Pulse Radiolysis of Methacryloyl-L-proline Methyl Ester in Dilute Aqueous Solution

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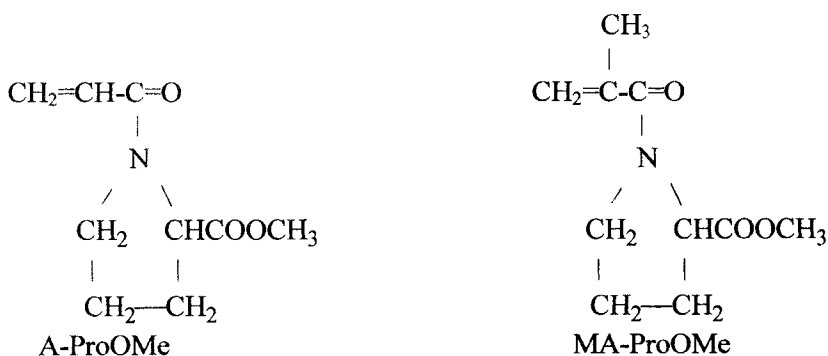CNR, Via P. Gobetti 101
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ABSTRACT

The reactions of hydroxyl radical, hydrogen atom and hydrated electron intermediates of water radiolysis with a hydrogel-forming monomer, methacryloyl-L-proline methyl ester (MA-ProOMe), were studied by pulse radiolysis in dilute aqueous solutions and compared with the reactions of the acrylic derivative (A-ProOMe). The spectral and kinetic characteristics of the first step of OH, H and e_{aq}^- reactions with the two monomers are very similar. There are considerable differences in the next steps. In neutral solutions, the electron adduct of A-ProOMe decays in slow radical-radical reactions. The adduct of MA-ProOMe, however undergoes a fast irreversible protonation resulting in α-carboxyalkyl radical. The oligomerization reactions occurring in MA-ProOMe solutions are slow, and under adopted pulse radiolytic conditions, they are observable only at high monomer concentrations. In A-ProOMe solutions the reaction is significantly faster.

INTRODUCTION

In our previous papers, the first steps of polymerization reactions of acrylic monomers were studied by pulse radiolysis [1, 2]. In [2] the reactions between the reactive intermediates of water radiolysis (OH, H and e_{aq}^-, having radiation chem-ical yields of G = 2.7, 0.55 and 2.7 species/100 eV absorbed energy) and acryloyl-L-proline methyl ester (A-ProOMe) were studied in dilute aqueous solutions (concentration (1 mmol dm^{-3}) and the absorption spectra and the kinetic char-acteristics of the intermediates were determined. Under similar conditions [2] we studied the reactions of the methacrylic derivative, methacryloyl-L-proline methyl ester (MA-ProOMe) and compared the reactivities of the two monomers.

$$CH_2{=}CH\text{-}C{=}O$$
$$|$$
$$N$$
$$/ \quad \backslash$$
$$CH_2 \quad CHCOOCH_3$$
$$| \qquad |$$
$$CH_2{-}CH_2$$

A-ProOMe

$$CH_3$$
$$|$$
$$CH_2{=}C\text{-}C{=}O$$
$$|$$
$$N$$
$$/ \quad \backslash$$
$$CH_2 \quad CHCOOCH_3$$
$$| \qquad |$$
$$CH_2{-}CH_2$$

MA-ProOMe

Pulse radiolysis of aqueous solutions of a methacrylic ester derivative was studied in the case of cyclohexyl methacrylate (CMA) [3]. The behavior of this compound in comparison with several acrylate derivatives e.g. ethyl- and hydroxyethyl acrylate [1, 4, 5] was found to be quite different. For instance, the electron adduct of CMA decays quickly even in neutral solutions with a first order reaction, whereas in acrylates at neutral pH the first order decay, under the usual experimental conditions (concentration 0.1-1 mmol dm^{-3}, dose/pulse 5-20 Gy) cannot compete effectively with the second order adduct-adduct reactions [1, 2, 4, 5].

EXPERIMENTAL

Details of the experimental technique are described in the previous publications [1, 2]. MA-ProOMe was synthesized by the method described in Reference 6. The solutions were freshly prepared using Milli-Q (Millipore) triply distilled water. The pH was set by HCl or NaOH.

Pulse radiolysis experiments with optical detection were performed by means of two different setups. In Bologna, Italy, the pulse irradiations (10-50 ns) were made with the 12 MeV linear accelerator of the FRAE Institute [7] on samples in Suprasil cells of 5 cm optical path length. The radiation dose per pulse (10-100 Gy) was monitored by means of a charge collector plate placed behind the cell and calibrated with O_2 saturated solution of 0.01 mol dm^{-3} KSCN and by taking G_{500} $_{nm}$ = 2.15·10^4 (100 eV)$^{-1}$ mol^{-1} dm^3 cm^{-1}.

α-carboxyalkyl radical   β-carboxyalkyl radical
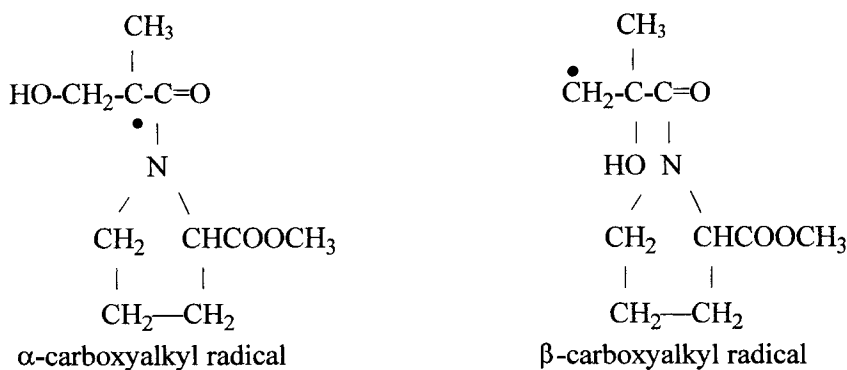
In Budapest, Hungary, the pulse radiolytic measurements were carried out with a 4 MeV linear accelerator of the Institute of Isotopes with pulse duration of 80 ns or 800 ns and dose per pulse values of 10 Gy or 40-100 Gy in 1 cm cell [8].

TABLE 1. Spectral and Kinetic Characteristics of OH, H and e_{aq}^- Reactions with MA-ProOMe and A-ProOMe

	MA-ProOMe	A-ProOMe
Reactions of OH radicals		
Rate constant, k mol^{-1} dm^3 s^{-1}	4.8·10^9	5.5·10^9
λ_{max}, nm	410	480
ε_{max}, mol^{-1} dm^3 cm^{-1}	620	860
Decay rate constant, 2k mol^{-1} dm^3 s^{-1}	2.5·10^8	5·10^8
Reactions of H atoms		
Rate constant, k mol^{-1} dm^3 s^{-1}	5·10^9	≈2·10^9
λ_{max}, nm	400	460
ε_{max}, mol^{-1} dm^3 cm^{-1}	740	970
Reactions of hydrated electrons		
Rate constant, k mol^{-1} dm^3 s^{-1}	5.8·10^9	1·10^{10}
λ_{max}, nm	≈310	290 [b]
ε_{max}, mol^{-1} dm^3 cm^{-1}	[a]	8000 [b]
Decay rate constant, 2k mol^{-1} dm^3 s^{-1}	[a]	1.3·10^9
Oligomerization reactions		
Propagation, k mol^{-1} dm^3 s^{-1}	8·10^3	1.4·10^5
Termination, 2k mol^{-1} dm^3 s^{-1}	3·10^7	6·10^7

[a]Due to the fast β protonation the data were not determined;
[b]Protonated electron adduct.

RESULTS AND DISCUSSION

Reaction of the Monomer with OH, H and e_{aq}^-

The spectral and kinetic characteristics of the intermediates formed from MA-ProOMe are collected in Table 1 and compared with the data obtained in the previous work [2] for A-ProOMe.

The *OH radicals* (as obtained in N_2O saturated solutions) enter in radical addition reaction to the C=C double bond of MA-ProOMe with a rate constant of
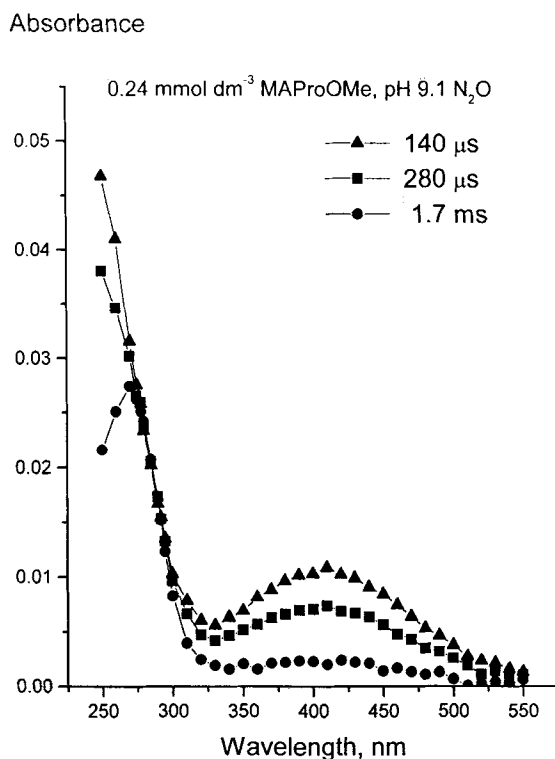
Absorbance

Figure 1.   Absorption spectra obtained in N_2O saturated 0.24 mmol dm^{-3} MA-ProOMe solution at pH = 9.1. The curves were taken 140 μs, 280 μs and 1.7 ms after 50 ns pulses of electrons. Dose/pulse 63 Gy.

$4.8 \cdot 10^9$ mol^{-1} dm^3 s^{-1}, a typical value for acrylic and methacrylic esters [9]. The adduct has the same absorption spectrum with λ_{max} at 410 nm (Figure 1) both in neutral and alkaline solutions. The absorption maximum wavelength is shifted to the red in comparison with the spectra of radicals of simple acrylic acid esters like ethyl acrylate (λ_{max} = 310 nm [4, 5]), *vice-versa* it is shifted to the blue with respect to the absorbance of A-ProOMe (480 nm). The OH radical may add to the α or to the β carbon atom of the C=C double bond with respect to the carbonyl group, and so -α or β-carboxyalkyl radical may form. The wavelength of the absorption maximum of the β-carboxyalkyl radical should be the same as that of the simple alkyl radicals (like hexyl, λ_{max} $\approx$ 250 nm [10]). Therefore, the maximum at about 410 nm should belong to the α-carboxyalkyl radical where the unpaired electron is in conjugation with the oxygen and nitrogen atoms. Its formation is preferred for

both energetic and steric reasons. Assuming that all the addition occurs on β positions, and taking the G-value of attacking radicals as 6, the extinction coefficient is calculated as $\varepsilon_{max} = 620$ mol^{-1} dm^3 cm^{-1}. This value is higher than that found for radicals produced from simple esters like ethyl acrylate with $\varepsilon_{max} = 400$ mol^{-1} dm^3 cm^{-1} [3-5], but it is lower than that measured for the radical produced from A-ProOMe (860 mol^{-1} dm^3 cm^{-1}).

In the *H atoms* reactions (in 0.5 mol dm^{-3} *tert*-butanol containing aqueous solutions saturated with argon, at pH = 1.8) a spectrum similar to that obtained with OH radicals was found. In the case of the H atom adduct, the maximum was found at a shorter wavelength, at $\lambda_{max} = 400$ nm, and the extinction coefficient is calculated to be somewhat higher, $\varepsilon_{max}= 740$ mol^{-1} dm^3 cm^{-1}, than that found for the OH adduct.

The decay of α-carboxyalkyl radicals formed in reactions of OH radicals or H atoms, at low solute concentrations, was found to follow a second order reaction with a 2k of $2.5 \cdot 10^8$ mol^{-1} dm^3 cm^{-1}, and no residual absorbance was found above 320 nm. In the reaction of OH radicals in alkaline solutions, however, there is a residual absorbance with a peak at 290 nm (Figure 1, circle points). Similar behavior was also observed in the reaction of A-ProOMe and hydroxyethyl- and ethyl acrylate [1, 2, 4, 5]. Such a residual absorbance is due to the disproportionation product of the α-carboxyalkyl radical (β-hydroxy-methacryloyl-L-proline methyl ester). In alkaline solution the OH group ionizes and the ion has strong absorbance in the UV. It is noteworthy that the formation of this type of compound was not mentioned in the radiolysis of CMA [3].

A complex absorption spectrum forms in the *hydrated electrons* reaction (Figure 2). At early times, (the circle points show the spectrum 140 ns after the electron pulse) the absorbance above 350 nm is due to the absorption of the hydrated electron (it has λ_{max} at 720 nm with $\varepsilon_{max}= 18500$ mol^{-1} dm^3 s^{-1} [11]). The adduct decays quickly (within several hundred ns) and the spectrum shown by triangle points 4.2 μs after the pulse is a spectrum of an α-carboxyalkyl type radical [1-5, 12-15]. Comparison of the triangle curves of Figures 1 and 2 supports this view. As it was suggested before in connection with the electron adducts of several acrylic esters [2, 4, 5, 12, 13], the radical forms in an irreversible protonation at the β carbon atom (see Scheme 1). The absorbance with a peak around 300 nm (shown by dotted line) should be due to the electron adduct. This intermediate decays so rapidly that its spectrum could be obtained only qualitatively, by correcting the 350 ns absorbance for the contributions of both the unreacted e_{aq}^- and the already produced α-carboxyalkyl radical. The λ_{max} of A-ProOMe and CMA electron adducts were found at 290 nm.
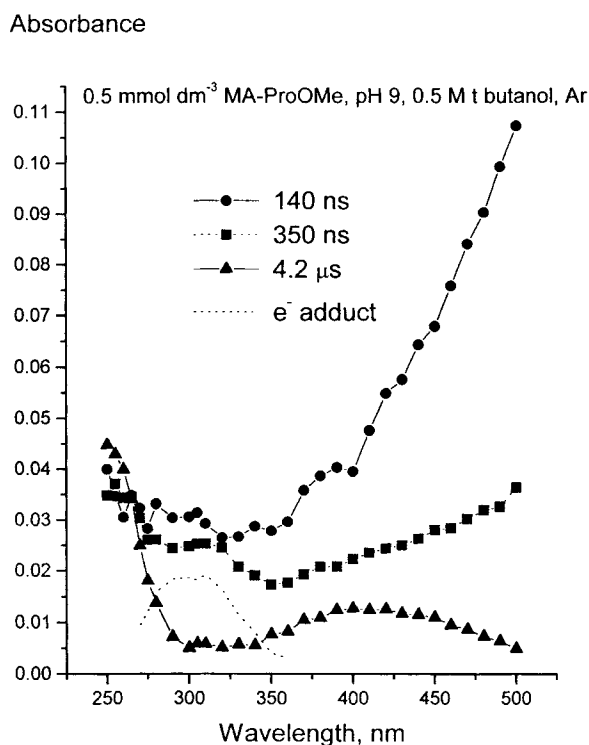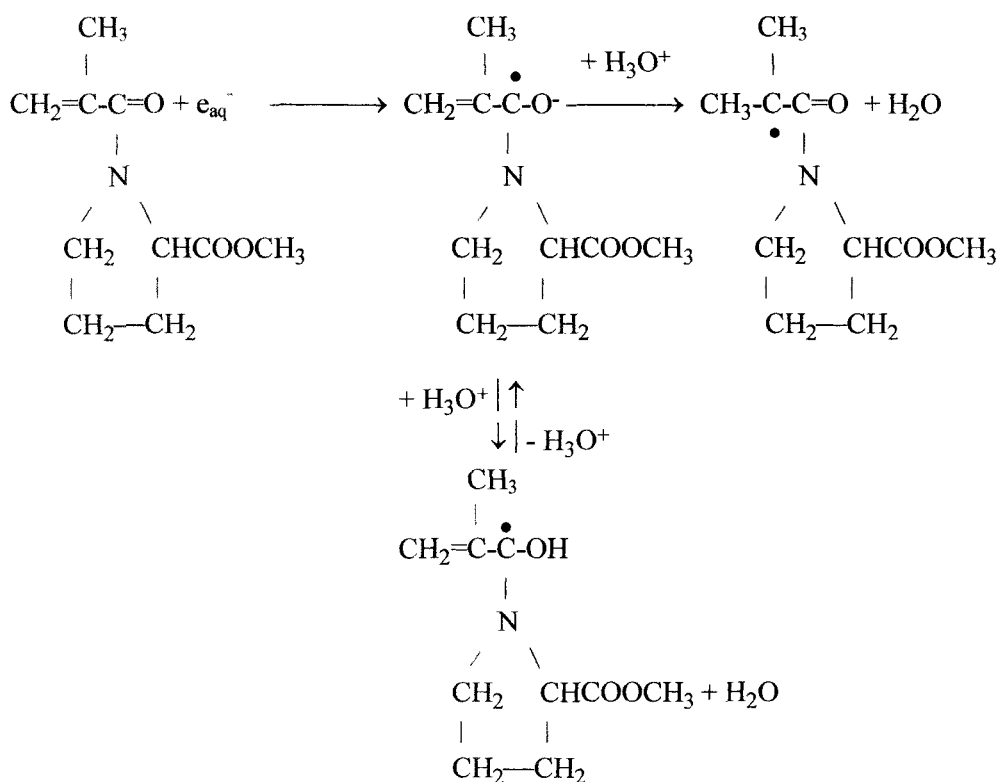
Absorbance

Figure 2. Absorption spectra obtained in Ar saturated 0.5 mmol dm^{-3} MA-ProOMe solution at pH = 9 containing 0.5 M t-butanol. The curves were taken 140 ns, 350 ns and 4.2 μs after 50 ns pulses. The dotted line shows the spectrum of the electron adduct obtained as described in the text. Dose/pulse 63 Gy.

In addition to the irreversible protonation, the adduct should also be involved in reversible protonation on the carbonyl oxygen. The pK_a of this reversible protonation is probably at high pH (~8-10) similar to that of the acrylamide derivatives [13]. In the case of A-ProOMe not much difference was found between the spectra of protonated and not protonated forms.

In neutral solutions, the decay of the MA-ProOMe electron adduct is fast, whereas that of the A-ProOMe adduct is slow [2]. As it was mentioned in the Introduction in the case of CMA, also fast decay was noted [3]. The authors attributed this fast decay to anionic polymerization reactions. We suspect, however, that in their case also β protonation caused the decay. The decay of the methacrylic acid electron adduct was also found to be faster than that of the acrylic acid (rate constant $4.5 \cdot 10^5$ s^{-1} and $2 \cdot 10^5$ s^{-1} [13,1 4]). Therefore, it seems to be a general

$$
\begin{array}{ccc}
\text{CH}_3 & \text{CH}_3 & \text{CH}_3 \\
| & | \quad \bullet \quad +\text{H}_3\text{O}^+ & | \\
\text{CH}_2=\text{C-C}=\text{O} + \text{e}_{aq}^- \longrightarrow \text{CH}_2=\text{C-C-O}^- \longrightarrow \text{CH}_3\text{-C-C}=\text{O} + \text{H}_2\text{O} \\
| & | & \bullet \; | \\
\text{N} & \text{N} & \text{N} \\
/ \quad \backslash & / \quad \backslash & / \quad \backslash \\
\text{CH}_2 \quad \text{CHCOOCH}_3 & \text{CH}_2 \quad \text{CHCOOCH}_3 & \text{CH}_2 \quad \text{CHCOOCH}_3 \\
| \quad\quad | & | \quad\quad | & | \quad\quad | \\
\text{CH}_2\text{---CH}_2 & \text{CH}_2\text{---CH}_2 & \text{CH}_2\text{---CH}_2
\end{array}
$$

$$
+\text{H}_3\text{O}^+ \; | \uparrow
$$
$$
\downarrow | \; \text{-H}_3\text{O}^+
$$
$$
\text{CH}_3
$$
$$
|\; \bullet
$$
$$
\text{CH}_2=\text{C-C-OH}
$$
$$
|
$$
$$
\text{N}
$$
$$
/ \quad \backslash
$$
$$
\text{CH}_2 \quad \text{CHCOOCH}_3 + \text{H}_2\text{O}
$$
$$
| \quad\quad |
$$
$$
\text{CH}_2\text{---CH}_2
$$

Scheme 1

observation that substituting the hydrogen on the acrylic part at the α-carbon atom by a methyl group accelerates the decay of the electron adduct in irreversible protonation. This acceleration may be due to the slight electron releasing power of the methyl substituent that may increase the negative charge density in β position. Electron density calculations are in agreement with this suggestion.

Oligomerization Reactions

In order to study and compare the OH radical induced oligomerization reactions of MA-ProOMe and A-ProOMe monomers, the decay of the α-carboxyalkyl radical was studied in a series of experiments at a constant dose/pulse value (17 Gy) and varying the monomer concentration. In Figures 3 and 4, the reciprocal radical concentrations are shown as a function of time. In both monomer solutions at the lowest concentration investigated, 0.1 mmol dm^{-3}, the time
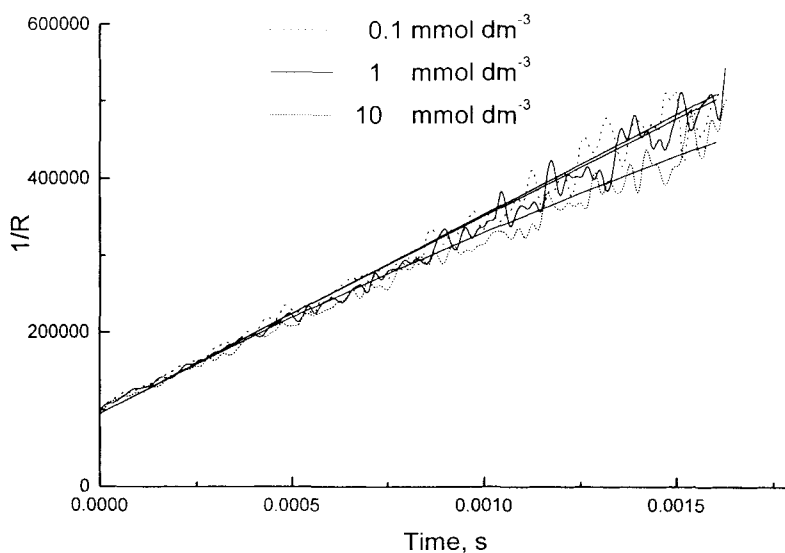
Figure 3.   Reciprocal radical concentrations taken in 0.1, 1 and 10 mmol dm^{-3} MA-ProOMe N_2O saturated solutions as a function of time. The solid lines were obtained by simulation (as described in [1]), (λ = 400 nm, pH~6.
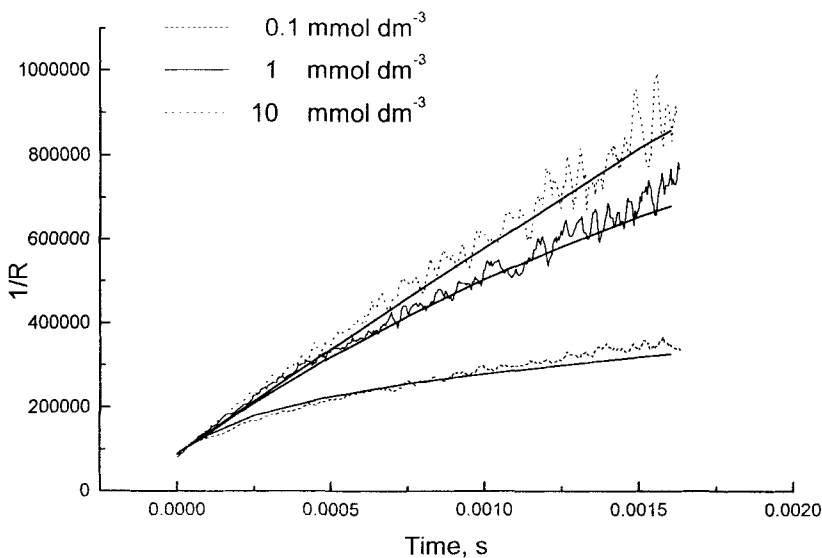

Figure 4.   Reciprocal radical concentrations taken in 0.1, 1 and 10 mmol dm^{-3} A-ProOMe N_2O saturated solutions as a function of time. The solid lines were obtained by simulation (as described in [1]), (λ = 480 nm, pH~6.

dependence is linear with slopes of $2k = 2.5 \cdot 10^8$ and $5 \cdot 10^8$ mol^{-1} dm^3 s^{-1}, respectively, indicating that the decay of the α-carboxyalkyl radicals takes place in self termination reactions and under the experimental conditions applied the oligomerization reactions are slow as compared to the termination. When the concentration was increased by one or two orders of magnitude, underlinear deviation of the curves was found in A-ProOMe solutions. The curves bending down can be attributed to the oligomerization reactions [1, 15]. The longer oligomeric radicals diffuse more slowly, and also may take up a globular structure with a hidden radical site that slows down the rate of termination [1]. The deviation from the linearity in MA-ProOMe solutions is much smaller than in A-ProOMe solutions, which may show that MA-ProOMe has a much lower reactivity in propagation reactions than A-ProOMe. Therefore, even at relatively high monomer concentrations the monomer radicals decay in radical-radical reactions. Low reactivity was also found in γ-radiolytic polymerization studies [16].

In order to estimate the rate constant of the α-carboxyalkyl radical + monomer reaction (propagation) and that of the reactions of two oligomeric radicals (term-ination), simulation studies, similar to those applied in Reference 1 to ethyl- and hydroxyethyl acrylate, were carried out. 6-10 oligomerization steps were considered in the simulations, and, as it is shown in Figures 3 and 4, good agreement was found between the simulated and measured curves. The results show (see Table 1) that the rate constant of the propagation reaction in A-ProOMe solutions ($1.4 \cdot 10^5$ mol^{-1} dm^3 s^{-1}) is more than an order of magnitude higher then in MA-ProOMe solutions ($8 \cdot 10^3$ mol^{-1} dm^3 s^{-1}). However, there is not much difference between the rate constants of termination for the two monomers ($6 \cdot 10^7$ and $3 \cdot 10^7$ mol^{-1} dm^3 s^{-1}, respectively).

CONCLUSIONS

As is evident from Table 1, the spectral and kinetic characteristics of the first step of OH, H and e_{aq}^- reactions with A-ProOMe and MA-ProOMe are very similar. The absorption maximum of the α-carboxyalkyl radical formed in OH or H addition to MA-ProOMe is at a somewhat lower wavelength than that of the radical produced in the analogous reactions of A-ProOMe. This lower λ_{max} makes the radical obtained from MA-ProOMe more similar to the radicals produced from simple alkyl acrylates than the radical formed from A-ProOMe.

Although the first step of the radical reactions is similar for the two monomers, the next steps may show considerable differences. In neutral unbuffered

solutions the electron adduct of A-ProOMe decays in slow radical-radical reactions. The adduct of MA-ProOMe, however, undergoes a fast irreversible protonation resulting in (-carboxyalkyl radical.

In MA-ProOMe solutions the oligomerization reactions are slow and under the conditions applied they are hardly observable even at monomer concentration as high as 10 mmol dm^{-3}. In A-ProOMe solutions the reaction is more than an order of magnitude faster, therefore hydrogel formation from this compound can be carried out with application of much lower doses.

ACKNOWLEDGEMENTS

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