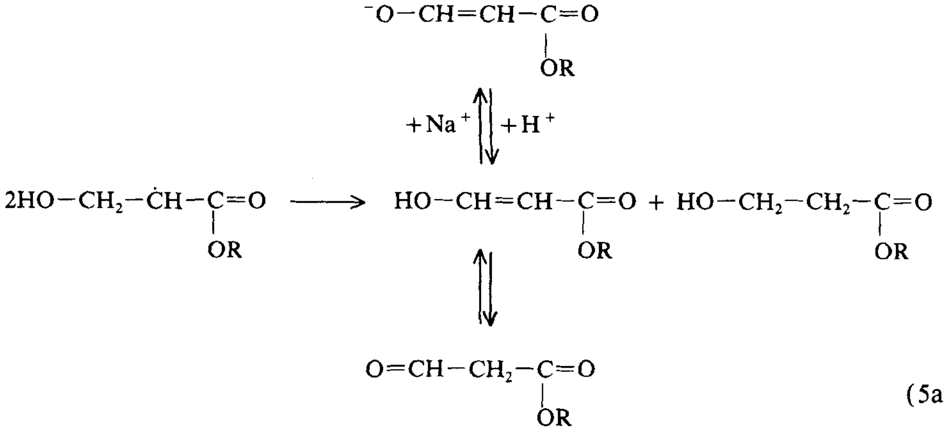
The extinction coefficient in the maximum (300-320 nm) is found to be 510 mol^{-1}·dm^3·cm^{-1}, whereas from Curves A in Figs. 1 and 2, ϵ_{max} = 430 and 480 mol^{-1}·dm^3·cm^{-1} are calculated. Therefore the absorbance with a maximum at $\lambda \approx 300$ nm found in N_2O-saturated solutions of EA and HEA belongs to the α-carboxy alkyl radical produced by OH addition to the double bond:



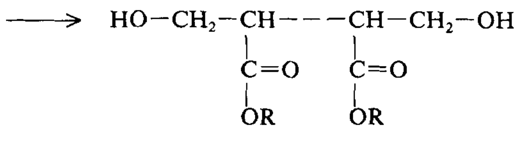
$$\mathrm{CH_2{=}CH{-}\underset{\displaystyle OR}{\underset{|}{C}}{=}O} + \mathrm{OH} \longrightarrow \mathrm{HO{-}CH_2{-}\dot{C}H{-}\underset{\displaystyle OR}{\underset{|}{C}}{=}O} \qquad (4)$$

A similar reaction of H atoms makes some contribution to the α-carboxy alkyl radical yield; in this case there is —H instead of —OH in the β position.

At low acrylate concentrations (≤1 mmol·dm^{-3}) and relatively high dose/pulse values (≥30 Gy), the decay of the transient signal occurs close to second-order kinetics:



$$\begin{tikzcd} & \mathrm{{}^-O{-}CH{=}CH{-}\underset{OR}{C}{=}O} \arrow[d, shift left, "+H^+"] & \\ 2\,\mathrm{HO{-}CH_2{-}\dot{C}H{-}\underset{OR}{C}{=}O} \arrow[r] & \mathrm{HO{-}CH{=}CH{-}\underset{OR}{C}{=}O} \arrow[u, shift left, "+Na^+"] \arrow[d, shift left] & + \ \mathrm{HO{-}CH_2{-}CH_2{-}\underset{OR}{C}{=}O} \\ & \mathrm{O{=}CH{-}CH_2{-}\underset{OR}{C}{=}O} \arrow[u, shift left] & \end{tikzcd} \qquad (5a)$$

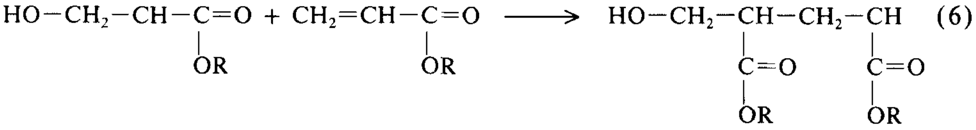


$$\longrightarrow \mathrm{HO{-}CH_2{-}\underset{\underset{\displaystyle OR}{\displaystyle C{=}O}}{CH}{-}{-}{-}\underset{\underset{\displaystyle OR}{\displaystyle C{=}O}}{CH}{-}CH_2{-}OH} \qquad (5b)$$

The $2k_5$ rate parameters were found to be 1.4×10^9 and 1.0×10^9 mol^{-1}·dm^3·s^{-1}. The hydroxy acrylic acid esters formed in Eq. (5a) are in keto-enol equilibria with the keto form. In alkaline media the enol form ionizes to give permanent light absorption with a maximum at 268 nm (Curves C in Figs. 1 and 2). The $G\epsilon_{268nm}$ value was determined as 6600 and 6300 (100 eV)$^{-1}$·mol^{-1}·dm^3·cm^{-1} for EA and HEA, respectively, by applying a high dose/pulse and a low acrylate concentration in the measurements. The remaining absorbance was observed in gamma radiolysis as well. For the determination of the extinction coefficient, the compound was synthesized in the usual way with ethyl acetate and ethyl formiate as the starting compounds: $\epsilon_{268\mathrm{nm}} = 6200\ \mathrm{mol}^{-1}\cdot\mathrm{dm}^3\cdot\mathrm{cm}^{-1}$. The G value of the formation of radicals in Reaction (5a) was calculated to be 1.0 by using this extinction coefficient. The k_{5a}/k_{5b} ratio is 0.6.

Due to the formation of a light-absorbing end-product that has a higher G value than the intermediate in alkaline solutions at around 268 nm, in time, increasing rather than decreasing light absorption was found (Fig. 3, Curve B). Second-order fittings gave similar rate parameters here also as with decaying absorbances, indicating that the buildup of a signal is due to the decay of the hydroxy carboxy alkyl radicals.

The absorption spectra remained essentially the same when the acrylate concentration was increased above 1 $\mathrm{mmol}\cdot\mathrm{dm}^{-3}$; however, departure from second-order behavior became more obvious. This can be attributed to the startup of oligomerization reactions. These reactions produce higher molecular weight radicals that terminate more slowly than lower molecular weight ones.



$$\mathrm{HO{-}CH_2{-}CH{-}\underset{\underset{OR}{|}}{C}{=}O + CH_2{=}CH{-}\underset{\underset{OR}{|}}{C}{=}O \longrightarrow HO{-}CH_2{-}\underset{\underset{\underset{\underset{OR}{|}}{C{=}O}}{|}}{CH}{-}CH_2{-}\underset{\underset{\underset{\underset{OR}{|}}{C{=}O}}{|}}{CH}} \qquad (6)$$

Above 1 $\mathrm{mmol}\cdot\mathrm{dm}^{-3}$ concentration in N_2O-saturated solutions, a small fraction of e_{aq}^- reacts with the acrylate. In any further reaction of the electron adduct, α-carboxy alkyl radicals may also form—as was mentioned before.

Determination of the Rate Parameter of the First Propagation Step in Gamma Radiolysis

The formulation rate of the stable light-absorbing species, hydroxy acrylic acid ester, was used to determine the rate parameter of the first propagation step. For gamma radiolysis applying steady-state kinetics, the following relation was developed:

$$M/M_0 = 1 - abJ\left[\sqrt{[1 + (bJ)^{-1}]} - 1\right] \qquad (7)$$

where M_0 is the low acrylate concentration and high dose rate limit of the $G\epsilon_{300\mathrm{nm}}$ value (when no propagation occurs) for hydroxy acrylic acid ester

M is the $G\epsilon_{300\mathrm{nm}}$ value measured in the solution

a is a parameter that equals 1 when all the dimer, trimer, etc. radicals terminate in reaction with monomer radicals. At the other extreme, when the termination occurs with higher molecular weight radicals only, it has a value of 2

b $\equiv k_6^2/2k_5$, the ratio of the square of propagation and of the self-termination rate parameter

J $\equiv [\mathrm{Ac}]^2/I$, where [Ac] is the concentration of acrylate and I is the formation rate of radicals ($\mathrm{mol}\cdot\mathrm{dm}^{-3}\cdot\mathrm{s}^{-1}$)

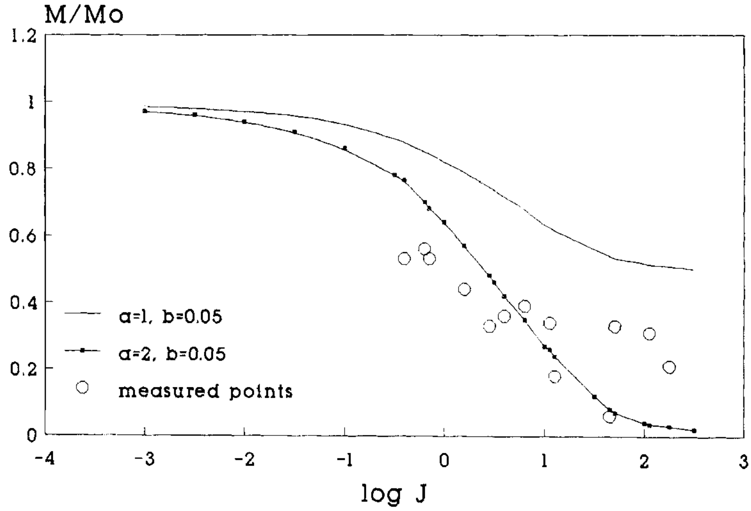


FIG. 4. Normalized hydroxy acrylic acid ethyl ester yields as a function of log J = log $[Ac]^2/I$. The solid curves were calculated according to Eq. (7) taking $a = 1$, $b = 0.05$ and $a = 2$, $b = 0.05$.

The acrylate concentration was varied between $[Ac] = 0.3$ and 3 mmol·dm^{-3} and the rate of radical production between $I = 8 \times 10^{-8}$ and 3×10^{7} mol·dm^{-3}·s^{-1} (Figs. 4 and 5). Here also, corrections were made to take into account the reactions of the electron adduct. Taking $2k_5$ as determined before and accepting

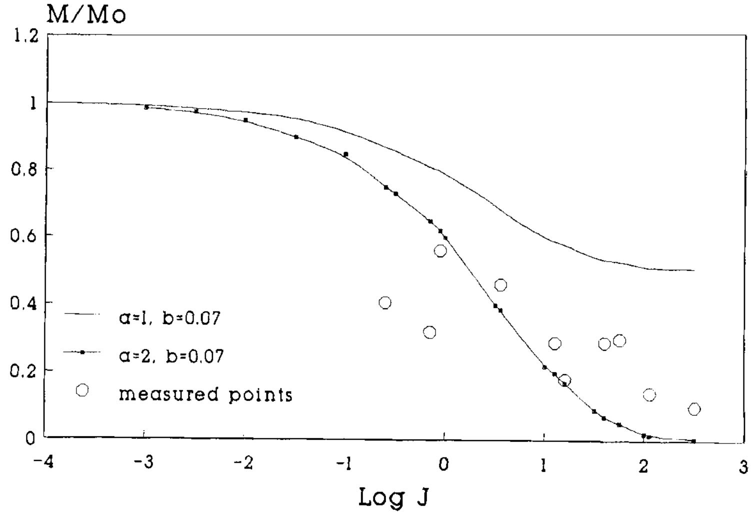


FIG. 5. Normalized hydroxy acrylic acid hydroxy ethyl ester yields as a function of log J = log $[Ac]^2/I$. The solid curves were calculated according to Eq. (7) taking $a = 1$, $b = 0.07$ and $a = 2$, $b = 0.07$.

$b = 0.05$ and $0.07\ \mathrm{mol^{-1}\cdot dm^3\cdot s^{-1}}$, k_6 was found to be $8 \times 10^3\ \mathrm{mol^{-1}\cdot dm^3\cdot s^{-1}}$ for both acrylates.

KINETIC PARAMETERS OF POLYMERIZATION

The OH radicals are produced only during the pulse, and at the end of the pulse their transformation into monomer radicals is nearly complete under our conditions. Since the absorption spectra did not change with time after the pulse, we suppose that the dimer, trimer, etc. radicals have practically the same absorption spectra as the monomer radicals, and we also suppose they have the same extinction coefficient. Observing the absorbance at the maximum, at $\lambda \approx 300$ nm, we can monitor the actual radical concentration: $[\mathrm{R}^{\cdot}] = \Sigma_i[\mathrm{R}_i^{\cdot}]$. The time behavior can be expressed by the relation:

$$\Sigma_i \frac{d[\mathrm{R}_i^{\cdot}]}{dt} = -\Sigma_{ij}k_{t,ij}\,[\mathrm{R}_i^{\cdot}][\mathrm{R}_j^{\cdot}] \tag{8}$$

where $k_{t,ij}$ is the termination rate parameter of the reaction of the *i*th and *j*th radicals and $[\mathrm{R}_i^{\cdot}]$ and $[\mathrm{R}_j^{\cdot}]$ are the radical concentrations. Introducing the average termination rate parameter, $\bar{k}_t$, as in the usual treatment, Eq. (8) is transformed into

$$\Sigma_i \frac{d[\mathrm{R}_i^{\cdot}]}{dt} = -2\bar{k}_t\{\Sigma_i[R_i^{\cdot}]\}^2$$

$$2\bar{k}_t = \frac{d(1/\Sigma_i[R_i^{\cdot}])}{dt} \tag{9}$$

Therefore, the slope of the reciprocal of the radical concentration-time curve is equal to the actual average termination rate parameter. Figures 6 and 7 show just after the pulse the slopes of the reciprocal radical concentration curves are close to that characteristic for the oligomerization-free conditions. However, at higher acrylate concentrations there is a definite departure from the linearity of the curves, indicating a more complex mechanism including oligomerization reactions. For example, in 5 $\mathrm{mmol\cdot dm^{-3}}$ EA solutions under the conditions used, 300 μs after the pulse the termination rate parameter is only half of the starting value.

The rate parameters of termination ($2\bar{k}_t$) calculated from the aftereffect measurements are average values. In order to estimate the individual rate parameters of each step of the polymerization, a computer program based on numerical integration was applied. In the simulation calculations, generally 6–8 oligomerization steps were taken into account and all the possible reactions between the radicals were considered (propagation as well as termination). Starting with the measured values of radical concentration just after the pulse (these are the concentrations of radicals containing one monomer unit), this program calculated the concentrations of individual radicals of different chain lengths as a function of time. Estimated values of the individual termination rate parameters were used for the calculations. The sum of the computed radical concentrations of different chain lengths results in a curve which shows the change of total radical concentration with time. In the case of good simulation, this curve should be very near to that measured in the pulse radiolysis

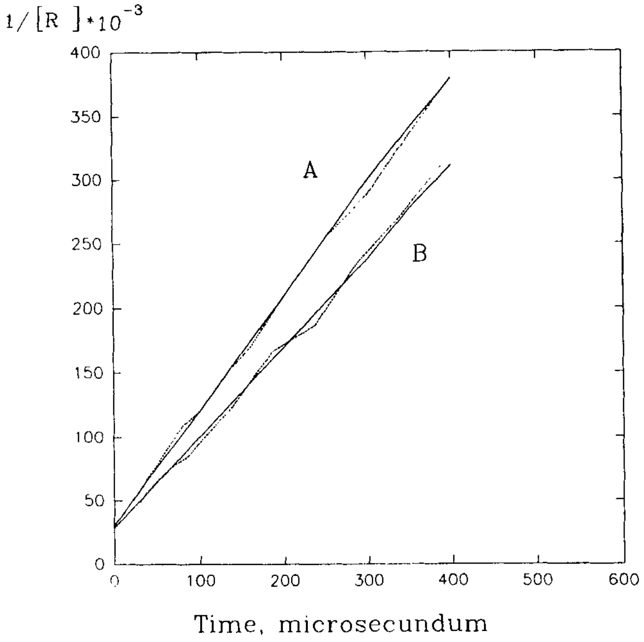


FIG. 6. Measured (dotted curves) and calculated (solid curves) values of reciprocal radical concentrations in aqueous EA solutions as a function of time. Monomer concentrations: A = 1 mmol·dm^{-3}, B = 5 mmol·dm^{-3}.

experiments. The difference between the computed and measured curves indicates that the estimations of the individual rate parameters were erroneous. In this case another row of calculations was started with new estimated kinetic parameters. This iteration was continued until the computed and measured values of the total radical concentration practically agreed.

The rate parameter calculated from the slope of the reciprocal of the radical concentration–time curve at zero time was used as the starting value for the estimation of the individual termination rate parameters. Different acrylate concentrations and initial radical concentrations were simulated for both the EA and HEA curves. In Figs. 6 and 7 the dashed curves are taken from the measurements while the solid curves are the results of simulations. Figure 8 shows the concentrations of individual radicals calculated for a 100-mmol·dm^{-3} solution with a starting radical concentration of 4.5×10^{-5} mol·dm^{-3}. The sets of rate parameters used in simulating the measured curves are shown in Table 1. After the second oligomerization step it was not necessary to change the values of the termination rate parameters.

The rate parameter of propagation (k_p) used for the calculations was 8×10^3 in each propagation step. Only this k_p value and the k_t values summarized in Table 1 resulted in good agreement between the measured and calculated total radical concentration at different monomer concentrations. By using a different set of parameters, this agreement existed only at one monomer concentration. Therefore, we believe that the estimated individual rate parameters given in Table 1 are very close to the real rate parameters.

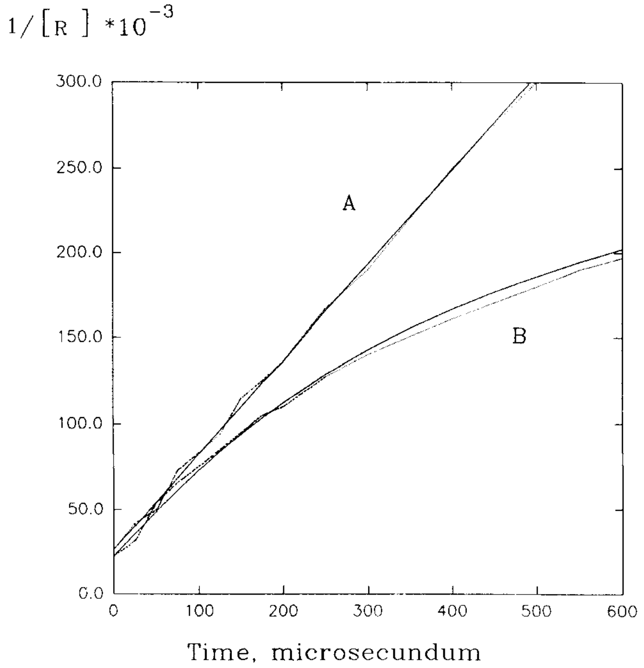


FIG. 7. Measured (dotted curves) and calculated (solid curves) values of reciprocal radical concentrations in aqueous HEA solutions as a function of time. Monomer concentrations: A = 1 mmol·dm^{-3}, B = 100 mmol·dm^{-3}.

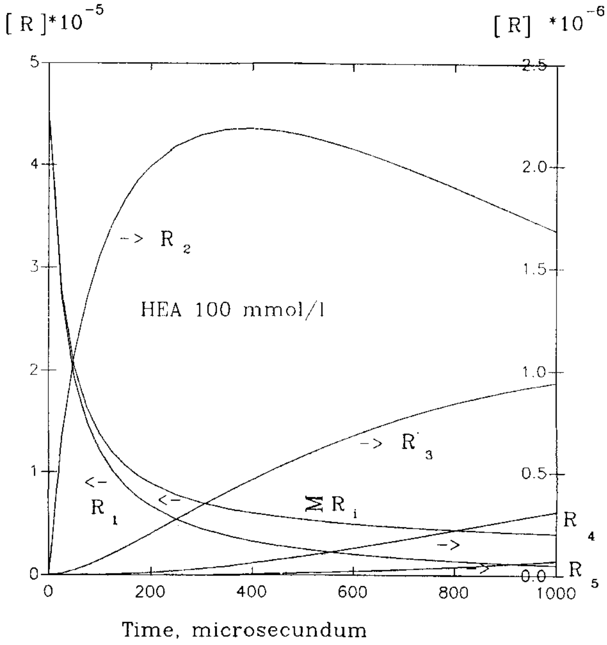


FIG. 8. The calculated concentrations of individual radicals of different chain lengths as a function of time.

TABLE 1. Rate Parameters Used in Simulating the Measured Radical Concentrations. k_{tij} Indicates the Termination Rate Parameter of the *i*th and *j*th Polymeric Radicals

Rate parameters	EA	HEA
k_{t11}	4.2×10^8	2.8×10^8
k_{t12}	8.4×10^7	6.0×10^7

As discussed before, at low acrylate concentration and high dose/pulse value the termination rate parameters ($2k_5$) of monomeric radicals are 1.4×10^9 and 1.0×10^9 $\mathrm{mol^{-1} \cdot dm^3 \cdot s^{-1}}$, i.e., $k_5 = k_{t11}$ was found to be 7×10^8 and 5×10^8 $\mathrm{mol^{-1} \cdot dm^3 \cdot s^{-1}}$. Better agreement was found in the simulation experiments when we took somewhat smaller values, 4.2×10^8 and 2.8×10^8 $\mathrm{mol^{-1} \cdot dm^3 \cdot s^{-1}}$. For good modeling, however, the rate parameters of termination reactions for the dimer, trimer, etc. radicals should be taken to be an order of magnitude smaller than those of the monomeric radicals. Such a large difference cannot be explained simply by a slowing down of diffusion. By using estimated diffusion coefficients, our calculations indicated a decrease in the rate parameter by a factor of 2 between monomer and tetramer radicals. The change in the nature of the terminating radical (in a monomer radical, surrounding the radical site is $HO{-}CH_2{-}CH{-}COOR$, in oligomer radicals it is $-CH_2{-}CH{-}COOR$), the steric hindrance caused by side groups, as well as the increasing hydration caused by the increased number of OH groups, may slow down the termination rate considerably.

CONCLUDING REMARKS

In the pulse radiolysis of aqueous solutions of EA and HEA, α-carboxy alkyl radicals were identified by their light absorption spectra. The radicals form by OH addition to the double bond of the acrylates. Changes in the kinetic curves with an increase of monomer concentration indicate there are several oligomerization steps during the interval investigated.

The pulsed radiolysis method, together with a computer program, seems to be applicable for determining the rate parameters of propagation and termination at the very beginning of the polymerization reaction. The rate parameter of propagation was found to be 8×10^3 in each propagation step, while the rate parameter of termination for dimer, trimer, etc. radicals was found to be an order of magnitude smaller than those of the monomeric radicals, as shown in Table 1. This decrease can be explained partly by a decrease in diffusion of longer radical chains in addition to the steric hindrance caused by increasing hydration.

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