Free-Radical-Induced Chain Breakage and Depolymerization of Poly(methacrylic acid): Equilibrium Polymerization in Aqueous Solution at Room Temperature

Piotr Ulanski,[a, b] **Eberhard Bothe,**[a] **Knut Hildenbrand,**[a] **and Clemens von Sonntag***[a]

Abstract: Hydroxyl radicals, generated by ionizing radiation in N_2O saturated aqueous solutions, abstract H atoms from poly(methacrylic acid) at the methyl and methylene groups, and radicals **1** and **2** are formed, respectively. The reactions of the poly(methacrylic acid) radicals were investigated by pulse radiolysis (using optical and conductometric detection), EPR, product analysis, and kinetic simulations. The conductometric detection allowed us to measure the rate of chain scission and monomer release. Under conditions in which the polymer is largely deprotonated, the primary radical **1** abstracts a hydrogen ($k = 3.5 \times 10^2\,s^{-1}$) from the methylene group, and this yields the more stable secondary radical **2**. This radical undergoes chain scission by β-fragmentation ($k = 1.8\,s^{-1}$), and the terminal (end-of-chain) radical **3** is formed. The polymer radicals terminate only slowly ($2k = 80\,dm^3\,mol^{-1}\,s^{-1}$). This allows effective depolymerization (depropagation) to take place ($k = 0.1\,s^{-1}$). The yield of monomer release is higher than the original radical yield by up to two orders of magnitude. Once monomer is formed, it reacts with **3** (propagation, $k = 15\,dm^3\,mol^{-1}\,s^{-1}$), and a situation close to an equilibrium radical polymerization is approached. From these data, the equilibrium monomer concentration is calculated at $6.7 \times 10^{-3}\,mol\,dm^{-3}$ at room temperature. The standard entropy of propagation is estimated at -185 to $-150\,J\,mol^{-1}\,K^{-1}$. Because the monomer reaches concentrations in the millimolar range, the $^{\bullet}OH$ radicals increasingly react with monomers (results in oligomerization) rather than with the polymer. This effect is reflected by, for example, a lowering of chain-scission yields upon prolonged irradiation. In acid solutions, the decay of the polymer radicals becomes much faster (estimated at about $10^7\,dm^3\,mol^{-1}\,s^{-1}$ at pH 3.5), and monomer release is no longer observed.

Keywords: EPR spectroscopy · kinetics · polymerizations · pulse radiolysis · radical reactions

Introduction

Poly(methacrylic acid), together with poly(acrylic acid), belongs to a group of the simplest synthetic polyelectrolytes. Basic data on their synthesis and applications[1] as well as their properties and solution behavior have been compiled.[2, 3] Besides many similarities, there are marked differences, in particular in the conformational transitions of these two polyelectrolytes.[2–15] While poly(acrylic acid) changes its conformation with increasing ionization relatively smoothly from coil-like to rodlike, many properties of poly(methacrylic acid) change stepwise at a degree of ionization between 0.2 and 0.3; this indicates a sharp conformational transition in this range. The fully protonated poly(methacrylic acid) seems to adopt a hypercoiled structure (coils of tight, compact conformation), in which an unfavorable contact between the methyl groups and water is avoided,[16–20] and when its molecular weight exceeds 10^4 Da, it probably forms several tightly packed clusters connected by short extended polymer chains.[18]

At present, poly(methacrylic acid) is mainly used for thickeners and gelling agents, ion-exchange resins, flocculating agents, binders, adhesives, and soil conditioners.[1] A relatively new and potentially promising application of synthetic polyelectrolytes is the formation of stimuli-sensitive hydrogels. These products have the beneficial properties of conventional hydrogels currently used in pharmacy,[21–23] but they also respond to environmental stimuli (for example, pH, ionic strength, additives, temperature, electric field, and light), usually by a pronounced change in their dimensions.[24–30] Because of this, they are now tested as chemical valves,

---

[a] Prof. Dr. C. von Sonntag, Dr. P. Ulanski, Dr. E. Bothe
Dr. K. Hildenbrand
Max-Planck-Institut für Strahlenchemie
Stiftstrasse 34–36, P.O. Box 101365
45413 Mülheim an der Ruhr (Germany)
Fax: (+49) 208-306-3951
E-mail: vonsonntag@mpi-muelheim.mpg.de

[b] Dr. P. Ulanski
Permanent address
Institute of Applied Radiation Chemistry
Technical University of Lodz, Wroblewskiego 15
93-590 Lodz (Poland)

0947-6539/00/0621-3922 $ 17.50+.50/0

micro-sensors, selective membranes, drug-delivery systems, and artificial muscles (e.g. refs. [31–36]). Ionizing radiation is one of the basic tools for the synthesis and sterilization of hydrogels for medical use, because of the high product purity, easy process control, as well as the possibility to combine synthesis and sterilization in a single step.[23, 37] The investigation of the underlying radiation-induced (i.e. free-radical-induced) processes is thus of considerable interest.

Recently we reported the free-radical-induced reactions of poly(acrylic acid) in aqueous solution,[38–43] and also touched on those of poly(methacrylic acid);[44, 45] this supplemented earlier studies[46–50] on the latter topic. We now present a complete account of our studies on poly(methacrylic acid).

For the present study, it is important to recall that at high pH, where poly(methacrylic acid) chains are fully charged, the strong repulsive electrostatic forces prevent a recombination of polymer radicals. In this respect, the present system fulfils one prerequisite for equilibrium radical polymerization (for a review see ref. [51]). Furthermore, it will be shown that once terminal radicals are produced by β-fragmentation of the initially formed midchain radicals generated randomly along the polymer chains, depolymerization and polymerization occur side by side. Such a system should resemble "living radical polymerization" (cf. refs. [52–54]), here however without deactivation, that is, without a reversible transformation of the terminal radicals into a dormant form.

Under our conditions, no monomer is initially present, but its concentration builds up rapidly upon depolymerization. In the absence of radical termination and assuming a simple equilibrium ($P^{\bullet} \rightleftharpoons P^{\bullet} + M$), the monomer concentration will approach a steady state.

The Dainton–Ivin equation [Eq. (a)],[51, 55, 56] is shown below.

$$T_c = \Delta H_p / [\Delta S_p^0 + R \times \ln([M]_{eq})] \qquad \text{(a)}$$

In this equation, T_c is the ceiling temperature, ΔH_p the enthalpy of propagation, and ΔS_p^0 the entropy of propagation in the standard state (i.e. at a monomer concentration, or more precisely activity, of unity), R is the gas constant, and $[M]_{eq}$ the equilibrium monomer concentration. The ceiling temperature, at which depolymerization and polymerization proceed at equal rates, decreases upon lowering the monomer concentration. Thus in very dilute solutions, the ceiling temperature can drop even to room temperature. Similarly, for a given temperature, lower than the ceiling temperature for bulk monomer, an equilibrium monomer concentration can develop, when the polymer radicals are very long-lived. In the present paper, it will be shown that the poly(methacrylic acid) system closely approaches these conditions.

Experimental Section

Residual monomer and solvent were removed from poly(methacrylic acid) (Polysciences) by drying in vacuo for 2 h at 40 °C, dissolving in water by stirring overnight at R.T., and dialysis (tangential flow, Minitan, Millipore: membrane of a nominal molecular weight cut off at 10 kDa). The remaining monomer content was below 0.1 % (*w*/*w* of dry polymer), as estimated from the lifetime of the hydrated electron in pulse radiolysis,[44] by formaldehyde determination after ozonation (cf. ref. [57]), and by ion chromatography. Solutions were filtered through a 5 µm-pore-size filter (Minisart, Sartorius). All the glassware and apparatus parts used to prepare, purify, and irradiate poly(methacrylic acid) solutions were previously soaked overnight in aqueous EDTA solution (disodium salt, 1×10^{-3} mol dm^{-3} at 50 °C), in order to remove traces of transition metal ions that may cause unwanted side reactions (cf. ref. [41]). Stock solutions of purified poly(methacrylic acid), made up in Milli-Q filtered (Millipore) water, were stored in the dark (note ref. [58]) and used within two weeks. Storage within this period did not affect the molecular weight. The weight-average molecular weight of the purified poly(methacrylic acid) was 2.8×10^5 Da, as measured by the low-angle laser light scattering (see below).

Aqueous sodium perchlorate solutions were purified from traces of transition metal ions by shaking with Chelex-100 chelating resin (Bio-Rad) for 4 h at R.T. and subsequent decantation. All other chemicals were used without further purification.

The pH was adjusted with $HClO_4$, NaOH, or KOH as required. Prior to irradiation, solutions were saturated for 1 h with N_2O (or Ar in the EPR experiments with photochemical generation of radicals) purified by an Oxisorb column (Messer-Griesheim).

γ-Irradiations were carried out with a panoramic ^{60}Co-γ-source (Nuclear Engineering) at a dose rate of 0.092 Gy s^{-1} or 3.7 Gy s^{-1}. For pulse radiolysis measurements, a Van de Graaff accelerator, which generated 0.4–4 µs pulses of 2.8 MeV electrons, equipped with optical and conductometric detection systems was used.[59, 60] After each pulse, the cell was refilled with a fresh solution. Fricke dosimetry (cf. ref. [61]) was used for γ-irradiations, while for optical and conductometric pulse experiments thiocyanate and dimethyl sulfoxide dosimetries[62–64] were applied.

Methacrylic acid was identified and quantified by ion chromatography (Dionex 2010i; Ion-Pac AS9-SC column; eluent: 1×10^{-3} mol dm^{-3} $NaHCO_3$) after ultrafiltration (Amicon TCF10 system with a Diaflo YM10 membrane) at pH 3 in order to remove polymeric material.

Post-irradiation spectral changes (λ-16, Perkin-Elmer) under anoxic conditions were followed in a gastight quartz cell equipped with a purging device (cf. ref. [65]).

EPR spectra were recorded on a laboratory-built X-band spectrometer with 100 kHz modulation equipped with an interface (Stelar, Mede) and a PC. For in situ experiments, the aqueous solutions with poly(methacrylic acid) and H_2O_2 were purged with argon, pumped through the quartz cell of the flow system, and irradiated in the cavity of the EPR instrument with unfiltered focused light from an argon plasma light source (GAT, Bremerhaven).

In the spin-trapping experiments, the samples were irradiated either with γ-rays or with unfiltered UV light from a xenon lamp (LX300UV Cermax, ICL Technology, Sunnyvale) and transferred to the quartz cell of the EPR instrument. The spin trap, 2-methyl-2-nitrosopropane (Sigma), was either present during γ-irradiation or added afterwards.

Weight-average molecular weights were determined by low-angle laser light scattering (Chromatix KMX-6 equipped with He/Ne laser, $\lambda =$ 633 nm, scattering angle 6–7°) in $NaClO_4$ (0.02 mol dm^{-3}) at pH 10 with freshly filtered (0.45 µm; Millex HA, Millipore) solutions. The refractive index increment (d*n*/d*c*) for poly(methacrylic acid) in this solvent was determined with a laser differential refractometer (Chromatix KMX16, $\lambda = 633$ nm) at 20 °C to be 0.253 cm^3 g^{-1}.

Poly(methacrylic acid) radicals have a very long lifetime, and, to avoid their reaction with oxygen, the irradiated samples were kept unopened overnight in the dark prior to analysis.

Simulations were performed on a standard PC with Chemical Kinetics Simulator software (version 1.01), developed by IBM at the Almaden Research Center.

Results and Discussion

The free-radical generating system: In the present study, poly(methacrylic acid) radicals were generated in dilute aqueous solution by ionizing radiation. The proportion of the energy of the ionizing radiation absorbed by each component of the system can be approximated by its weight fraction, that is, in the case of dilute polymer solutions (concentrations $<1\,\mathrm{g\,dm^{-3}}$ were used in this work), the absorption of ionizing radiation by the polymer itself can be neglected. Thus, the free-radical reactions are induced by the radicals created during the absorption of the ionizing radiation by water [cf. reaction (1)]. In this context, it is important to recall that ^{60}Co-γ-rays and high-energy electrons (e.g. 2.8 MeV electrons used in pulse radiolysis) lead to identical free-radical yields.[66] The radiation-chemical yields are expressed as G values (units: $10^{-7}\,\mathrm{mol\,J^{-1}}$). The radiolysis of water yields $^{\bullet}$OH radicals, hydrated electrons, and hydrogen atoms [reaction (1), $G(^{\bullet}\mathrm{OH}) \approx G(\mathrm{e^-_{aq}}) = 2.8\times10^{-7}\,\mathrm{mol\,J^{-1}}$,

$$\mathrm{H_2O} \xrightarrow[\text{radiation}]{\text{ionizing}} \mathrm{e^-_{aq}},\ {}^{\bullet}\mathrm{OH},\ \mathrm{H^{\bullet}},\ \mathrm{H_2O_2},\ \mathrm{H_2},\ \mathrm{H^+},\ \mathrm{OH^-} \qquad (1)$$

$G(\mathrm{H^{\bullet}}) = 0.6\times10^{-7}\,\mathrm{mol\,J^{-1}}$]. The hydrated electrons can be readily converted into further $^{\bullet}$OH by saturating the solution with $\mathrm{N_2O}$ [cf. reaction (2), $k = 9.1\times10^{9}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$].[67] Thus,

$$\mathrm{e^-_{aq}} + \mathrm{N_2O} \rightarrow {}^{\bullet}\mathrm{OH} + \mathrm{N_2} + \mathrm{OH^-} \qquad (2)$$

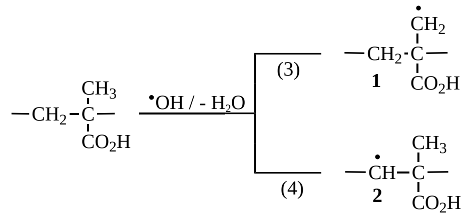
the $\mathrm{N_2O}$ containing system consists of 90% $^{\bullet}$OH and only 10% $\mathrm{H^{\bullet}}$, and since H atoms also undergo H abstraction (see below), albeit at a lower rate, we can add them to the OH radical yield without inducing a major error.

The reactivity of hydrated electrons towards poly(methacrylic acid) is too low ($k < 4\times10^{6}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$)[44] to compete with reaction (2) under our experimental conditions. At pH 8.4, when the poly(methacrylic acid) is deprotonated, $^{\bullet}$OH radicals react faster ($1.2\times10^{8}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$, with respect to monomer units) than at pH 3.1 ($3.1\times10^{7}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$),[44] when poly(methacrylic acid) is protonated (reported values[49] are higher due to the lower molecular weight of the polymer in that study). The pH effect on the rate is mainly attributed to different conformations of the polyelectrolyte chain (and thus to different reaction geometries). It also reflects the electrophilic property of the $^{\bullet}$OH radical, which leads to a faster reaction with the anions of carboxylic acids than with their protonated forms.[40, 67] The rate of reaction of $^{\bullet}$OH radicals with polymers is lower than that for the corresponding low molecular-weight compounds. A detailed discussion of this aspect can be found elsewhere.[68–71]

In some of the EPR experiments, $^{\bullet}$OH radicals were also generated by photolytic cleavage of $\mathrm{H_2O_2}$ added to the samples.

Reaction of $^{\bullet}$OH radicals with poly(methacrylic acid): Hydroxyl radicals react with low molecular-weight carboxylic acids by abstraction of carbon-bound hydrogens. In poly(methacrylic acid), there are two sites for OH radical attack: methyl and methylene groups [reactions (3) and (4); formation of radicals **1** and **2**].

In their reactions with carboxylic acids, $^{\bullet}$OH radicals show little selectivity,[40, 72] and also in the present case both sites are attacked to a significant extent. Judging from studies on small carboxylic acids[40, 73] and poly(acrylic acid),[41] there is no evidence of a noticeable attack at the carboxylic group.



The initial absorption spectrum of radicals **1** and **2** (Figure 1) shows an increasing absorbance towards shorter wavelengths and a shoulder localized at 320 nm (cf. also ref. [49]).

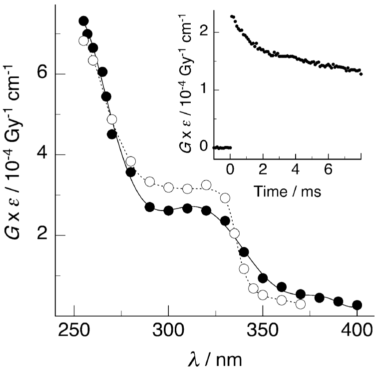
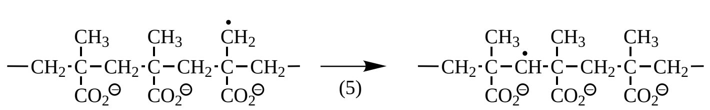


Figure 1. Pulse radiolysis of $\mathrm{N_2O}$ saturated aqueous solution of poly(methacrylic acid). Initial absorption spectra (10 µs after the pulse) of polymer radicals at pH 3.5 (●) and at pH 8.5 (○). Polymer concentration $1\times10^{-2}\,\mathrm{mol\,dm^{-3}}$ and dose per pulse 7–22 Gy. Corrections for $^{\bullet}$OH recombination have been made. Inset: decay of absorbance at 320 nm at pH 7.5.

The spectra observed at low and high pH are very similar. β-Carboxyalkyl radicals like **1** and **2** usually exhibit a featureless spectrum with a maximum localized below 250 nm.[72] Spectra of simple α-carboxyalkyl radicals have a maximum at around 280–320 nm; the maximum is red-shifted by 30–60 nm upon deprotonation.[72] Such radical structures, however, cannot be formed in our system at this initial stage. Also the location of the shoulder in the present case does not exhibit the typical red shift. Therefore the shoulder in the spectrum must be a feature of radicals **1** and/or **2**. Data on further spectral changes, in particular those that accompany the chain-scission reaction (see below), indicate that the shoulder in the initial absorption spectrum can essentially be attributed to radical **1**.

H transfer from the methylene group to the $-\mathrm{CH_2^{\bullet}}$ radical (conversion of 1 → 2): The lifetimes of the radicals of deprotonated poly(methacrylic acid) are very long (see below), and therefore moderately slow reactions may precede recombination. Within 10 ms, that is, at times when recombination is still minimal under our conditions, a change in the absorption spectrum is observed. While the absorbance at the low-wavelength side remains unchanged, there is a pronounced decrease in absorption at around 320 nm (inset in Figure 1). This can be attributed to an intramolecular H transfer from a methylene group to radical **1** [reaction (5);



$$\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\dot{\text{C}}\text{H}_2}{\text{C}}}\text{—CH}_2\text{—} \xrightarrow[(5)]{} \text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—}\dot{\text{C}}\text{H-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—}$$

1 **2**

$k = 3.5 \times 10^2\ s^{-1}$]. This transforms the initially formed primary radical **1**, possibly via a six-membered transition state, into the secondary radical **2**, which is of lower energy (the difference in bond dissociation energies is ca. $12\ kJ\,mol^{-1}$, cf. refs. [74, 75]). After this transformation, radical **2** is the dominating radical in our system.

Analogous radical transfer processes are well-known from the free-radical chemistry of low molecular-weight species (e.g. intermolecular hydrogen transfer from 2-propanol to the β-hydroxypropyl radical, $k \approx 10^3\ dm^3 mol^{-1} s^{-1}$).[76] An example of intramolecular transfer in polymers is the poly(vinyl alcohol) system, in which a secondary radical is transformed into a tertiary one ($k = 4.6 \times 10^2\ s^{-1}$).[77] With fully protonated poly(acrylic acid),[41] the intramolecular conversion of the secondary radical into the tertiary one is $\approx 150\ s^{-1}$, that is, slower. This is understood, because the tertiary hydrogen in poly(vinyl alcohol) is more loosely bound than its counterpart in poly(acrylic acid). Upon deprotonation of poly(acrylic acid), the rate of H transfer drops to $0.7\ s^{-1}$. Under these conditions, the poly(acrylic acid) assumes a less flexible rodlike conformation, and since the same five-membered transition state (not very favorable in H transfer reactions) would still be possible after deprotonation, this drop in reactivity may be taken as an indication that H transfer from more distant sites takes place in this system and also with poly(vinyl alcohol).

Chain scission: In the absence of O_2, free-radical-induced chain scission is not typical for uncharged polymers in solution, since the recombination of the polymer radicals is fast, and the relatively slow scission reactions (by means of β-fragmentation) cannot compete effectively. However, in the case of charged (deprotonated) poly(acrylic acid), for which the radicals are long-lived because of the electrostatic repulsive forces, chain scission becomes a pronounced process.[41] Also with poly(methacrylic acid) in O_2-free aqueous solution a pronounced decrease in the average molecular weight[46, 47, 49, 50] is observed (see also our data below).

The kinetics of chain scission can be followed by pulse radiolysis. However, standard spectrophotometric detection is usually of little help, because spectral changes are in general not pronounced and cannot be attributed with certainty to chain breakage (cf. the transformation reactions discussed above). Therefore, two alternative time-resolved detection methods are applied, namely detection by light scattering[78, 79] and, for polyelectrolytes, conductometry.[80–83] The latter method is very sensitive, that is, very low doses per pulse can be applied. Conductometric detection of chain scission is based on the fact that in solution the majority of the counterions of a polyion forms a loose cloud (condensed counterions), which cannot leave the potential valley of the polyion, and thus these counterions do not contribute to the conductivity. When a chain scission occurs and the broken ends diffuse apart, the electrostatic potential around the newly formed chain ends is lowered, and a few counterions are released into the bulk solution. This leads to an increase in conductivity (for a detailed description see ref. [80]). The method has been successfully applied in studies on chain scission in natural and synthetic polyelectrolytes.[41, 80–83]

When an electron pulse is applied to a dilute solution of deprotonated poly(methacrylic acid), a pronounced increase in conductivity is observed (Figure 2).

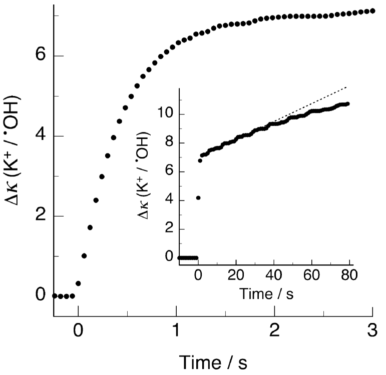
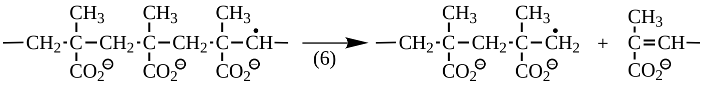


Figure 2. Pulse radiolysis of N_2O saturated aqueous solution of poly(methacrylic acid). Conductivity changes (expressed as the released number of K^+ per $^{\bullet}OH$) as a function of time. Polymer concentration $4 \times 10^{-4}\ mol\,dm^{-3}$, pH 8.5, and dose per pulse 2 Gy. The slope given by the dotted line in the inset represents the rate of monomer release (see text below).

This process consists of two kinetically separated parts. The fast step occurs within the first few seconds, followed by a further slow increase on the timescale of minutes (inset in Figure 2). We attribute the fast step of conductivity increase to chain breakage [β-scission of radicals **2**, reaction (6)].



$$\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—}\dot{\text{C}}\text{H—} \xrightarrow[(6)]{} \text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{-}\underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{—}\dot{\text{C}}\text{H}_2 + \underset{\text{CO}_2^{\ominus}}{\overset{\text{CH}_3}{\text{C}}}\text{=CH—}$$

2 **3** **4**

In this reaction, two chain fragments are formed; one bears a primary terminal radical **3**, and the other carries the olefinic element **4**. As expected, the reaction is of first-order kinetics, and the half-life is independent of the dose per pulse (0.02–5 Gy). The pH range 7–9 is most suitable for the measurement of counterion release without disturbance from other effects (see below). There, the rate constant of chain scission is $k = 1.8\ s^{-1}$, which is almost independent of pH (Figure 3).

The scission of poly(methacrylic acid) is faster by nearly two orders of magnitude than that of poly(acrylic acid) ($k = 0.025\ s^{-1}$).[41] This difference may be attributed to differences in the stability of the break-initiating radicals [the tertiary radicals of *poly*(*acrylic acid*) are considered to be more stable than the secondary ones in *poly*(*methacrylic acid*)]. For poly(methacrylic acid), a much higher rate constant of chain scission ($k = 1.4 \times 10^4\ s^{-1}$) has been reported before.[49] This value was arrived at on the basis of the influence of

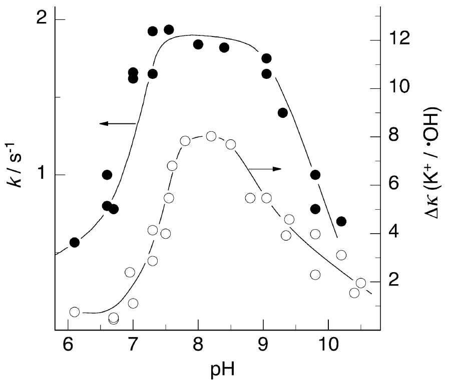


Figure 3. Pulse radiolysis of N_2O saturated aqueous solutions of poly(methacrylic acid). Rate (●, left axis) and amplitude (○, right axis) of the fast conductivity increase as a function of pH. Polymer concentration 2.5×10^{-4} mol dm^{-3} and dose per pulse 2 Gy.

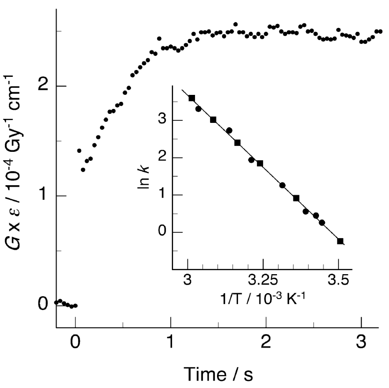


Figure 4. Pulse radiolysis of N_2O saturated aqueous solutions of poly(methacrylic acid) at pH 7.5. Absorbance change at 320 nm as a function of time (for changes at shorter times see Figure 1). Inset: Arrhenius plot of the spectral (●, cf. main graph) and conductivity (■, cf. Figure 2 main graph) changes at pH 8.5.

benzoquinone on radiation-induced viscosity changes. Depolymerization (see below) has not been taken into consideration, and the high yield of monomer might have led to this large overestimation. Our measurements were done by a more direct method, and we believe that the earlier value has to be revised.

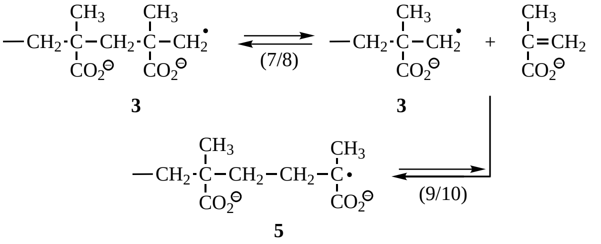
The lower curve in Figure 3 illustrates the amplitude dependence of the fast conductivity increase on the pH. This dependence does not reflect changes in scission yields, but rather the influence of pH on the efficiency of counterion release. If the pH is lowered, the carboxylate groups become protonated, and at an average charge spacing (≥ 0.7 nm), that is, before the polymer is fully protonated, counterions are no longer condensed.[84] At pH > 9, addition of excess base increasingly leads to screening effects, and the efficiency of counterion release decreases. A similar decrease (data not shown) is observed, when equivalent amounts of neutral salt, $NaClO_4$, were added to solutions of fully dissociated poly(methacrylic acid).

At optimum conditions, on average 7–8 counterions are released per chain break (Figure 3, lower curve). This value is close to that reported for DNA and polynucleotides (8.5 ions per break)[81] and similar to that found for poly(acrylic acid) (5.3 ions per break).[41]

Concomitantly with the fast step of conductivity increase, a second change in the absorption spectrum is observed (Figure 4).

The absorbance at 320 nm rises again, after its decrease in the ms range, and the original shoulder (cf. Figure 1) reappears. Since the kinetics of this process, including the activation parameters ($E_a = 64$ kJ mol^{-1}, $\Delta H^{\ddagger} = 62$ kJ mol^{-1}, $\Delta S^{\ddagger} = -29$ J mol^{-1} K^{-1}),[45] are identical to those of the conductivity change (cf. inset in Figure 4), these spectral changes must be due to chain scission, that is, to the transformation of radical **2** into radical **3**. This is in agreement with our assignment of the initial shoulder at 320 nm to radical **1**, since radical **3** has a structure very similar to that of radical **1** (both are primary β-carboxyalkyl radicals).

Depolymerization: γ-Irradiated deoxygenated aqueous solutions of poly(methacrylic acid) bleach iodine and $KMnO_4$.[49] This has been attributed to the formation of unsaturated structures (cf. structure **4**) formed upon chain scission. In our preliminary reports, we have shown that this effect must be mainly due to the high amounts of monomer, that is, methacrylic acid, that are released upon irradiation.[44, 45] Under certain conditions, the methacrylic acid yield reaches $G = 500 \times 10^{-7}$ mol J^{-1}, that is, the monomer yield is two orders of magnitude higher than that of polymer radicals. Thus in our system, an efficient depolymerization takes place by means of a chain reaction [reaction (7)]. In contrast, no significant depolymerization occurs with poly(acrylic acid) under otherwise equal conditions.[41]



$$\text{—CH}_2\text{·}\overset{\text{CH}_3}{\underset{\text{CO}_2^{\ominus}}{\text{C}}}\text{–CH}_2\text{·}\overset{\text{CH}_3}{\underset{\text{CO}_2^{\ominus}}{\text{C}}}\text{–}\dot{\text{C}}\text{H}_2 \underset{(7/8)}{\rightleftharpoons} \text{—CH}_2\text{·}\overset{\text{CH}_3}{\underset{\text{CO}_2^{\ominus}}{\text{C}}}\text{–}\dot{\text{C}}\text{H}_2 + \overset{\text{CH}_3}{\underset{\text{CO}_2^{\ominus}}{\text{C}}}\text{=CH}_2$$

3 **3**

$$\text{—CH}_2\text{·}\overset{\text{CH}_3}{\underset{\text{CO}_2^{\ominus}}{\text{C}}}\text{–CH}_2\text{–CH}_2\text{–}\overset{\text{CH}_3}{\underset{\text{CO}_2^{\ominus}}{\text{C}}}\bullet \underset{(9/10)}{\rightleftharpoons} \mathbf{3}$$

5

The final monomer concentration (measured after 24 h to allow all radicals to decay, that is, the irradiated samples were left unopened during this period) depends on pH (Figure 5), on the radiation dose (Figure 6), on the dose rate, on the polymer concentration (Figure 7), and on the presence of neutral salt (inset in Figure 5).

The explanation of some of these features is straightforward. For example, the pH dependence of the monomer yield (Figure 5) must be related to the lifetime of the radicals. This increases (see below) from milliseconds for uncharged poly(methacrylic acid) radicals up to minutes for fully deprotonated ones [cf. also the poly(acrylic acid) system].[41] The slow (see below) depolymerization [reaction (7)] can only become effective, when the competing termination of **3** and **5** is slowed down by repulsive coulombic forces. Like protonation, the addition of salt (cf. Figure 5, inset) reduces the radical lifetime by charge-screening effects, which make the polymer chains more flexible and enhance the encounter frequency of the polymer radicals.

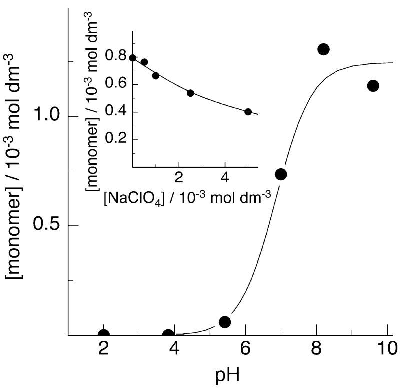


Figure 5. γ-Radiolysis of N_2O saturated solutions of poly(methacrylic acid). Final methacrylic acid concentration at a dose of 22.2 Gy (initiating radical concentration $= 1.33 \times 10^{-5}$ mol dm^{-3} and dose rate 0.0921 Gy s^{-1}) as a function of pH. Inset: The same as a function of the salt concentration at pH 9.5. Polymer concentration 1×10^{-2} mol dm^{-3} (main graph) and 5×10^{-3} mol dm^{-3} (inset). The samples were kept unopened for 24 h prior to analysis.

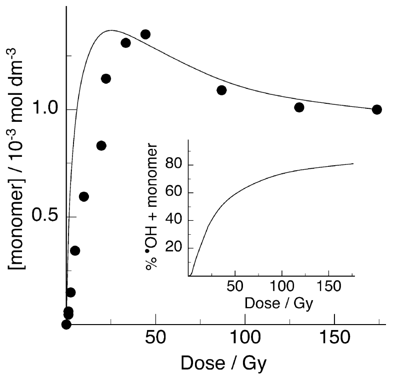


Figure 6. γ-Radiolysis of N_2O saturated solutions of poly(methacrylic acid) at pH 9.6. Final methacrylic acid concentration as a function of dose. Dose rate 0.092 Gy s^{-1} and polymer concentration 1×10^{-2} mol dm^{-3}. The samples were kept unopened for 24 h prior to analysis. The solid line has been obtained by simulation by using the values given in Table 1. Inset: Fraction of $^{\bullet}OH$ radicals scavenged by methacrylic acid during the whole irradiation time as calculated by simulation (see text below).

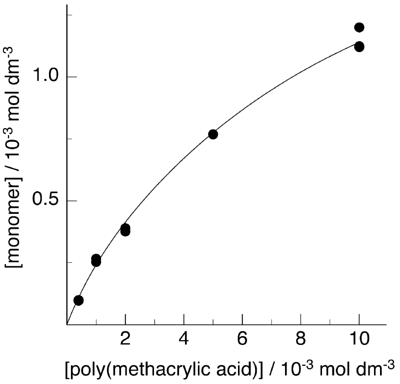
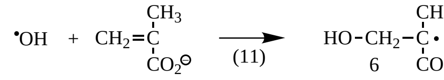


Figure 7. γ-Radiolysis of N_2O saturated solutions of poly(methacrylic acid) at pH 9.6. Final methacrylic acid concentration as a function of polymer concentration. Dose 22.2 Gy (initiating radical concentration $= 1.33 \times 10^{-5}$ mol dm^{-3}) and dose rate 0.092 Gy s^{-1}. The samples were kept unopened for 24 h prior to analysis. The solid line has been obtained by simulation by using the values given in Table 1.

Formation of methacrylic acid during exposure to radiation lowers the yields of polymer radicals, since $^{\bullet}OH$ radicals are effectively scavenged by methacrylic acid [reaction (11), $k \approx 2 \times 10^{10}$ dm^3 mol^{-1} s^{-1};[85, 86] cf. inset in Figure 6]. This competition is one of the reasons for the pronounced dependence of monomer formation on the poly(methacrylic acid) concentration (Figure 7; for a further contribution to this effect see below).



$$^{\bullet}OH + CH_2{=}\underset{CO_2^{\ominus}}{\overset{CH_3}{C}} \xrightarrow[(11)]{} HO{-}CH_2{-}\underset{CO_2^{\ominus}}{\overset{CH_3}{C}}{\bullet} \quad 6$$

Reaction (11) initiates polymerization by means of dimer, trimer, and oligomer radical formation (for a study on the early stages of methacrylic acid polymerization see ref. [87]). These low molecular-weight radicals will disappear quite rapidly by self-termination and possibly by reacting with the long-chain terminal radicals **3** and **5**. These reactions are mainly responsible for the decrease in the monomer yield at the longer irradiation times (Figure 6).

It has to be taken into account that depolymerization is reversible, that is, once methacrylic acid is present in the system, polymerization takes place as well [e.g. reactions (8) and (10)]. This aspect will be discussed in more detail below.

EPR spectra and formation of α-carboxyalkyl radicals 5: Three methods have been used to generate poly(methacrylic acid) radicals for EPR experiments.

1) γ-Irradiation followed by transfer of the sample to the EPR spectrometer.
2) γ-Irradiation with concomitant or subsequent spin-trapping using 2-methyl-2-nitrosopropane.
3) in situ UV irradiation in the presence of hydrogen peroxide.

When poly(methacrylic acid) radicals were generated at pH 3.5 by either γ-rays or UV light in the absence of a spin trap, EPR signals were too low for an assignment. At this pH, the radicals are short-lived, and no detectable radical concentration builds up, not even under in situ UV irradiation. However in the presence of a spin trap, spectra could be recorded (Figure 8), although the signals fade away a few

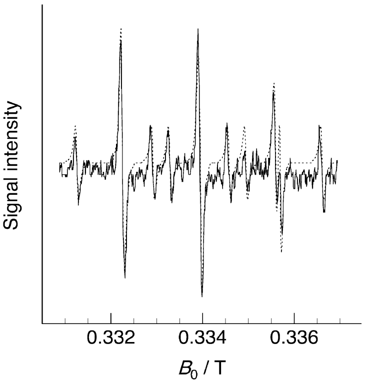


Figure 8. γ-Irradiation of a N_2O saturated solution of poly(methacrylic acid) (20×10^{-3} mol dm^{-3}) in the presence of 2-methyl-2-nitrosopropane (4×10^{-3} mol dm^{-3}) at pH 3.5. EPR spectrum (first derivative) of the spin adduct. Solid line: experimental spectrum; dotted line: simulation with parameters given in the text.

minutes after the end of irradiation due to the low stability of the 2-methyl-2-nitrosopropane adducts in acid solutions (cf. ref. [88]).

In the presence of the spin trap, the spectra of γ- and UV-irradiated samples are similar. They can be interpreted as an overlay of two spectra. A dominant structure is a triplet of triplets ($a_N = 1.634$ mT, $a_H(2) = 0.999$ mT), that can be attributed to radical **1** and/or to the terminal radical **3**. Another, weaker signal is a triplet ($a_N = 1.70$ mT) with no splitting by H atoms. This is attributed to the adduct of the terminal radical **5**. The observation of the spin adduct of this radical indicates that some of the precursor radicals, for example, **1** and **2**, do not react with the spin trap efficiently (the polymer chain is tightly coiled at this pH). If some of the radicals **3** are scavenged with the spin trap, depolymerization and subsequent re-polymerization to **5** [reactions (7) and (9)] must be reduced. This is partially counterbalanced by an increased rate of polymerization at low pH (cf. refs. [89–91]).

At high pH, the long lifetime of the poly(methacrylic acid) radicals allows their EPR spectra to be recorded on samples without a spin trap, even after γ-irradiation and transfer to the EPR spectrometer (the transfer took ca. 2 min). In these samples, and also in UV-irradiated ones, the dominating spectrum consists of sixteen lines (Figure 9), whose coupling constants are $a_H(3) = 2.19$ mT, $a_H(1) = 0.66$ mT, and $a_H(1) = 1.785$ mT.

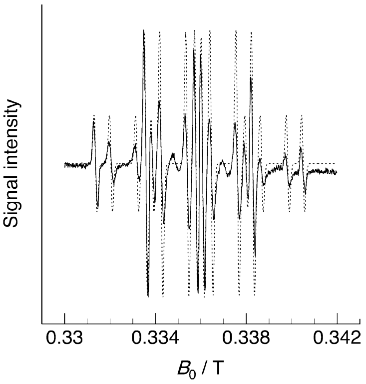


Figure 9. In situ UV irradiation of argon saturated aqueous solution of H_2O_2 containing poly(methacrylic acid) at pH 9.8 and 15 °C. Solid line: experimental EPR spectrum (first derivative); dotted line: spectrum simulated with the coupling constants given in the text. The line-width effects in the experimental spectrum are due to a slow exchange between the two nonequivalent methylene positions.

We attribute this spectrum to the terminal radical **5**; the quartet results from the methyl β-protons and two different doublet splittings by two nonequivalent β-protons of the methylene group (cf. the terminal radicals of methacrylic acid dimers and trimers).[87] When the spin trap is added *after* recording these spectra, the signal is replaced (data not shown) by a triplet ($a_N = 1.70$ mT) with relatively broad lines ($\Delta\nu 0.2$ mT); this is expected for the spin adduct of radical **5** immobilized by repulsive electrostatic forces of the carboxylate groups. These data indicate that the mechanisms, which convert radicals **3** into radicals **5** [e.g. reactions (7) and (9)], are quite effective, that is, equilibria (7)–(10) are mainly on the side of **5** under these conditions.

Generally, vinyl-type monomers polymerize by adding preferentially at the side of unsubstituted carbons (steric hindrance and radical stabilization are invoked as the most important reasons, cf. refs. [92–94]). In our system, this enriches α-carboxylalkyl radicals **5** [cf. reaction (9)] at the expense of β-carboxylalkyl radicals **3**, formed by chain scission and by monomer addition [reactions (6) and (8)]. Based on the few data available, one can expect that in a typical radical polymerization the ratio between the head-to-head and head-to-tail structures usually does not exceed 1:100.[92] Simulations indicate that if a ratio of 1:100 is assumed for the rate constants of addition at substituted and unsubstituted carbons [reactions (8) and (9)], after about two minutes, when these addition reactions become more important, **5** starts to dominate over **3**. This explains why in the EPR spectra radicals **5** dominate despite the fact that originally only radicals **3** are formed in the scission reaction [cf. reaction (6)].

There is potentially a further process that can additionally enhance the transformation of **3** into **5**. If our starting poly(methacrylic acid) contains about 1% head-to-head junctions, the unzipping process, when it reaches such a junction, will transform the terminal radical **3** into radical **5**.

In the case of in situ UV irradiation, there is a given chance that the short-chain radicals, which result from $^{\bullet}OH$ attack on the released monomer and subsequent propagation steps, will contribute. However, they have a structure analogous to **5**, and thus cannot be detected separately.

Lifetime of radicals: The most direct method of following the decay of radical concentration is EPR spectroscopy. However, the application of this technique for the present kinetic study has some limitations. Relatively high radical concentrations are required for obtaining good signals. Thus, kinetic experiments could only be done by in situ UV irradiation of H_2O_2/poly(methacrylic acid) solutions. Here, however, the initial radical concentration is not exactly known. Therefore, the conditions for kinetic EPR measurements differ from other long-timescale experiments, and the experiments cannot be compared on a *quantitative* basis, for example, with the monomer-release data. Higher initial radical concentrations imply faster bimolecular decay. Nevertheless, at an initial radical concentration higher than typically obtained by γ-irradiation, a half-life as high as 45 s is observed for the fully dissociated poly(methacrylic acid) at pH 9.8 (Figure 10). If the pH is lowered to 8.0 under the same conditions, the half-life is shortened to approximately 5 s (inset in Figure 10). At pH 3.5, the decay of the now uncharged poly(methacrylic acid) radicals is so fast that no ESR signal could be recorded.

The termination of charged polymer radicals may also be followed by the decay of their UV absorbance (Figure 11). An N_2O saturated poly(methacrylic acid) solution was subjected to γ-irradiation for 15–60 s at high dose rate, and the decay of absorption was followed spectrophotometrically. The EPR experiments (cf. Figures 9 and 10) show that under such conditions (high pH, many seconds after irradiation) the main polymeric radical is **5**. The UV spectrum expected for such α-carboxyalkyl radicals is characterized by a maximum or a shoulder at around 320 nm (for the spectra of analogous

0947-6539/00/0621-3928 $ 17.50+.50/0

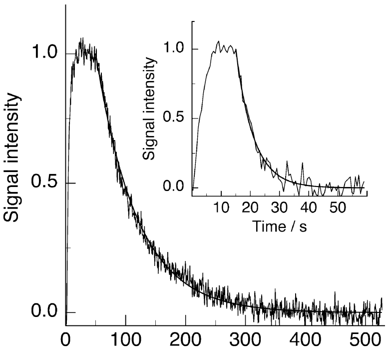


Figure 10. Buildup and decay of the EPR signal generated by UV photolysis of a solution containing poly(methacrylic acid) and H_2O_2 at pH 9.8 (main graph) and 8.0 (inset). The illumination periods were 50 s and 15 s, respectively.

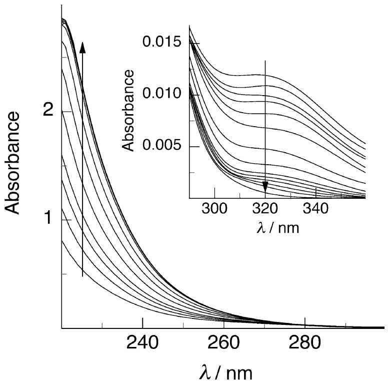


Figure 11. γ-Irradiation (15 s, dose 56 Gy) of N_2O saturated solution of poly(methacrylic acid) (1×10^{-2} mol dm^{-3}) at pH 9.7. Spectra recorded 72, 127, 182, 238, 361, 540, 787, 1222, 1805, 2910, 3770, 6482, 12600, and 22500 s after the end of irradiation. Main graph: from bottom to top; inset: from top to bottom.

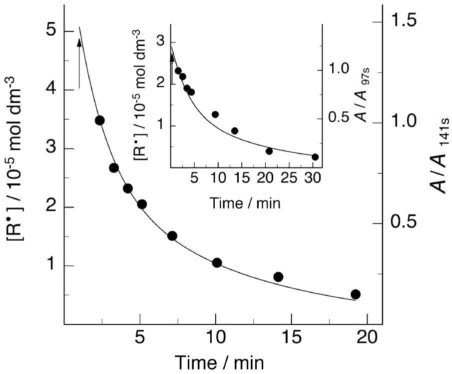


Figure 12. γ-Irradiation of N_2O saturated solution of poly(methacrylic acid) (1×10^{-2} mol dm^{-3}) at pH 9.7. Relative changes in absorbance at 320 nm (●, right axis) after 60 s of irradiation (dose 224 Gy, main graph) and after 15 s of irradiation (56 Gy, inset). Radical concentrations obtained by simulation (solid line, left axis) by using the rate constants listed in Table 1. Arrows denote the end of irradiation.

radicals, see ref. [72]). The short-wavelength part of the observed spectrum (Figure 11) is dominated by the growing absorption of the monomer released. However, the monomer does not absorb at $\lambda \geq 300$ nm, and the decay at $\lambda = 320$ nm can be attributed to the termination of the poly(methacrylic acid) radicals **5**.

At two different doses, the decay of the long-chain radicals **5** could be reasonably modeled by assuming a bimolecular reaction with a rate constant of $2k = 80$ dm^3 mol^{-1} s^{-1} (Figure 12). This value also allowed us to simulate the kinetics of monomer release adequately (see below).

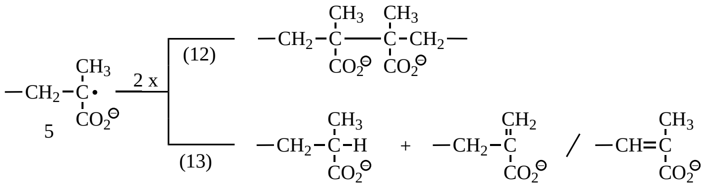
From our pulse radiolysis data, the intermolecular bimolecular decay rate constant of poly(methacrylic acid) radicals at pH 3.5 (almost fully protonated acid) is estimated at $2k \approx 10^7$ dm^3 mol^{-1} s^{-1}. Precise measurements regarding such *inter*molecular rate constants are difficult, because of the low absorption coefficients of the radicals and the necessity of using low doses to avoid formation of multiple radical sites at one macromolecule (otherwise the measured decay kinetics would be dominated by *intra*molecular recombination, which can be very fast).[69, 95]

With *uncharged* alkyl-type radicals [for poly(methacrylic acid) in the acidic range], the recombination is usually close to diffusion-controlled. For small molecules, the rate constant of this reaction is typically in the order of 10^9 dm^3 mol^{-1} s^{-1}. With polymer radicals, the rate constant of termination drops. According to the Smoluchowski equation, this is caused by the lower diffusion coefficient of polymers. In addition, the termination of polymer radicals requires segmental diffusion of the radical sites for their mutual encounter (cf. refs. [92, 96]). Experimental data can be described by $k_t = \mathrm{A} \times P_n^{-b}$,[97] where A is a constant, and P_n is the number-average degree of polymerization. Values of $b = 0.16-0.18$ were reported for the bulk polymerization of styrene and methyl methacrylate.[98, 99] Rate constants for uncharged polymer radicals with molecular weights similar to our poly(methacrylic acid) sample are in the order of $2k = 10^7-10^8$ dm^3 mol^{-1} s^{-1}.[96, 100–102]

Recombination of *charged* radicals is slowed down by coulombic repulsive forces. Radicals derived from simple carboxylic acids of single, double, and triple negative charge recombine approximately 2, 20, and over 100 times slower than the radicals of the corresponding fully protonated acids.[43] This tendency continues with an increasing number of charges on the radical-bearing molecule (e.g. by incorporation of an increasing number of ionic monomers into an unionized polymer[103]), and the recombination of polyelectrolyte radicals eventually becomes very slow. For radicals of fully dissociated poly(acrylic acid)[41, 43] and poly(styrene sulfonate),[104] half-lives of many minutes to hours have been observed in aqueous solutions at room temperature. Although in the latter case the authors tended to attribute the very long lifetime of the radical to the stabilizing effect of the aromatic ring, the example of poly(acrylic acid) clearly indicates that electrostatic forces alone are capable of exerting such a strong retarding effect.

Especially during the long-lasting post-irradiation period, termination will be mainly by radical **5**, which can combine as well as disproportionate [reactions (12) and (13)].

Kinetics of monomer release: Two independent experimental methods were used to follow the kinetics of depolymerization. Since the depolymerization is slow, and the lifetime of polymer radicals is long under our experimental conditions,



$$2\,\left[-CH_2-\overset{CH_3}{\underset{CO_2^{\ominus}}{C}}\bullet\right]\ (\mathbf{5}) \xrightarrow{(12)} -CH_2-\overset{CH_3}{\underset{CO_2^{\ominus}}{C}}-\overset{CH_3}{\underset{CO_2^{\ominus}}{C}}-CH_2-$$

$$\xrightarrow{(13)} -CH_2-\overset{CH_3}{\underset{CO_2^{\ominus}}{C}}-H \;+\; -CH_2-\overset{CH_2}{\underset{CO_2^{\ominus}}{\overset{\|}{C}}} \;/\; -CH=\overset{CH_3}{\underset{CO_2^{\ominus}}{C}}$$

most of the monomer is formed *after* irradiation. The monomer released *during* irradiation is largely consumed by reacting with $^\bullet OH$ (cf. Figure 6).

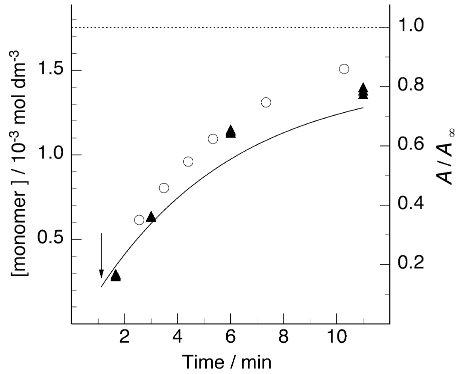


Figure 13. γ-Irradiation of N_2O saturated solution of poly(methacrylic acid) (1×10^{-2} mol dm^{-3}) at pH 9.7. Rise in monomer concentration after 1 min of irradiation (224 Gy) monitored by cysteamine addition (▲, left axis; solid line: simulation by using the rate constants listed in Table 1) and absorbance A at 225 nm relative to its final value A_∞ (○, right axis). The arrow denotes the end of irradiation; the final values (experiments and simulation) are given by the broken line.

One of the methods to determine the kinetics of the depolymerization made use of the very rapid quenching of the polymer radicals by cysteamine [$P^\bullet + RSH \rightarrow PH + RS$; for α- and β-carboxyalkyl radicals of poly(acrylic acid)[41] $k \approx 1 \times 10^7$ dm^3 dm^{-1} s^{-1} and $k = 8 \times 10^7$ dm^3 dm^{-1} s^{-1}]. N_2O saturated poly(methacrylic acid) solutions were γ-irradiated for 15–60 s, and the reactions allowed to proceed for a given time. The radicals were then quenched by the addition of deoxygenated cysteamine solution through a septum while stirring vigorously. After ultrafiltration, methacrylic acid concentrations were determined. The kinetics of monomer release are shown in Figure 13 (triangles), together with the final methacrylic acid concentration (broken line) obtained by keeping the samples for 24 h without the addition of scavenger.

Another set of kinetic data for monomer release was obtained spectrophotometrically at 225 nm, when methacrylic acid strongly absorbs [ε(225nm) $= 1.2 \times 10^3$ dm^3 mol^{-1} cm^{-1}; Figures 11 and 13]. Although at this wavelength some overlay from the absorbance of radicals [ε(225nm) $\leq 2 \times 10^3$ dm^3 mol^{-1} cm^{-1}, cf. ref. [72], where spectra of similar radicals have been measured down to 235 nm] and other stable products takes place, their contribution is not great, because of their low concentration compared with the amount of methacrylic acid released.

The monomer release data obtained by radical quenching and by spectroscopy agree and can be reasonably simulated (solid line in Figure 13) using the rate constants listed in Table 1. The most valuable pieces of information extracted from these data are the rate constants of depolymerization (depropagation) and propagation.

Table 1. List of reactions and their rate constants used in the simulation of OH radical-induced reactions of deprotonated poly(methacrylic acid). Second-order rate constants are given as k (not $2k$). The rate constant of reaction 1 is expressed in dm^3(mol of monomer units)$^{-1}$ s^{-1}. The units for first-order reactions are s^{-1} and for second-order reactions dm^3 mol^{-1} s^{-1}. Explanation of symbols: P = polymer chain, M = monomer, and $SC^\bullet$ = short-chain (oligomer) radical.

	Reaction	Eq. in the text	Rate constant	References
1	$^\bullet OH + P \rightarrow \mathbf{2}$	(4)	1.1×10^8	refs. [44, 45]
2	$\mathbf{2} \rightarrow \mathbf{3} + P$	(6)	1.8	refs. [44, 45], and this work
3	$\mathbf{3} \rightarrow \mathbf{3} + M$	(7)	0.1	this work
4	$\mathbf{5} \rightarrow \mathbf{5} + M$		0.1	this work
5	$SC^\bullet \rightarrow SC^\bullet + M$		0.1	this work
6	$\mathbf{3} \rightarrow \mathbf{5} + M$		1×10^{-3}	assumed as 1% of **3–5**
7	$\mathbf{5} \rightarrow \mathbf{3} + M$	(10)	1×10^{-3}	assumed as 1% of **3–5**
8	$\mathbf{3} + M \rightarrow \mathbf{5}$	(9)	15	this work
9	$\mathbf{5} + M \rightarrow \mathbf{5}$		15	this work
10	$\mathbf{3} + M \rightarrow \mathbf{3}$	(8)	0.15	assumed as 1% of **8–9**
11	$\mathbf{5} + M \rightarrow \mathbf{3}$		0.15	assumed as 1% of **8–9**
12	$SC^\bullet + M \rightarrow SC^\bullet$		5×10^2	this work
13	$\mathbf{2} + \mathbf{2} \rightarrow P$		40	this work
14	$\mathbf{2} + \mathbf{3} \rightarrow P$		40	this work
15	$\mathbf{2} + \mathbf{5} \rightarrow P$		40	this work
16	$\mathbf{3} + \mathbf{3} \rightarrow P$		40	this work
17	$\mathbf{3} + \mathbf{5} \rightarrow P$		40	this work
18	$\mathbf{5} + \mathbf{5} \rightarrow P$		40	this work
19	$\mathbf{2} + SC^\bullet \rightarrow P$		$1-4 \times 10^4$	this work
20	$\mathbf{3} + SC^\bullet \rightarrow P$		$1-4 \times 10^4$	this work
21	$\mathbf{5} + SC^\bullet \rightarrow P$		$1-4 \times 10^4$	this work
22	$SC^\bullet + SC^\bullet \rightarrow$ oligomer		1×10^6	this work
23	$\mathbf{3} \rightarrow SC^\bullet + M$		calculated for each set of irradiation conditions (see text)	
24	$\mathbf{5} \rightarrow SC^\bullet + M$		calculated for each set of irradiation conditions (see text)	
25	$^\bullet OH + M \rightarrow SC^\bullet$	(11)	2.1×10^{10}	ref. [86]

Depolymerization proceeds with $k = 0.1$ s^{-1}. The same value is found in pulse radiolysis with conductometric detection, when the initial slope of the slow part of conductivity increase is analyzed (inset in Figure 2, broken line). Extrapolations of high-temperature data for solution radical polymerization or calculations based on the equilibrium data (see below) of other methyl-substituted vinyl polymers lead to room-temperature depropagation rate constants of a similar order of magnitude to our value for poly(methacrylic acid). For 25 °C, we calculate: $k_d = 0.6$ s^{-1} for poly(methyl methacrylate),[100, 105] $k_d = 1.2$ s^{-1} for poly(α-methylstyrene),[106] $k_d = 0.5$ s^{-1} for poly(n-dodecyl methacrylate),[107] and $k_d = 0.7$ s^{-1} for poly(n-butyl methacrylate).[107]

For the main pathway of *propagation*, that is, monomer addition that leads to **5** [e.g. reaction (9)], a rate constant of $k = 15$ dm^3 mol^{-1} s^{-1} is found in the fitting procedure. This value is considerably lower than the propagation rate constants at room temperature for uncharged methacrylic systems (methacrylic acid in acidic solution, $k = 4.1 \times 10^3$ dm^3 mol^{-1} s^{-1},[108] $k = 2.3 \times 10^3$ dm^3 mol^{-1} s^{-1};[109] methacrylic acid in methanol, 470 dm^3 mol^{-1} s^{-1};[110] methyl methacrylate in water,[111] $k = 3 \times 10^3$ dm^3 mol^{-1} s^{-1}). Therefore we conclude that the propagation rate of charged reactants is slower by two orders of magnitude. Here an electrostatic potential barrier must be overcome, when a monomeric methacrylate anion approaches a terminal radical of a strongly charged poly(methacrylic acid) chain. Low rate constants of propagation, as well as relatively high (as compared with acrylic acid) equilibrium monomer concentration allow us to explain the failure of the first attempts[112] to polymerize methacrylic acid in alkaline aqueous solution. Polymerization under these conditions is in fact possible, but its overall rate is lower by more than an order of magnitude than in acidic media, in which all species are protonated.[89–91]

The rate of propagation strongly depends on the chain length of the propagating radical. The low value given above (15 dm^3 mol^{-1} s^{-1}) only applies to long-chain radicals. For the short-chain radicals formed by OH induced oligomerization [reaction (11) and consecutive propagation steps], an average value of 500 dm^3 mol^{-1} s^{-1} has been chosen for the simulation. This is still lower than that of uncharged species of unknown chain length (see above) and the addition of a methacrylate ion to a monomer radical which has been estimated at 2×10^5 dm^3 mol^{-1} s^{-1}.[87] This value may be on the high side if one considers that it is based on an assumed bimolecular termination rate constant of 2×10^9 dm^3 mol^{-1} s^{-1}. For charged species, termination rate constants are typically considerably lower.[43]

Equilibrium concentration of monomer: As depolymerization and polymerization are slow processes, the equilibrium monomer concentration cannot be fully reached during the long lifetime of the radicals ($2k = 80$ dm^3 mol^{-1} s^{-1}). This concentration, however, can be calculated for the present system from the rate constants of polymerization and depolymerization that have been obtained by simulation (cf. Table 1). If $[\mathrm{M}]_{\mathrm{eq}} = k_{\mathrm{d}}/k_{\mathrm{p}}$, we obtain $[\mathrm{M}]_{\mathrm{eq}} = 6.7 \times 10^{-3}$ mol dm^{-3}. The highest monomer concentration reached in our experiments, under competing radical termination, was quite similar, 2×10^{-3} mol dm^{-3}.

The value of $[\mathrm{M}]_{\mathrm{eq}}$ can also be obtained by the Dainton–Ivin equation (see Introduction), provided both the enthalpy and entropy of propagation are known for a given monomer/solvent pair. To our knowledge, the entropy of propagation of methacrylate anions in water is not known. Nevertheless, a comparison with other systems is still possible. Calculations for methyl methacrylate in *o*-dichlorobenzene, based on thermodynamic data in ref. [105] at 25 °C, give $[\mathrm{M}]_{\mathrm{eq}} = 2 \times 10^{-3}$ mol dm^{-3}, not far from the present value.

An estimation of the standard entropy of propagation in the current system may be obtained from our $[\mathrm{M}]_{\mathrm{eq}}$ value, and the values for the enthalpy of propagation are reported[113, 114] for methacrylic acid in aqueous solution (these data were probably obtained under conditions, in which the monomer was largely protonated). From the spread of literature values given for ΔH_{p}, one arrives at a standard $\Delta S^{\circ}_{\mathrm{p}}$ (for monomer concentration of 1 mol dm^{-3}), which ranges from -185 to -150 J mol^{-1} K^{-1}. These values are somewhat more negative than -130 J mol^{-1} K^{-1} (approximate) typical for nonionic acrylic polymers (cf. refs. [100, 105]). The solvation shell of a *polyelectrolyte* will be ordered to a larger extent than that of a monomeric ion. Thus, the incorporation of the latter into the charged polymer may be connected with a greater entropy loss than the attachment of a monomer to a noncharged chain.

A comparison of the methacrylic acid with the acrylic acid system may be interesting. In an attempt to estimate the equilibrium monomer concentration of the latter, we assume $\Delta S^{\circ}_{\mathrm{p}}$ to be equal to the mean of our values for methacrylate and the enthalpy of propagation equal to that known for acrylic acid in water ($\Delta H_{\mathrm{p}} = -77.5$ kJ mol^{-1}).[113] This estimate leads only to $[\mathrm{M}]_{\mathrm{eq}} \approx 9 \times 10^{-6}$ mol dm^{-3}. In fact, not more than mere traces of acrylic acid were found after γ-irradiation of dissociated poly(acrylic acid)[41] under conditions similar to those in the present study. In vinyl systems, there is the general observation that methyl substitution at the vinyl function slows down the rate of propagation.[106, 115, 116] Thus, the lower $[\mathrm{M}]_{\mathrm{eq}}$ of the acrylic acid system, as compared with the methacrylic acid system, will certainly be partly due to a faster rate of propagation for acrylic acid, but if the differences in the rates of chain breakage[45] are a good guide, our data suggest that a slower depropagation will contribute to this effect.

Changes in molecular weight: As a result of chain scission [reaction (6)] and depolymerization [reactions (7) and (10)], the molecular weight of poly(methacrylic acid) decreases upon γ-irradiation (inset in Figure 14); this effect has also been reported previously.[46, 47, 49, 50]

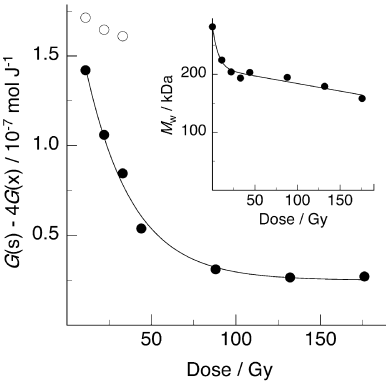


Figure 14. γ-Radiolysis of N_2O saturated solutions of poly(methacrylic acid) (1×10^{-2} mol dm^{-3}) at pH 9.6 and dose rate 0.092 Gy s^{-1}. $G(\mathrm{s}) - 4G(\mathrm{x})$ (see text) as a function of dose. The samples were kept unopened for 24 h prior to analysis. Inset: weight-average molecular weight as a function of dose. Values (○) after correction for OH radical scavenging by monomer formed during irradiation (cf. Figure 6, inset).

Based on the mechanism described above, one would expect that the actual yield of chain breaks, $G(\mathrm{s})$, for deprotonated poly(methacrylic acid) should be close to the initial yield of radicals generated in the system, that is, $G(\mathrm{s}) \approx 6 \times 10^{-7}$ mol J^{-1}. This expectation is supported by the pulse radiolytic conductivity data (cf. Figure 2), in which, before radical termination, the yield of counterion release is close to this value. Upon radical termination, however, this initially high yield of chain breaks is counteracted by the recombination of radicals. Therefore, the final decrease in molecular weight must be lower than calculated from the initial G(s). Measurements of final weight-average molecular weight, M_w, after completion of all radical reactions (Figure 14), provide only the difference in the yields of scission G(s) and *inter*molecular radical recombination G(x) according to Equation (b).[117–119]

$$G(\mathrm{s}) - 4G(\mathrm{x}) = 2\,(M_{\mathrm{w}}^{-1} - M_{\mathrm{w0}}^{-1})c/D\rho \qquad \text{(b)}$$

In the equation, M_{w0} and M_w are the weight-average molecular weights (in $\mathrm{g\,mol^{-1}}$) before and after irradiation with a dose D (in $\mathrm{Gy \equiv J\,kg^{-1}}$), c is the concentration of polymer in $\mathrm{g\,dm^{-3}}$, and ρ is the solution density in $\mathrm{kg\,dm^{-3}}$.

In a simple case, $G(\mathrm{s}) - 4G(\mathrm{x})$ should remain constant during irradiation. In our system, however, $G(\mathrm{s}) - 4G(\mathrm{x})$ decreases with dose (Figure 14). We attribute this drop mainly to effective $^{\bullet}$OH scavenging by the released monomer (cf. inset in Figure 6). Values corrected by allowing for this effect are also shown in Figure 14.

The value of $G(\mathrm{s}) - 4G(\mathrm{x})$ cannot exceed $0.25 \times G(\mathrm{s})$, that is, $1.5 \times 10^{-7}\,\mathrm{mol\,J^{-1}}$, when all of the scission-generated terminal radicals decay by intermolecular recombination only. However, in our system, this value may be higher, because radicals **5** can also disproportionate. Moreover, intense depolymerization takes place which leads to a reduction in average molecular weight and thus to an increase in the apparent scission yield. A rough estimation shows that depolymerization leads to an apparent increase of $G(\mathrm{s}) - 4G(\mathrm{x})$ in the order of 35%. Thus without depolymerization, this value is about $1.4 \times 10^{-7}\,\mathrm{mol\,J^{-1}}$, that is, close to the above value of $1.5 \times 10^{-7}\,\mathrm{mol\,J^{-1}}$, and it seems that disproportionation of radical **5** is not of major importance.

In this context it may be worth mentioning that as a consequence of the high efficiency of scission, it is not possible (in the absence of crosslinking agents) to form a wall-to-wall hydrogel with poly(methacrylic acid) by free-radical-induced reactions, not even in acid solution.[45]

Kinetic simulation: Kinetic simulations were carried out to test, whether the proposed reaction mechanism can describe our experimental results not only in a qualitative way but also on a quantitative basis. The goal is a set of rate constants that enables the simulation of key features, especially the long-timescale processes such as depolymerization and radical termination. These rate constants (partially known, assumed, and arrived at by simulation) are compiled in Table 1. After we demonstrated that some reactions are quite unimportant (e.g. the self-termination of $^{\bullet}$OH and the reaction of $^{\bullet}$OH with oligomers), these were omitted in order to reduce the simulation time. Moreover, reaction (5) is that fast that radical **1** cannot participate in further reactions, and it was assumed that radicals **2** were the only midchain radicals.

The simulation disregards the molecular weight distribution, and thus is not capable of taking into account the chain length dependence $k = \mathrm{f}(P_n)$ of rate constants. This effect has been approximated by dividing the radicals into two groups, according to their size. One comprises long-chain radicals **2**, **3**, and **5**. The second group consists of all monomer and oligomer radicals (SC$^{\bullet}$). This simple grouping allows us to take into account their difference in the rate constants which is especially important for the termination reactions.

The chain depolymerization reaction can, in principle, lead to complete unzipping of the chain, and the resulting small radical would have kinetic characteristics different from the original one. To mimic this phenomenon, a first-order process that transformed the end-chain radical into a short-chain radical was set up (reactions 23 and 24 in Table 1). The probability of this transformation was P_n times lower than the probability of a single depolymerization event, where P_n is the number-average degree of polymerization of a chain fragment after the initial chain scission [cf. reaction (6)]. In some cases, on average more than one radical per polymer chain was generated, and this causes shorter chain fragments. If one disregards these effects, there is poor agreement between experiment and simulation.

Only three of the total of 25 rate constants used in the simulation are known from the literature or our earlier measurements. Since it is impossible to treat the remaining 22 values as independent, unknown variables, the following assumptions have been made. All termination rate constants of long-chain polymer radicals (**2**, **3**, and **5**, reactions 13–18 in Table 1) are assumed to be equal, as are those for the various cross-combinations between long-chain and oligomer radicals (reactions 19–21). Equal rate constants are also assumed for depropagation events (reactions 3–5). Depropagation that crosses a head-to-head (or tail-to-tail) junction (reactions 6 and 7) is assumed to occur with a hundred times lower rate constant than that of the normal depropagation. The main propagation reactions (reactions 8 and 9) are described by one rate constant; the less probable ones (reactions 10 and 11) are assumed to occur one hundred times slower. In this way, the number of adjustable variables is reduced to only six. These were varied to obtain the best fit to all sets of experimental data.

It was further assumed that all the oligomer radicals SC$^{\bullet}$ are α-carboxyalkyl radicals (among others, radical **6**). Their steady-state concentration is much lower than that of the terminal polymer radicals (mainly due to the much faster recombination of SC$^{\bullet}$), and since the β-carboxyalkyl structures are expected not to exceed 1% of the total amount of the oligomer radicals, their concentration can be neglected.

In the ideal case, it should be possible to simulate all experimental data with one set of rate constants. As a result of the above simplifications, this is not quite possible in the present case. Although all experimental data can be reproduced well *qualitatively* with one set of fixed rate constants, good *quantitative* agreement can only be obtained by keeping all the rate constants fixed, except for the cross-combination rates between long- and short-chain radicals (reactions 19–21). To obtain quantitative agreement under different experimental conditions, these rate constants had to be varied within a factor of four (cf. Table 1). This variation may reflect the different sizes of the low molecular-weight radicals under the respective experimental conditions. If these simplifications are taken into account, the quality of simulation is satisfactory (cf. Figures 6, 7, 12, and 13), and we take this as a confirmation that our reaction scheme is capable of describing the data fairly well. It is comforting that fitting became fully inadequate, when the rate constants of major importance, for reactions 3–5, 8, 9, and 13–18, were varied by as little as 25%.

Conclusion

Besides providing a detailed description of the free-radical-induced processes in deoxygenated solutions of deprotonated poly(methacrylic acid), this study is the first example that shows a propagation-depropagation equilibrium of a polymer in aqueous solution [k(propagation) = 15 dm^{3}mol^{-1}s^{-1}, k(depropagation) = 0.1 s^{-1}]. The approach to the equilibrium is observable because the polymer radicals are long-lived, and the rate of propagation is slow.

The very slow propagation rate and the long lifetimes of the polymer radicals are the result of the electrostatic repulsive forces between the monomer anion and the highly negatively charged polymer radical. The slowness of propagation explains the difficulties encountered with the polymerization of methacrylic acid in neutral and alkaline aqueous solutions.

The effective unzipping reaction following the formation of a radical site on poly(methacrylic acid) is probably also the reason for its reported light-sensitivity in solution.[58]

The processes of chain breakage and subsequent monomer release should be taken into account when designing the formation of hydrogels and other biomaterials containing poly(methacrylic acid) by ionizing radiation or other free-radical generating systems.

Acknowledgements

The skillful technical assistance of R. Wagner, P. Höfer, and H. Niehaus is gratefully acknowledged. P.U. thanks the Alexander-von-Humboldt Foundation for a stipend.

---

[1] J. W. Nemec, W. Bauer in *Encyclopedia of Polymer Science and Engineering, Vol. 1* (Eds.: H. F. Mark, M. N. Bikales, C. G. Overberger, G. Menges, J. Kroschwitz), Wiley, New York, **1988**, pp. 211–234.

[2] P. Molyneux, *Water-Soluble Synthetic Polymers. Properties and Applications*, CRC, Boca Raton, **1987**.

[3] E. A. Bekturov, Z. K. Bakaouva, *Synthetic Water-Soluble Polymers in Solution*, Huethig & Wepf, Basel, **1986**.

[4] M. Mandel in *Encyclopaedia of Polymer Science and Engineering, Vol. 11* (Eds.: H. F. Mark, M. N. Bikales, C. G. Overberger, G. Menges, J. Kroschwitz), Wiley, New York, **1988**, pp. 739–829.

[5] V. Crescenzi, *Adv. Polym. Sci.* **1967**, *5*, 358–386.

[6] Z. Alexandrowicz, *J. Polym. Sci.* **1959**, *40*, 91–106.

[7] C. Tondre, R. Zana, *J. Phys. Chem.* **1972**, *76*, 3451–3459.

[8] A. Silberberg, J. Eliassaf, A. Katchalsky, *J. Polym. Sci.* **1957**, *23*, 259–284.

[9] R. Arnold, J. T. G. Overbeek in *Proc. Int. Colloq. Macromol. 1949*, D. B. Ceten's Uitgevers, Amsterdam, **1950**, pp. 314–328.

[10] V. Crescenzi, F. Quadrifoglio, F. Delben, *J. Polym. Sci. Polym. Chem. Ed.* **1972**, *10*, 357–368.

[11] E. Baumgartner, R. Fernandez-Prini in *Polyelectrolytes* (Eds.: K. C. Frisch, D. Klempner, A. V. Patsis), Technomic, Westport, **1976**, pp. 1–33.

[12] M. Moan, C. Wolff, J.-P. Cotton, R. Ober, *J. Polym. Sci. Polym. Symp.* **1977**, *61*, 1–8.

[13] M. Irie, W. Schnabel, *Macromolecules* **1986**, *19*, 2846–2850.

[14] J. Horsky, H. Morawetz, *Macromol. Chem.* **1988**, *189*, 2475–2483.

[15] A. F. Olea, H. Rosenbluth, J. K. Thomas, *Macromolecules* **1999**, *32*, 8077–8083.

[16] K. P. Ghiggino, K. L. Tan in *Polymer Photophysics* (Ed.: D. Philips), Chapman and Hall, London, **1985**, pp. 341–376.

[17] A. F. Olea, J. K. Thomas, *Macromolecules* **1989**, *22*, 1165–1169.

[18] B. Bednar, J. Trnena, P. Svoboda, S. Vajda, V. Fidler, K. Prochazka, *Macromolecules* **1991**, *24*, 2054–2059.

[19] Y. Kurimura, Y. Sairenchi, S. Nakayama, *Macromol. Chem. Macromol. Symp.* **1992**, *59*, 199–215.

[20] I. Soutar, L. Swanson, *Polymer* **1994**, *35*, 1942–1947.

[21] N. A. Peppas, *Hydrogels in Medicine and Pharmacy*, CRC, Boca Raton, **1986**.

[22] D. De Rossi, K. Kajiware, Y. Osada, A. Yamauchi, *Polymer Gels. Fundamentals and Biomedical Applications*, Plenum, New York, **1991**.

[23] J. M. Rosiak in *Radiation Effects on Polymers, Vol. 475* (Eds.: R. C. Clough, S. W. Shalaby), American Chemical Society, Washington, **1991**, pp. 271–299.

[24] A. S. Hoffman, *MRS Bull.* **1991**, *Sept. 1991*, 42–46.

[25] *Responsive Gels: Volume Transitions* (Ed.: K. Dusek), Springer, Berlin, **1993**.

[26] L. Brannon-Peppas, N. A. Peppas, *J. Controlled Release* **1991**, *16*, 319–330.

[27] I. Kaetsu, K. Uchida, Y. Morita, M. Okubo, *Radiat. Phys. Chem.* **1992**, *40*, 157–160.

[28] O. Hirasa, *J. Intel. Mater. Syst. Struct.* **1993**, *4*, 538–542.

[29] R. Yoshida, H. Ichijo, T. Hakuta, T. Yamaguchi, *Macromol. Rapid Commun.* **1995**, *16*, 305–310.

[30] J. Zhang, N. A. Peppas, *Macromolecules* **2000**, *33*, 102–107.

[31] T. Shiga, Y. Hirose, A. Okada, T. Kurauchi, *J. Intel. Mater. Syst. Struct.* **1993**, *4*, 553–557.

[32] N. S. Yoon, K. Kono, T. Takagishi, *J. Appl. Polym. Sci.* **1995**, *55*, 351–357.

[33] R. A. Siegel, *Nature* **1998**, *394*, 427–428.

[34] P. F. Kiser, G. Wilson, D. Needham, *Nature* **1998**, *394*, 459–462.

[35] A. M. Lowman, N. A. Peppas, *J. Biomater. Sci. Polym. Ed.* **1999**, *10*, 999–1009.

[36] S. H. Yuk, Y. H. Bae, *Crit. Rev. Ther. Drug Carrier Syst.* **1999**, *16*, 385–423.

[37] J. M. Rosiak, P. Ulanski, *Radiat. Phys. Chem.* **1999**, *55*, 139–151.

[38] P. Ulanski, J. M. Rosiak, *J. Radioanal. Nucl. Chem.* **1994**, 315–324.

[39] P. Ulanski, E. Bothe, K. Hildenbrand, J. M. Rosiak, C. von Sonntag, *Radiat. Phys. Chem.* **1995**, *46*, 909–912.

[40] P. Ulanski, E. Bothe, J. M. Rosiak, C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* **1996**, 5–12.

[41] P. Ulanski, E. Bothe, K. Hildenbrand, J. M. Rosiak, C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* **1996**, 13–22.

[42] P. Ulanski, E. Bothe, K. Hildenbrand, J. M. Rosiak, C. von Sonntag, *J. Chem. Soc. Perkin Trans. 2* **1996**, 23–28.

[43] P. Ulanski, E. Bothe, K. Hildenbrand, C. von Sonntag, J. M. Rosiak, *Nukleonika* **1997**, *42*, 425–436.

[44] P. Ulanski, E. Bothe, C. von Sonntag, *Radiat. Phys. Chem.* **1999**, *56*, 467–474.

[45] P. Ulanski, E. Bothe, C. von Sonntag, *Nucl. Instrum. Methods. Phys. Res. Sect. B* **1999**, *151*, 350–355.

[46] J. H. Baxendale, J. K. Thomas, *Trans. Faraday Soc.* **1958**, *54*, 1515–1525.

[47] P. Alexander, A. Charlesby, *J. Polym. Sci.* **1957**, *23*, 355–375.

[48] B. Ranby, J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers. Principles and Applications*, Wiley, London, **1975**.

[49] T. S. Chen, J. K. Thomas, *Radiat. Phys. Chem.* **1980**, *15*, 429–433.

[50] H. Nishide, M. D. Cho, T. Kaku, Y. Okamoto, *Macromolecules* **1993**, *26*, 2377–2379.

[51] S. C. Greer, *J. Phys. Chem. B* **1998**, *102*, 5413–5422.

[52] J.-S. Wang, K. Matyjaszewski, *Macromolecules* **1995**, *28*, 7901 – 7910.
[53] K. A. Davis, H. Paik, K. Matyjaszewski, *Macromolecules* **1999**, *32*, 1767 – 1776.
[54] V. Coessens, J. Pyun, P. J. Miller, S. G. Gaynor, K. Matyjaszewski, *Macromol. Rapid Commun.* **2000**, *21*, 103 – 109.
[55] F. S. Dainton, K. J. Ivin, *Nature* **1948**, *162*, 705 – 707.
[56] F. S. Dainton, K. J. Ivin, *Q. Rev. Chem. Soc.* **1958**, *12*, 61 – 91.
[57] P. Dowideit, C. von Sonntag, *Environ. Sci. Technol.* **1998**, *32*, 1112 – 1119.
[58] T. Völker, *Makromol. Chem.* **1961**, *44 – 46*, 107 – 122.
[59] C. von Sonntag, H.-P. Schuchmann, *Methods Enzymol.* **1994**, *233*, 3 – 20.
[60] E. Bothe, E. Janata, *Radiat. Phys. Chem.* **1994**, *44*, 455 – 458.
[61] A. Henglein, W. Schnabel, J. Wendenburg, *Einführung in die Strahlenchemie*, Verlag Chemie, Weinheim, **1969**.
[62] R. H. Schuler, L. K. Patterson, E. Janata, *J. Phys. Chem.* **1980**, *84*, 2088 – 2089.
[63] G. V. Buxton, C. R. Stuart, *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 279 – 281.
[64] D. Veltwisch, E. Janata, K.-D. Asmus, *J. Chem. Soc. Perkin Trans. 2* **1980**, 146 – 153.
[65] F. Weeke, E. Bastian, G. Schomburg, *Chromatographia* **1974**, *7*, 163 – 170.
[66] C. von Sonntag, *The Chemical Basis of Radiation Biology*, Taylor and Francis, London, **1987**.
[67] G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **1988**, *17*, 513 – 886.
[68] A. Behzadi, U. Borgwardt, A. Henglein, E. Schamberg, W. Schnabel, *Ber. Bunsen-Ges. Phys. Chem.* **1970**, *74*, 649 – 653.
[69] P. Ulanski, Zainuddin, J. M. Rosiak, *Radiat. Phys. Chem.* **1995**, *46*, 917 – 920.
[70] M. S. Matheson, A. Mamou, J. Silverman, J. Rabani, *J. Phys. Chem.* **1973**, *77*, 2420 – 2424.
[71] A. Behzadi, W. Schnabel, *Macromolecules* **1973**, *6*, 824 – 826.
[72] P. Neta, M. Simic, E. Hayon, *J. Phys. Chem.* **1969**, *73*, 4207 – 4213.
[73] M. N. Schuchmann, H. Zegota, C. von Sonntag, *Z. Naturforsch. B* **1985**, *40*, 215 – 221.
[74] J. Berkowitz, G. B. Ellison, D. Gutman, *J. Phys. Chem.* **1994**, *98*, 2744 – 2765.
[75] *CRC Handbook of Chemistry and Physics*, 67th ed. (Eds.: R. C. Weast, M. J. Astle, W. H. Beyer), CRC, Boca Raton, **1986**.
[76] H.-P. Schuchmann, C. von Sonntag, *Radiat. Phys. Chem.* **1988**, *32*, 149 – 156.
[77] C. von Sonntag, E. Bothe, P. Ulanski, A. Adhikary, *Radiat. Phys. Chem.* **1999**, *55*, 599 – 603.
[78] G. Beck, J. Kiwi, D. Lindenau, W. Schnabel, *Eur. Polym. J.* **1974**, *10*, 1069 – 1075.
[79] R. Lubis, J. Olejniczak, J. Rosiak, J. Kroh, *Radiat. Phys. Chem.* **1990**, *36*, 249 – 252.
[80] E. Bothe, D. Schulte-Frohlinde, *Z. Naturforsch. C* **1982**, *37*, 1191 – 1204.
[81] M. Adinarayana, E. Bothe, D. Schulte-Frohlinde, *Int. J. Radiat. Biol.* **1988**, *54*, 723 – 737.
[82] D. J. Deeble, E. Bothe, H.-P. Schuchmann, B. J. Parsons, G. O. Phillips, C. von Sonntag, *Z. Naturforsch. C* **1990**, *45*, 1031 – 1043.
[83] E. Bothe, G. A. Qureshi, D. Schulte-Frohlinde, *Z. Naturforsch. C* **1983**, *38*, 1030 – 1042.
[84] G. S. Manning, *Quart. Rev. Biophys.* **1978**, *11*, 179 – 246.
[85] P. Maruthamuthu, *Makromol. Chem. Rapid Commun.* **1980**, *1*, 23 – 25.
[86] M. Kumar, M. H. Rao, P. N. Moorthy, K. N. Rao, *Radiat. Eff. Express* **1988**, *1*, 167 – 173.
[87] B. C. Gilbert, J. R. L. Smith, C. E. Milne, A. C. Whitwood, P. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1994**, 1759 – 1769.
[88] K. Makino, M. M. Mossoba, P. Riesz, *J. Phys. Chem.* **1983**, *87*, 1074 – 1080.
[89] G. Blauer, *J. Polym. Sci.* **1953**, *11*, 189 – 192.
[90] S. H. Pinner, *J. Polym. Sci.* **1952**, *9*, 282 – 285.
[91] G. Blauer, *Trans. Faraday Soc.* **1960**, *56*, 606 – 612.
[92] G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, **1991**.
[93] O. Vogl, M. F. Qin, A. Zilkha, *Prog. Polym. Sci.* **1999**, *24*, 1481 – 1525.
[94] N. C. Billingham, A. Ledwith in *Reactivity, Mechanism and Structure in Polymer Chemistry* (Eds.: A. D. Jenkins, A. Ledwith), Wiley, London, **1974**, pp. 42 – 51.
[95] I. A. Raap, U. Gröllmann, *Makromol. Chem.* **1983**, *184*, 123 – 134.
[96] A. M. North in *Reactivity, Mechanism and Structure in Polymer Chemistry* (Eds.: A. D. Jenkins, A. Ledwith), Wiley, London, **1974**, pp. 143 – 152.
[97] O. F. Olaj, A. Kornherr, G. Zifferer, *Macromolecules* **1999**, *32*, 8800 – 8806.
[98] O. F. Olaj, P. Vana, *Macromol. Rapid Commun.* **1998**, *19*, 433 – 439.
[99] O. F. Olaj, P. Vana, *Macromol. Rapid Commun.* **1998**, *19*, 533 – 538.
[100] *Polymer Handbook*, 3rd ed. (Eds.: J. Brandrup, E. H. Immergut), Wiley, New York, **1989**.
[101] U. Borgwardt, W. Schnabel, A. Henglein, *Makromol. Chem.* **1969**, *127*, 176 – 184.
[102] S. Bywater, *J. Polym. Sci. Part A: Polym. Chem.* **1999**, *37*, 4467 – 4477.
[103] W. Görlich, W. Schnabel, *Eur. Polym. J.* **1973**, *9*, 1298 – 1296.
[104] D. Behar, J. Rabani, *J. Phys. Chem.* **1988**, *92*, 5288 – 5292.
[105] S. Bywater, *Trans. Faraday Soc.* **1955**, *51*, 1267 – 1273.
[106] D. Kukulj, T. P. Davis, *Macromolecules* **1998**, *31*, 5668 – 5680.
[107] R. A. Hutchinson, D. A. Paquet, S. Beuermann, J. H. McMinn, *Ind. Eng. Chem. Res.* **1998**, *37*, 3567 – 3574.
[108] N. I. Galperina, W. F. Gromov, P. M. Khomikovskii, A. D. Abkin, *Vysokomol. Soedin. Ser. B* **1975**, *17*, 674 – 677.
[109] J. Matuszewska-Czerwik, S. Polowinski, *Eur. Polym. J.* **1991**, *27*, 1335 – 1337.
[110] S. Beuermann, D. A. Paquet, J. H. McMinn, R. A. Hutchinson, *Macromolecules* **1997**, *30*, 194 – 197.
[111] L. Wojnarovits, E. Takacs, *Res. Chem. Intermed.* **1999**, *25*, 275 – 283.
[112] A. Katchalsky, G. Blauer, *Trans. Faraday Soc.* **1951**, *47*, 1360 – 1370.
[113] A. G. Evans, E. Tyrrall, *J. Polym. Sci.* **1947**, *2*, 387 – 396.
[114] K. G. McCurdy, K. J. Laidler, *Can. J. Chem.* **1964**, *42*, 818 – 824.
[115] R. A. Lyons, J. Hutovic, M. C. Piton, D. I. Christie, P. A. Clay, B. G. Manders, S. H. Kable, R. G. Gilbert, *Macromolecules* **1996**, *29*, 1918 – 1927.
[116] S. Beuermann, D. A. Paquet, J. H. McMinn, R. A. Hutchinson, *Macromolecules* **1996**, *29*, 4206 – 4215.
[117] A. Charlesby, *Atomic Radiation and Polymers*, Pergamon, Oxford, **1960**.
[118] D. G. E. Lemaire, E. Bothe, D. Schulte-Frohlinde, *Int. J. Radiat. Biol.* **1987**, *51*, 319 – 330.
[119] W. Schnabel, *Polymer Degradation. Principles and Practical Applications*, Hanser, München, **1981**.

Received: March 13, 2000 [F2363]