PERKIN 2

Hydroxyl-radical-induced reactions of poly(acrylic acid); a pulse radiolysis, EPR and product study. Part I. Deoxygenated aqueous solutions

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Hydroxyl radicals were generated radiolytically in N_2O-saturated dilute aqueous solutions of poly(acrylic acid), PAA. They abstract H-atoms from PAA both at the α- and β-position to the carboxy group. Using the pulse radiolysis technique the UV spectra of the PAA radicals were recorded. While the main absorption (λ_{max} < 250 nm) is due to both α- and β-type radicals, the α-radicals show long-wavelength shoulders at 290 and 330 nm at pH 3.5 and 10, respectively. At pH 10, where the lifetime of the radicals is very long (*e.g.* 20 min at pH 10 and a dose of 300 Gy), a 3.5-fold increase in the 330 nm absorbance was observed ($k = 0.7\ s^{-1}$). This is attributed to a conversion of β- into α-radicals, and from this result it is concluded that the primary yield of α-radicals is *ca.* 30%. The lifetime of the radicals strongly depends on pH. At low pH, where the polymer has a random-coil conformation, the radical decay is fast, whereas in neutral and basic solutions the repulsive electrostatic forces of the negative charges cause the polymer to assume a rod-like structure and prevent the radicals from ready approach. Their decay then becomes slow. This allows the radicals to fragment ($k = 0.025\ s^{-1}$ as determined by pulse conductometry at pH 8). As a consequence, scission dominates at high pH (determined as a decrease in the molecular weight using low-angle laser light-scattering). In acid solution crosslinking is the dominating process. However, the *inter*molecular crosslinking yield is low ($G \approx 0.1 \times 10^{-7}\ mol\ J^{-1}$), disproportionation of radicals, scission and *intra*molecular crosslinking (loop formation) being effective competing reactions. Cysteamine ($10^{-6}\ mol\ dm^{-3}$) prevents chain scission by H-donation and equally low concentrations of Fe^{II} ions exert a similar effect by an as yet unknown mechanism. EPR data support the long lifetime of the PAA radicals and the β- to α-radical conversion.

Poly(acrylic acid) (PAA), is one of the simplest synthetic organic polyelectrolytes, and has been used as a model macromolecule in a number of studies related to polyelectrolytic properties (for reviews see refs. 1–3). An important feature of polyelectrolytes in aqueous solution, reflected in macroscopic properties such as viscosity, is their dependence of chain conformation on pH and the presence of salts. In acidic solution the chains of anionic polyelectrolytes are coiled; with increasing neutralization the number of deprotonated functional groups increases and, owing to repulsive coulombic forces, the coil expands, and finally the chain attains a conformation which is close to a rigid rod. Addition of a low molecular weight electrolyte causes a screening effect on the forces acting between chain segments, allowing the macromolecule to gain a more compact conformation. It will be shown that these effects also play an important role in the behaviour of PAA-derived radicals.

The polyelectrolyte properties of PAA are of considerable practical importance in its use as a thickener for cosmetics, hydraulic fluids and petroleum recovery liquids, as an ion-exchange resin, as a suspending or flocculating agent and as an adhesive.[4] There is also an increasing interest in biomedical applications of PAA, either pure or as a polyelectrolyte complex, copolymer, composite or a grafted material. For example, contractile membranes, thromboresistant surfaces,[5] composites for implants[6] and high-performance dental cements[4,7] are among the tested PAA-based biomaterials. Hydrogels of PAA or its copolymers, owing to their ability to respond to environmental stimuli such as pH or ionic strength,[8] are investigated for their potential applications in biomedical devices, *e.g.* as a pore-size controlling agent in the membrane of an artificial pancreas. Since the treatment with ionizing radiation has been proven to be a convenient method of hydrogel formation and sterilization of polymeric biomaterials,[9,10] it seems that interaction of ionizing radiation with PAA in aqueous solution is worth studying in some detail.

The studies on the radiolysis of PAA (*i.e.* its OH-radical-induced reactions) may provide useful information for more complex biological polyelectrolytes such as DNA, poly(U), poly(A) or hyaluronic acid. Owing to the importance of these polymers, their radiation chemistry has been subjected to extensive studies (for reviews see refs. 11–13). It seems that the processes directly related to the polymeric or polyelectrolytic properties, such as strand breakage, counterion release, complex kinetics of radical decay, rate of oxygen addition to macroradicals and radical transfer reactions, show some common features for both the simple synthetic polyelectrolytes as PAA or poly(methacrylic acid) (PMA) and the above mentioned biopolymers.

There are only a few papers devoted to the radiolysis of PAA in aqueous solution. The rate constant of the reaction of OH radicals with PAA has been shown to depend on the molecular weight, salt concentration and on pH.[14] The latter observation has been recently confirmed for the same PAA sample as used in the present study.[15] The same tendency, *i.e.* increase in the rate constant of OH radicals with polymer upon deprotonation of carboxylic groups, has also been found for low molecular weight model systems such as 2,4-dimethylglutaric acid.[†,16] The

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[†] 2,4-Dimethylglutaric acid = 2,4-dimethylpentanedioic acid.

absorption spectrum of PAA-radicals has been published recently.[15,17] The observation of their very long life-times in deoxygenated alkaline solutions[15] is in line with studies on the influence of charge density on the rate of recombination of macroradicals.[18] Viscosity measurements,[19] gelation studies[20] and pulse conductometric studies[17] indicate that OH radical attack in dilute solutions causes PAA to degrade, the process being enhanced in alkaline solutions. Gel formation occurs, however, in deoxygenated solutions of sufficiently high PAA concentrations[20] and it is concluded that crosslinking and scission must occur side by side. EPR spectra of the radicals derived from low molecular weight carboxylic acids and PAA in aqueous solution have been reported[17,21,22] and efficient conversion of radicals in the β-position to the carboxy groups into α-radicals has been suggested.[17,23] The reaction of OH radicals with PAA has also been studied using Tb^{3+} fluorescence as a probe.[24]

The aim of the present work was to study in more detail the OH-radical-induced reactions of PAA in dilute, deoxygenated aqueous solutions, especially the factors influencing the kinetics and yield of the most conspicuous reactions of the macroradicals, *i.e.* the processes leading to chain scission and crosslinking.

Experimental

Poly(acrylic acid) (PAA; Aldrich), 700 kDa weight-average molecular weight (MW) as determined by low-angle laser light-scattering, was dried *in vacuo* at 80 °C for 2 h to remove traces of solvent, monomer and water. Monomer content in these samples was <0.1% as tested by the lifetime of the hydrated electron in alkaline PAA solutions upon pulse irradiation (hydrated electrons react rapidly with monomer anions on account of the C=C bond, $k = 5.7 \times 10^9$ dm^3 mol^{-1} s^{-1},[25] while they are practically unreactive towards PAA). Solutions in Milli-Q-filtered (Millipore) water were made by stirring overnight at 50 °C. In some experiments a PAA sample (Aldrich, MW = 90 kDa, supplied as 25% aqueous solution), was used as received. Tetranitromethane (TNM) was washed with water to reduce the background level of nitroform anion. All other chemicals were of analytical grade.

All the glassware used was soaked overnight in 10^{-3} mol dm^{-3} EDTA (di-sodium salt) solution at 50 °C and then rinsed with the solutions to be irradiated. This procedure was found to be indispensable for obtaining reproducible results. The rationale behind this treatment is that trace amounts of transition metal ions, like Fe^{II}, interfere with the reactions of long-lived PAA-radicals. This was confirmed by pulse radiolysis and light-scattering experiments (see below).

The pH, if different from the natural one, was adjusted with $HClO_4$, NaOH or KOH. Prior to irradiation, solutions were saturated for 1.5 h with N_2O purified by an Oxisorb column (Messer-Griesheim).

γ-Irradiations were carried out with a ^{137}Cs-γ-source (Oris IBL 437 C) at a dose rate of 0.17 Gy s^{-1} or with a panorama ^{60}Co-γ-source (Nuclear Engineering) at dose rates of 0.034–5.0 Gy s^{-1}. Pulse radiolysis experiments were performed with a 2.8 MeV van de Graaf accelerator generating electron pulses of 0.4–4 μs duration with optical and conductometric detection.[26,27] In optical measurements thiocyanate dosimetry[28] and for conductivity measurements dimethyl sulfoxide dosimetry was used.[29]

EPR experiments were performed on an X-band spectrometer with 100 kHz modulation equipped with a flow system. For time-resolved measurements a stopped-flow technique was used.[30] Radicals were generated by UV-irradiation *in situ* using an argon plasma light source (Gamma Analysentechnik). Spin-trapping experiments (2-methyl-2-nitrosopropane, Sigma) were carried out by adding a 5×10^{-3} mol dm^{-3} N_2O-saturated stock solution (*cf.* ref. 31) before or after γ-irradiation.

Post-irradiation spectral changes (λ-16, Perkin-Elmer) under anoxic conditions were followed in a quartz cell equipped with a purging device (*cf.* ref. 32).

Low-angle laser light-scattering (LALLS) measurements of the weight-average molecular weight were performed at λ = 633 nm (Chromatix KMX-6). PAA samples were analysed at pH 10 in 0.5 mol dm^{-3} $NaClO_4$ to ensure a compact conformation of the macromolecules required for the light-scattering measurements. The specific refractive index increment (dn/dc) of PAA was measured in 0.5 mol dm^{-3} $NaClO_4$ at pH 10 (Chromatix KMX-16 laser differential refractometer). After extrapolating the data to zero PAA concentration, dn/dc was found to be 0.30 cm^3 g^{-1} (λ = 633 nm, 20 °C). Dialysis of the polymer solution against the solvent (*cf.* ref. 33) did not influence the results in our system. Before carrying out the light-scattering measurements, samples were filtered with Minisart NML filters (5 μm, Sartorius) and subsequently with Millex HA filters (0.45 μm, Millipore). Because of the very long lifetime of PAA-radicals under anoxic conditions, the irradiated samples were kept closed for at least 24 h before analysis in order to avoid an interference with oxygen and subsequent enhanced PAA degradation.[34]

Results and discussion

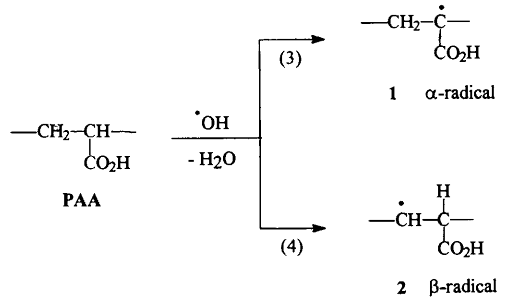
The radical-generating system

Upon irradiation of dilute, N_2O-saturated PAA solutions OH radicals and H atoms are formed in reactions (1) and (2). Under

$$H_2O \xrightarrow[(1)]{\text{ionizing radiation}} {}^{\bullet}OH,\ e_{aq},\ H^{\bullet},\ H^+,\ H_2,\ H_2O_2$$

$$N_2O + e_{aq} \xrightarrow[(2)]{} {}^{\bullet}OH + OH^- + N_2$$

such conditions the radiation-chemical yield of OH radicals is $G = 5.8 \times 10^{-7}$ mol J^{-1}, while the H atoms are formed with a G value of 0.6×10^{-7} mol J^{-1}.[11] The OH radicals react with PAA by H-abstraction both at the α- and β-positions to the carboxylic groups [reactions (3) and (4)]. The H atoms will also undergo H-abstraction reactions, albeit with lower rate constants than the OH radicals.



In the case of low molecular weight carboxylic acids, OH radicals do not react with the carboxylate group,[35,36] and we conclude that also in the case of PAA such a reaction, if it occurs at all, is of minor importance.

The overall rate constants of reactions (3) and (4) have been shown to depend on the molecular weight, on the pH and on the salt concentration.[14,15] While the dependence on the molecular weight is a general phenomenon of polymers (*cf.* refs. 37–39), the pronouced pH and ionic strength dependence is unique to polyelectrolytes. For the 700 kDa PAA sample used also in the present study k(${}^{\bullet}$OH + PAA) = 9.0×10^7 dm^3 mol^{-1} s^{-1} at pH 3.0 (where only a small fraction of carboxylic groups is deprotonated) and k(${}^{\bullet}$OH + PAA) = 2.2×10^8 dm^3 mol^{-1} s^{-1}

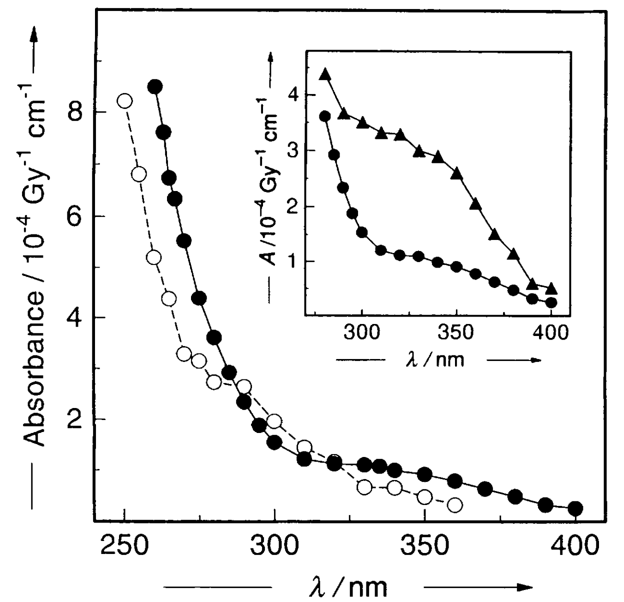


Fig. 1 Pulse radiolysis of N_2O-saturated PAA solutions (5 × 10^{-2} mol dm^{-3}), 40 Gy. Initial absorption spectra of PAA-derived radicals recorded 35 μs after the pulse (corrected for OH recombination). (○) pH 3.5, (●) pH 10.3. Inset: spectra recorded at pH 10.3 (●) 35 μs and (▲) 7.5 s after the pulse.

at pH 9.6 (where deprotonation is nearly complete) has been found.[15] The higher rate constant at the higher pH is due to two effects: a higher rate constant of OH radicals with the dissociated carboxylic acids and the expanded dimensions of the dissociated polymer compared with the coiled shape of protonated PAA, which leads to a higher collision frequency. The former effect has also been observed for the low molecular weight model compound 2,4-dimethylglutaric acid (2,4-DMGA), where the reaction of OH radicals with the dianion is 1.7 times faster than with the free acid.[16]

UV absorption spectra and the site of OH radical attack

Initial absorption spectra of PAA-radicals **1** and **2** show a main absorption band with a maximum below 250 nm and a shoulder at *ca.* 290 nm at pH 3.5 and near 330 nm at pH 10.3 (Fig. 1) and thus resemble the spectra of the radicals derived from the model compound 2,4-DMGA.[16] On the basis of the spectra of the radicals derived from simple, low molecular weight carboxylic acids[36,40] it is concluded that the radicals in the α-position to the carboxyl groups give rise to the (pH dependent) absorbances in the 290–330 nm range while α- and β-radicals both contribute to the stronger short-wavelength absorption. From these absorption spectra it can be concluded that α-radicals must be formed, but the α : β ratio cannot be assessed in this way.

An estimate, however, of the initial yield of α-radicals has been based on the following observation. At pH 10.3, when the radical–radical reactions are very slow, the absorbance at 350 nm, where only the α-radicals absorb, increases *ca.* 3.5-fold with time[17] (for details see below). If this transformation of β- into α-radicals is quantitative, the initial fraction of α-radicals should be about one-third, *i.e.* close to the fraction of tertiary H atoms in PAA. A similar ratio has been obtained at pH 7.6 from experiments using thiols as scavenger of the β-radicals (see below). A very low selectivity of OH-attack was also reported for low molecular weight carboxylic acids.[36] At low pH the α : β-ratio may be slightly different: the lower rate constant of the OH radicals with PAA at low pH and the product studies with the model system 2,4-DMGA indicate that there should be a lower proportion of α-radicals when the carboxylic groups are undissociated.[16] This has also been suggested for propionic acid.[36]

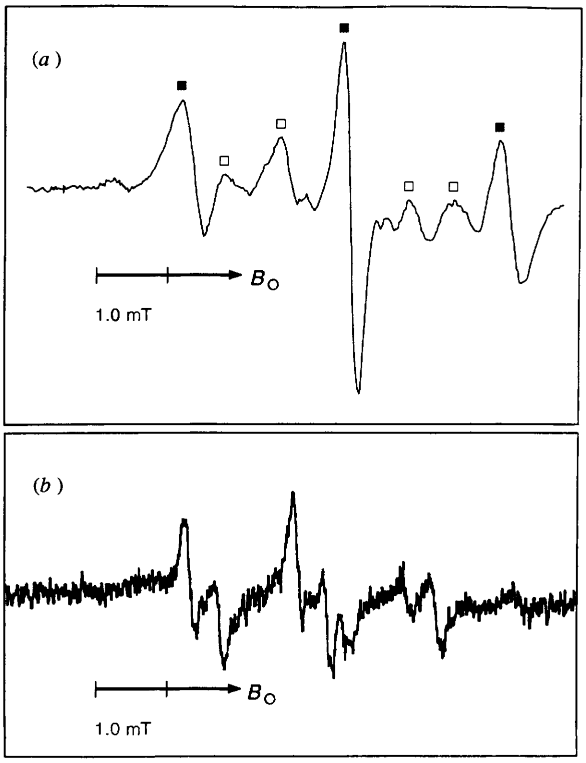


Fig. 2 (*a*) Steady-state EPR spectrum of PAA-derived radicals generated photochemically in a flow system; Ar-saturated 3.5 × 10^{-2} mol dm^{-3} PAA solution containing 3 × 10^{-3} mol dm^{-3} H_2O_2 and 3.5 × 10^{-2} mol dm^{-3} $NaClO_4$, pH 7.6. Assignment: (■) α-radical, (□) β-radical. (*b*) EPR spectrum recorded after γ-irradiation (300 Gy) of N_2O-saturated PAA solutions (1.25 × 10^{-2} mol dm^{-3}), containing 2-methyl-2-nitrosopropane (2.5 × 10^{-3} mol dm^{-3}), pH 10.

Identification of PAA radicals by EPR spectroscopy

PAA radicals were generated by UV irradiation of H_2O_2-containing PAA solutions. The steady-state EPR spectrum consists of two major features: a triplet and a broad, poorly resolved multiplet [Fig. 2(*a*)].

The triplet can be attributed to the α-radicals, assuming that the free rotation is highly restricted and one set of hydrogen atoms of the adjacent methylene groups is out of plane with respect to the unpaired electron, thus only the remaining two β-protons give rise to the observed splitting ($a_{\beta H}$ = 2.65 mT, see also EPR data for PAA irradiated in the solid state, *cf.* ref. 41 and references cited therein). A similar situation has been reported for γ-irradiated poly(ethyl acrylate), where one of the two β-couplings was zero and the other one 2.5 mT.[42] The same interpretation of the triplet signal obtained for acrylic acid oligomers and PAA in aqueous solution upon the action of Fenton-type reagents has been suggested recently.[21] The remaining weak signals we attribute to the β-radicals **2**. The asymmetry of peak positions is due to the anisotropies of the *g*-factor and α-coupling. The initial proportion between the intensity of both signals after photolysis does not reflect the proportions between radicals when they are generated radiolytically, since there is also some radical formation due to a direct photolysis of PAA.[43]

Spin-trapping experiments provide some evidence for an initial dominance of β-radicals. When a PAA solution was γ-irradiated at pH 10 in the presence of 2-methyl-2-nitrosopropane, the main feature of the subsequently recorded EPR spectrum was a triplet of doublets [Fig. 2(*b*)]. This we attribute to the structure **3**, the triplet resulting from the nitrogen splitting (a_N = 1.575 mT) and the doublet being due to the hydrogen

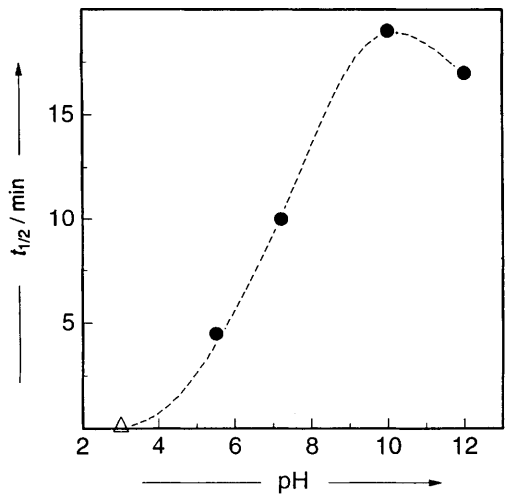


Fig. 3 First half-lives of PAA-derived radicals generated in N_2O-saturated, PAA solutions (10^{-2} mol dm^{-3}) by γ-irradiation (300 Gy), as a function of pH. Irradiation time 1 min. Values are based on the decay in UV-absorbance; (△) value estimated by pulse radiolysis.

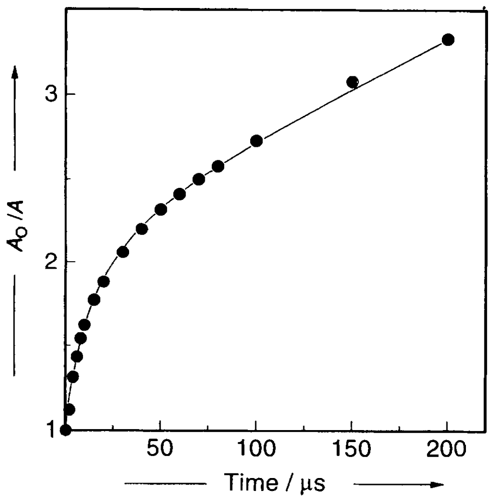
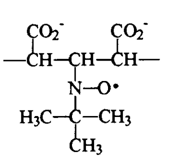


Fig. 4 Pulse radiolysis of N_2O-saturated PAA solutions (10^{-3} mol dm^{-3}), 72 Gy, pH 3. Second-order plot of the decay of PAA-derived radicals at 260 nm.



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atom in the β-position to the carboxylic group ($a_H = 0.375$ mT).

It is worth noting that when the spin-trap is added to the γ-irradiated PAA solution with some delay (*ca.* 1 min), *i.e.* after the completion of the β- to α-radical transformation (see below), a triplet attributed to the non-trapped α-radicals dominates, indicating that either the α-radicals of PAA do not effectively react with the spin-trap, or that the adduct formation is reversible.

Lifetime of PAA radicals

The 2,4-DMGA-derived radicals decay by second-order kinetics with rate constants of $2k = 4.0 \times 10^8$ dm^3 mol^{-1} s^{-1} at pH 3.2 (protonated radicals) and $2k = 1.3 \times 10^7$ dm^3 mol^{-1} s^{-1} at pH 10 (deprotonated radicals).[16] As measured by UV spectroscopy, the lifetimes of PAA radicals show a much stronger pH dependence (Fig. 3, *cf.* also Fig. 13).

A similar pH dependence and magnitude of the lifetimes were observed by EPR spectroscopy after photolytic generation of PAA radicals (data not shown). At low pH, where the segments of PAA chains may move more freely, the reactions between radical functions are relatively fast. With increasing deprotonation repulsive forces prevent an approach of two radical sites and the termination rates are reduced. At pH 10 the half-life of PAA macroradicals shows a dose dependence typical for a second-order reaction and at doses lower than those given in Fig. 3, half-lives of more than one hour are observed. In the case of poly(styrene sulfonate) such long radical lifetimes have been attributed to the presence of stabilized radical-cations.[44] In the present system such a stabilization mechanism is not possible and the long lifetime of the PAA radicals at high pH can only be attributed to repulsive electrostatic forces. The decrease in the radical lifetime observed at pH 12 compared with that measured at pH 10 may be due to screening effects at the higher ionic strength, but this effect was not investigated any further.

At low pH (*ca.* pH 3–3.5) the bimolecular radical terminating reactions are so fast that they can only be followed by pulse radiolysis. The decay of radicals does not follow simple second-order kinetics, but it becomes progressively slower, *i.e.* the incremental second-order rate constant decreases with time (Fig. 4).

Such an effect has been theoretically predicted[45] and recently experimentally observed in the case of poly(vinyl alcohol)[46] and poly(ethylene oxide).[39] It has been attributed to the non-homogeneous distribution of radicals. The decay process of the radicals may be divided into three classes: (*i*) reactions of two radicals within a cluster of radicals formed on one chain, probably originating from one spur (the contribution of this process is very low at our concentrations), (*ii*) reactions of radicals localized on the same chain, but not within a cluster and (*iii*) reactions of the radicals localized on separate chains. Radicals formed in close proximity (*i.e.* in a cluster) react fastest (their initial rate constant can be as high as $2k = 6 \times 10^9$ dm^3 mol^{-1} s^{-1}, an order of magnitude higher than the bimolecular decay of the 2,4-DMGA radicals at comparable pH, see above). Those localized on the same polymer chain, but further away, react more slowly. This process may require a considerable movement of chain segments. The slowest process is the reaction between radicals on separate chains and can only proceed upon a diffusion of both macromolecules. In addition, the formation of *intra*molecular crosslinks (loops) in the early stages of the radical reactions within the polymer chain may reduce the flexibility of the chain segments and hence further decrease the rate of reaction.

Conversion of β-radicals into α-radicals

The long lifetimes of PAA macroradicals allow first-order reactions to compete succesfully with the second-order termination processes (6) and (7). In the absence of oxygen, such first-order reactions are not observed in the 2,4-DMGA system at low concentrations.[16] However, at very high concentrations of simple carboxylic acids an *inter*molecular H-transfer yielding α-radicals is observed.[22]

As has been reported before in PAA the β-radicals also rearrange into α-radicals [reaction (5)].[17,23] This β- to α-radical conversion has been followed by monitoring the increase in absorbance at wavelengths where mainly the α-radicals absorb (*cf.* insets in Figs. 1 and 10) and was confirmed by EPR measurements where an increase in the α-radical triplet and a decay of the signals attributed to the β-radicals was observed.[17] At pH 10 the half-life of this process is 1.0 s (*cf.* also ref. 15). It does not significantly depend on the dose (radical concentration), the molecular weight of PAA or its concentration,

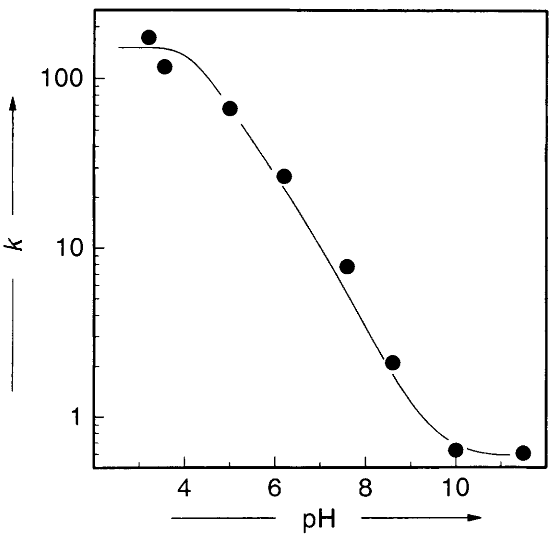
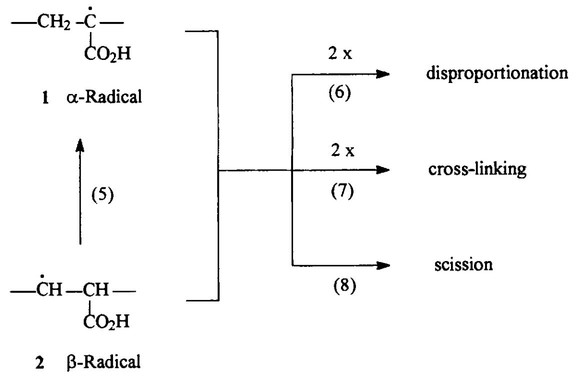


Fig. 5 Pulse radiolysis of N_2O-saturated PAA solutions (10^{-2} mol dm^{-3}), 11 Gy. First-order rate constant of the β- to α-radical conversion (measured at 320 nm) as a function of pH.



but shows a pronounced pH dependence. With decreasing pH this β- to α-radical conversion becomes drastically faster (Fig. 5).

Reaction (5) seems not to be due to a 1,2-H-shift, but rather must occur by H-abstraction from a position at some distance along the chain. In this aspect this reaction resembles the rate of termination reactions which also strongly depend on the pH. In both cases two relevant chain segments may have to approach each other closely for the processes to occur.

The temperature dependence of the rate of the β- to α-radical conversion has been measured between 10 and 60 °C at pH 3, 7.7 and 10.1. The Arrhenius plots were found to be linear over the entire temperature range (Fig. 6). The activation enthalpies $\Delta H^{\ddagger}$ (in kJ mol^{-1}) and entropies $\Delta S^{\ddagger}$ (in J mol^{-1} K^{-1}) are 33 and −88 at pH 3, 52 and −55 at pH 7.7 and 53 and −66 at pH 10.1.

At least two processes must contribute to these activation parameters: segmental motions of the polymer chain and the H-transfer reaction. At present it is impossible to disentangle these two components. Note that at pH 3 a hydrogen is transferred from the α-position to a protonated carboxy group; at the more alkaline pH values the carboxylic group is deprotonated. This may facilitate the abstraction reaction, but the polymer is more rigid thus impeding the segmental motions.

Yields of chain scission and crosslinking

When PAA solutions are irradiated, the molecular weight of the polymer changes owing to the formation of scissions [reaction (8)] and crosslinks [reaction (7)]. The disproportionation reaction (6) does not affect the molecular weight. The

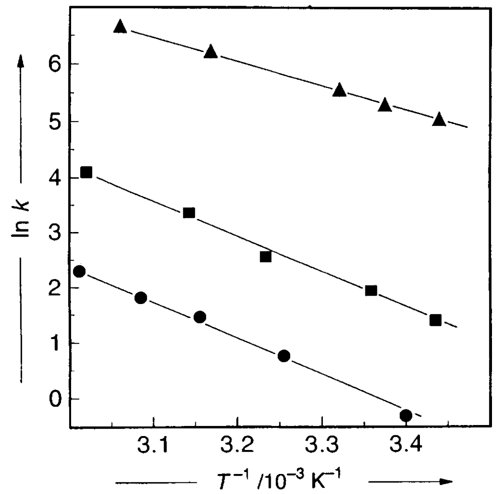


Fig. 6 Pulse radiolysis of N_2O-saturated PAA solutions (3.5 × 10^{-2} mol dm^{-3}), 20–50 Gy. Temperature dependence of the rate constant of the β- to α-radical conversion (measured at 320 nm). (▲) pH 3.0, (■) pH 7.7, (●) pH 10.1.

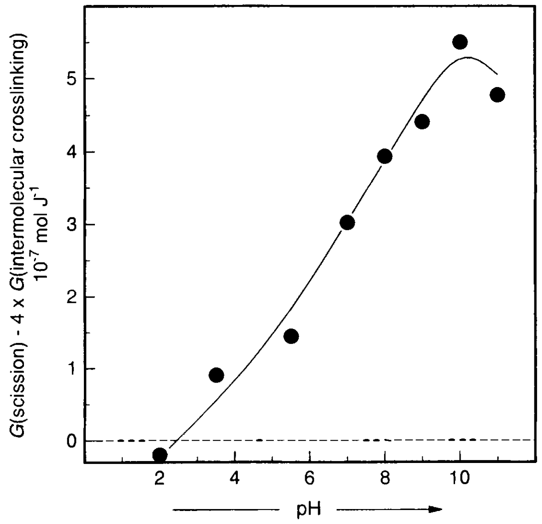


Fig. 7 Radiation-chemical yields of chain scission and *inter*molecular crosslinking as a function of pH. Values obtained by LALLS measurements of weight-average molecular weight of PAA before and after γ-irradiation (8 Gy, dose rate 0.033 Gy s^{-1}) of N_2O-saturated PAA solutions (10^{-2} mol dm^{-3}). Samples were kept closed for at least 24 h after irradiation.

relationship between the weight-average molecular weights before (MW_0) and after irradiation (MW) and the G values of scission [G(S)] and *inter*molecular crosslinks [G(XL)] is given by eqn. (9) (*cf.* refs. 47–49). Here c_{PAA} denotes PAA

$$G(S) - 4G(XL) = 2(MW^{-1} - MW_0^{-1})c_{PAA}D^{-1}\rho^{-1} \quad (9)$$

concentration in g dm^{-3}, D is the dose in Gy (J kg^{-1}) and ρ is the solution density in kg dm^{-3}. The pH dependence of G(S) − 4G(XL) calculated from the molecular weight measurements according to eqn. (9) is shown in Fig. 7. It is seen that at pH > 9 G(S) − 4G(XL) approaches G(˙OH). This may be taken as evidence that in this pH range crosslinking must be of minor importance. Since chain scission is a relatively slow process ($t_{\frac{1}{2}} \approx 30$ s, see below), long lifetimes of the PAA radicals are required and chain scission can appear to a greater extent only when the radicals have a longer lifetime than the time constant of this process. At the dose rates and PAA concentrations used in these experiments this condition is met at pH > 6.

Towards lower pH the lifetime of the radicals decreases and the chance of the radicals to disproportionate and to crosslink

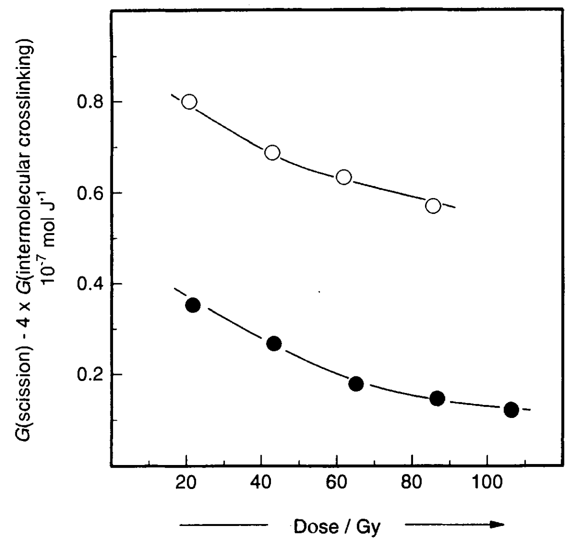


Fig. 8 Radiolysis of N_2O-saturated PAA solutions: (○) 1 × 10^{-2} mol dm^{-3}, pH 3.5; (●) 1 × 10^{-3} mol dm^{-3}, pH 4 (dose rate 0.033 Gy s^{-1}). *G*(scission) – *G*(*inter*molecular crosslinking) as a function of dose.

increases, thus preventing the scission reaction otherwise occurring. Therefore *G*(S) – 4*G*(XL) decreases and, at the lowest pH used, crosslinking exceeds scission (Fig. 7). Its yield remains, however, small [*G*(XL) – 0.25*G*(S) < 0.1 × 10^{-7} mol J^{-1}].

Crosslinking arises from dimerization of polymer radicals and the condition of eqn. (9) that they react *inter*molecularly is fulfilled only if the number of radicals per molecule, Z_R, is smaller than 1.[45] At the relatively low polymer concentrations used in our experiments this condition is not met at the higher doses. Hence with increasing dose, *intra*molecular crosslinking (loop formation) increasingly occurs. *Intra*molecular crosslinking leads to a decrease in the observable yield of both crosslinking and scissions.

Fig. 8 shows two examples for such behaviour at two different polymer concentrations. It is seen that the decline is more pronounced at the lower PAA concentration, where Z_R is higher; for 10^{-2} mol dm^{-3} PAA solutions the yields measured at 85 Gy are reduced to 71% and to 41% for 10^{-3} mol dm^{-3} PAA solutions when compared with their yields at 20 Gy. The *G* values given in Fig. 7 were based on measurements at low doses (*i.e.* low Z_R values) in order to minimize the effect of *intra*molecular crosslinking. Nevertheless, at low pH one expects a remaining influence. Thus, while at pH 3.5 and a PAA concentration of 10^{-2} mol dm^{-3}, *G*(S) – 4*G*(XL) = 0.9 × 10^{-7} mol J^{-1} is obtained and lowering the concentration 10-fold halved this value (even after an extrapolation to zero dose; Fig. 8).

At least three effects may contribute to the low yield of *inter*molecular crosslinking. (*i*) The PAA model, 2,4-dimethylglutaric acid, showed that less than one half of the radicals dimerize, while the major part disproportionates. Thus disproportionation may also be the dominating process in the reaction of PAA radicals. (*ii*) There is a strong preference for the radicals to decay by *intra*molecular reactions (see above) and the resulting loops are not detected in molecular weight measurements. (*iii*) A part of the radicals decay with rate constants of < 10^5 dm^3 mol^{-1} s^{-1}. At our dose rate these live more than 10 s and stand a good chance of undergoing scission.

It is recalled that irradiation at low pH of more concentrated PAA solutions at sufficiently high doses leads to the formation of a hydrogel.[20,50] This is not in contradiction with the above considerations, since the high PAA concentrations considerably reduce the relative likelihood of *intra*molecular crosslinking (loop formation). The possibility of promoting crosslinking or degradation by choosing an adequate dose rate, pH and PAA concentration is of practical importance for the radiation-induced formation and/or sterilization of PAA-based biomaterials.

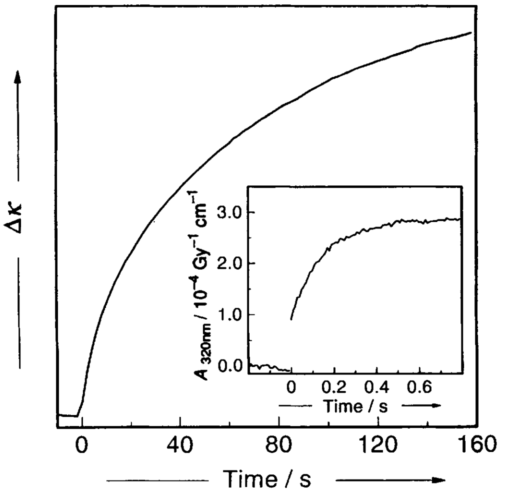


Fig. 9 Pulse radiolysis of N_2O-saturated PAA solutions (2.7 × 10^{-4} mol dm^{-3}), pH 8.0. Conductivity increase after a 2 Gy pulse. Inset: absorbance increase at 320 nm [N_2O-saturated PAA solutions (10^{-2} mol dm^{-3}), pH 7.6, 11 Gy].

Kinetics of chain scission

The kinetics of chain scission in PAA at pH 7–10 can be conveniently followed by pulse radiolysis with conductometric detection, since the process of chain breakage in polyelectrolytes is accompanied by the effect of counterion release.[51] A schematic description of the processes involved is given in ref. 23. The high electric field of the polyelectrolyte chain causes condensation of counterions. When after chain breakage the two fragments diffuse apart, the effective electrostatic potential at the two (smaller) polyelectrolyte molecules formed is lowered and some of the condensed counterions are released into the bulk solution. This causes an increase in conductivity. When related to chain scission in DNA and polynucleotides, the observed conductivity increase corresponds to a release of 8.5 K^+ ions per chain break.[52] In the case of PAA the conductivity increase shown in Fig. 9 corresponds to *G*(K^+ release) = 29 × 10^{-7} mol J^{-1}, *i.e.* 5.3 K^+ ions are released per PAA radical initially formed.

Since the scission reaction is a unimolecular process, a first-order increase of conductivity is expected. In accordance with this, the half-life of the conductivity build-up was found to be independent of the dose/pulse. The overall conductivity increase is, however, not well represented by a single rate constant. From Fig. 9 it is seen that there is a considerable conductivity increase even after times longer than 3 min. The reason for this may be a slow H-abstraction by end-chain radicals from mid-chain positions leading to subsequent further chain breakage.

The inset of Fig. 9 shows the kinetics of the β to α transformation at a similar pH. It is seen that this transformation is much faster than the conductivity build-up. From this we conclude that the α-radicals are the precursors of chain breakage.

Fig. 10 shows the pH dependence of the size of the conductivity increase. At pH ⩽ 6.5 PAA is only a weak polyelectrolyte since the protons are covalently bound and do not constitute a condensed counterion atmosphere which generates the conductivity increase. Consequently, the amplitude of the conductivity signal becomes very small at lower pH values (see Fig. 10). In addition to this effect, loop formation becomes of increasing importance at low pH thus preventing strand breakage and hence counterion release. The decrease in the amplitude at high pH is due to the increased counterion

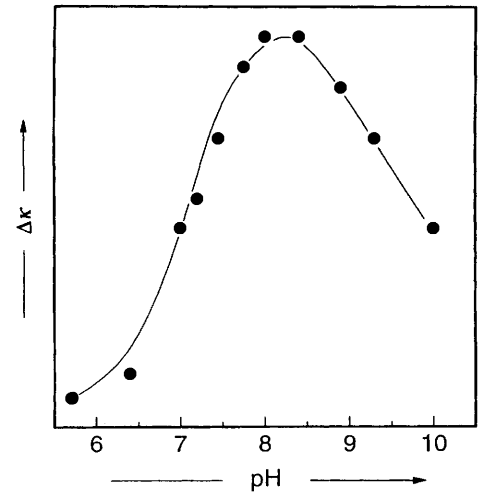


Fig. 10 Pulse radiolysis of N_2O-saturated PAA solutions (2.5×10^{-4} mol dm^{-3}), 2 Gy. Amplitude of conductivity increase as a function of pH.

concentration at elevated pH. The effect of counterion release per break is less efficient at higher ionic strength because of screening effects of the electrostatic forces. For PAA this could not be verified by salt addition because of experimental problems with baseline stability at longer times. Measurements with poly(methacrylic acid), however, showed that similar decreases of the conductivity amplitude can be achieved when, instead of NaOH, an equimolar concentration of $NaClO_4$ is added (unpublished results).

In the range where PAA is a strong polyelectrolyte and the conductivity method can be applied (pH 7–10), the half-life of the conductivity increase did not vary by more than a factor of two.

Radical scavenging by tetranitromethane

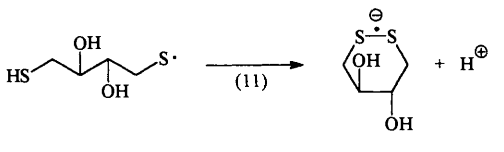
When one of the macroradicals is of a reducing nature, such as the α-hydroxyalkyl radical derived from poly(vinyl alcohol),[46] it can be selectively oxidized by tetranitromethane (TNM) and its fraction can be calculated from the yield of nitroform anion (one-electron reduction product of TNM absorbing strongly at 350 nm). In contrast, in the presence of TNM PAA radicals yielded an absorption with $\lambda_{max} = 310$ nm ($k = 1.0 \times 10^6$ dm^3 mol^{-1} s^{-1}, Fig. 11) which is typical for TNM-adducts.[53] Formation of a similar adduct has also been observed for the 2,4-DMGA system.[54] These adduct radicals do not decay on the pulse radiolysis timescale yielding nitroform anions, confirming the expectation that neither the β- nor the α-radicals have pronounced reducing properties. Thus, the TNM method cannot be used for the determination of the α/β-radical ratio in the case of PAA.

Radical scavenging by thiols

Thiols are known to react with many carbon-centred radicals ($R^{\bullet}$) by H-donation [reaction (10)]. With uncharged molecules

$$R^{\bullet} + R'SH \longrightarrow RH + R'S^{\bullet} \qquad (10)$$

the rate constant of reaction (10) does not depend much on the thiol (*cf.* ref. 11). However, in their reactions with charged macroradicals the charge of the thiol has a very pronounced effect on the observed rate constant.[55–57] Thus the positively-charged cysteammonium ion (the pK_a of its ammonium group is at 10.85)[58] is expected to react quickly with the negatively charged PAA radicals, whereas the neutral thiol dithiothreitol (DTT) should react more slowly. In the latter case, the resulting thiyl radical readily forms the (ring-closed) disulfide radical anion [reaction (11)] which can be detected by its strong



absorption at 390 nm ($\varepsilon = 5900$ dm^3 mol^{-1} cm^{-1}).[59]

When cysteamine, at a concentration of only 1×10^{-6} mol dm^{-3}, was added ([PAA] = 2.5×10^{-4} mol dm^{-3}, N_2O-saturated, pH 8, 2 Gy/pulse), the conductivity increase observed in the absence of cysteamine was fully suppressed. Thus cysteamine must react effectively with the PAA-radicals, thereby preventing the chain scission reaction.

The kinetics of the reaction of cysteamine with the PAA radicals was investigated in pulse radiolysis of N_2O-saturated PAA solutions (1×10^{-2} mol dm^{-3}, pH 7.4, dose/pulse 4.5 Gy) with optical detection. In such solutions the absorption at 260 nm was constant for at least 1 s, indicating correspondingly long lifetimes of both α- and β-radicals. The β to α transformation (measured at 330 nm) proceeded with a half-life of *ca.* 0.15 s. When 3×10^{-6} mol dm^{-3} cysteamine was added, the lifetime of the absorption at 260 nm was found to be drastically reduced; *ca.* 95% of the absorption decayed in two steps within 0.1 s. The fast component made up 68% of the decay and proceeded with a half-life of 2.5 ms. The kinetics of the slow component of 32% contribution could be determined less reliably owing to its smaller contribution and longer half-life. However, a value of 15–20 ms may serve as an estimate. At 330 nm there is no component with kinetics that correspond to the fast component at 260 nm. Therefore we assign the fast and the slow component to the reactions of β- and α-radicals, respectively, with cysteamine. Note that in the calculations of the above contributions, allowance was made for a small residual and permanent absorption generated in the decay of cysteamine radicals ($\varepsilon \approx 100$ dm^3 mol^{-1} cm^{-1} at 260 nm), as witnessed from measurements with similar cysteamine solutions in the absence of PAA.

On increasing the cysteamine concentration to 6×10^{-6} and 1×10^{-5} mol dm^{-3} the half-lives of both components decreased. From the slopes of plots of the reciprocal half-lives of the UV-absorbance decay *vs.* the cysteamine concentrations, rate constants for the reaction of α- and β-PAA radicals with

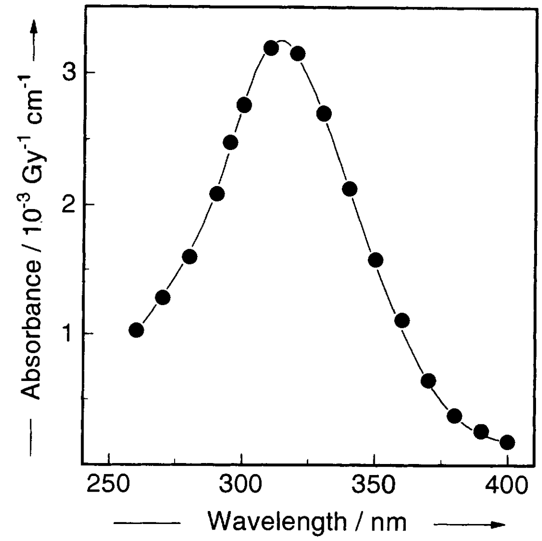


Fig. 11 Pulse radiolysis of N_2O-saturated PAA solutions (10^{-2} mol dm^{-3}), containing 6.7×10^{-4} mol dm^{-3} TNM, pH 7.5, 3 Gy. Absorption spectrum of the tetranitromethane PAA adduct radicals, 8 ms after pulse.

cysteamine of (0.5–1.5) × 10^7 and 8 × 10^7 dm^3 mol^{-1} s^{-1} were obtained. For reasons given above, the rate constant for α-radicals must be regarded as a rough estimate only.

These high apparent rate constants occur mainly because cysteamine is positively charged at pH 7.4 and hence contributes to the counterion atmosphere in the immediate vicinity of the polyelectrolyte and is present there in high concentrations. Similar observations were made with DNA and thiols of different charges.[56]

The high efficiency of cysteamine to scavenge PAA radicals was also used to demonstrate by an additional method the long times required for chain breakage. Aliquots of N_2O-saturated cysteamine solution (yielding a final concentration of 1 × 10^{-4} mol dm^{-3}) were added through a septum to PAA samples at 60 and 300 s after γ-irradiation (90 s, 0.18 Gy s^{-1}). The yields of chain breakage were then determined by LALLS and compared with the value obtained for the sample irradiated without subsequent cysteamine addition. The relative yields of scission were 69% at 60 s and 83% at 300 s. Although exact kinetic data cannot be derived from these results (mainly because of the non-negligible irradiation time), it can be concluded that the main part of chain breaks occur within minutes of irradiation. This agrees well with the conductivity data. Even after 5 min, *G*(scission) is still lower than in the sample with no scavenger added ('infinite' reaction time). This indicates that some scission occurs even at longer times. This is in line with the observation of a slow component of conductivity increase.

Dithiothreitol (DTT) and 2-sulfanylethanol (2-SE) are both uncharged at pH 7.5–8 and hence lower rate constants for their reactions with PAA radicals are expected. Indeed, in similar experiments as described above for cysteamine with optical detection ([PAA] = 7 × 10^{-2}, [DTT] or [2-SE] = 5 × 10^{-5}–2 × 10^{-4} mol dm^{-3}, N_2O-saturated, pH 7.6) rate constants of 1.2 × 10^6 and 7 × 10^5 dm^3 mol^{-1} s^{-1} were obtained for the reaction of PAA radicals with DTT and 2-SE, respectively. In contrast to cysteamine, the decay of the UV absorbance was not complete. A wavelength-depending fraction of the absorbance remained constant for more than 1 s after the thiol-induced decay (half-lives 3–20 ms) even at the highest DTT concentration used. This provides evidence that only one kind of the PAA radicals react with DTT and 2-SE within 1 s. Note that the thiol-induced decay is much faster than the β- to α-radical transformation at the same pH ($t_{\frac{1}{2}}$ = 100 ms at pH 7.6) *i.e.* the thiols may react with the β-radicals prior to their transformation into α-radicals. Fig. 12 shows the spectrum after completion of the thiol reaction. It shows a shoulder at *ca.* 330 nm which is taken as evidence that the β-radicals react with the rate constant given above, leaving behind the unreactive α-radicals. This agrees with the observation on the higher reactivity of β-radicals towards cysteamine. Because of the long half-lives of > 3 s of PAA α-radicals at all thiol concentrations used, their rates of reaction with DTT and 2-SE must be < 10^3 dm^3 mol^{-1} s^{-1}.

The yield of β-radicals in PAA can be calculated from the yield of the disulfide radical anion after completion of the thiol reaction. Since these radical anions decay bimolecularly concomitantly with their slow formation, low doses/pulse have to be used to avoid an underestimation of their yield. An extrapolation of measurements at different doses to zero dose yielded a value of 68% for β-radical formation on PAA upon OH radical attack at pH 7.6.

The yield of α-radicals can be calculated from the remaining absorption after the 2-SE reaction if one assumes that in the absence of 2-SE (or DTT), all β-radicals are transformed into α-radicals, *i.e.* that the absorption coefficient of the α-radicals is known. This yields a value of 25% α-radical formation in PAA. This sums up to 93% for total radical formation. Possibly the value for α-radicals is somewhat too low because it is based on absorption measurements 70 ms after the pulse (after the DTT or 2-SE reaction) where some bimolecular decay of α-radicals might have occurred.

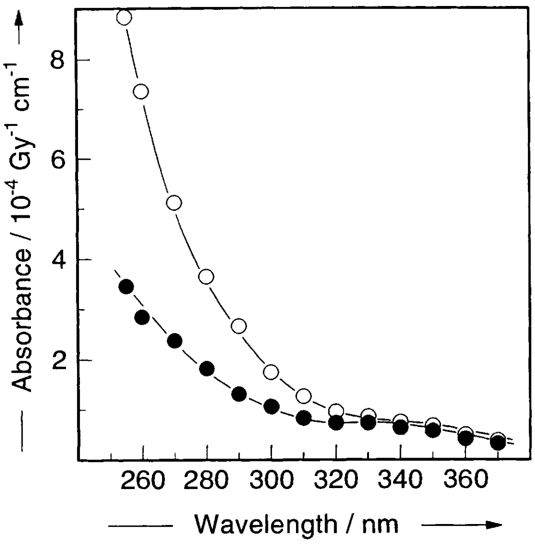


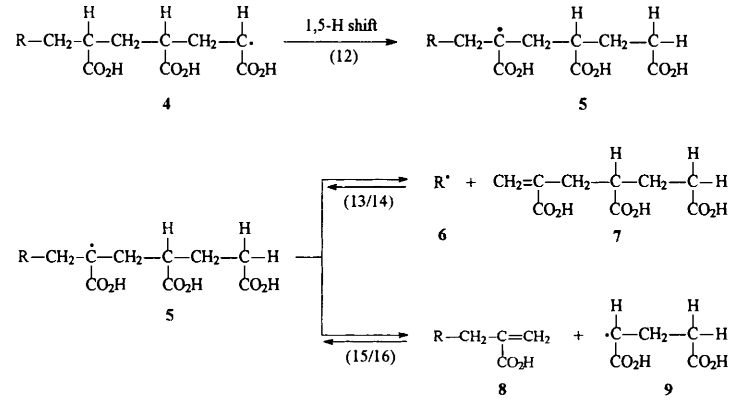
Fig. 12 Pulse radiolysis of N_2O-saturated PAA solutions (7 × 10^{-2} mol dm^{-3}) in the absence (○) and presence (●) of 2-sulfanylethanol (10^{-4} mol dm^{-3}), pH 7.4, 19 Gy, 70 ms after the pulse. A correction of 12% for the reaction of OH radicals with 2-sulfanylethanol has been made.

Effect of Fe^{II} ions

It has been recognized before that contaminations with small amounts of transition metal ions, notably iron, may cause a poor reproducibility in certain experiments, especially when the PAA radicals are long-lived.[23] For this reason in the present study all glassware has been carefully cleaned with EDTA solutions prior to use. Direct proof that Fe^{II} ions do in fact interact with the PAA radicals has been obtained by scission yield measurements. γ-Irradiation of 1 × 10^{-2} mol dm^{-3} N_2O-saturated PAA solutions at pH 7 containing deliberately added 1.9 × 10^{-6} mol dm^{-3} of Fe^{II} ions resulted in a four-fold reduction in the yield of scission and in the presence of 1.9 × 10^{-5} mol dm^{-3} Fe^{II} ions scission was almost completely suppressed. In addition, in a pulse radiolysis experiment, 1 × 10^{-6} mol dm^{-3} Fe^{II} ions reduces the amplitude of the conductivity increase more than 10-fold and also causes a significant decrease in the half-life of this process. The mechanism of the effect of such small concentrations of (complexed) Fe^{II} ions is not yet understood. Experiments are in progress to study this reaction further.

The 1,5-H shift reaction

The EPR spectrum of PAA radicals observed at times much longer than the half-life of strand breakage, however, is predominantly that of an internal α-radical, in agreement with a recent EPR study on the OH-radical-induced polymerization of acrylic acid.[21] There it has been proposed that the terminal α-radicals **4** generate a mid-chain α-radical **5** by a 1,5-H-shift [reaction (12)]. However, this interpretation raises the question whether depolymerization [reactions (13) and (15)] ensues during the long lifetime of the α-radicals at pH 10. It should be possible to determine the terminal methylene groups (*cf.* compounds **7** and **8**) formed in reactions (13) and (15) by ozonation. Ozonation of acrylic acid yields formaldehyde with a 50% yield.[60] The formaldeyde yield of γ-irradiated and subsequently ozonated PAA samples was $G(CH_2O) \approx 2.0 \times 10^{-7}$ mol J^{-1}, *i.e.* not more than 80% of the PAA radicals eventually yielded $CH_2{=}CR_2$-groups. Such



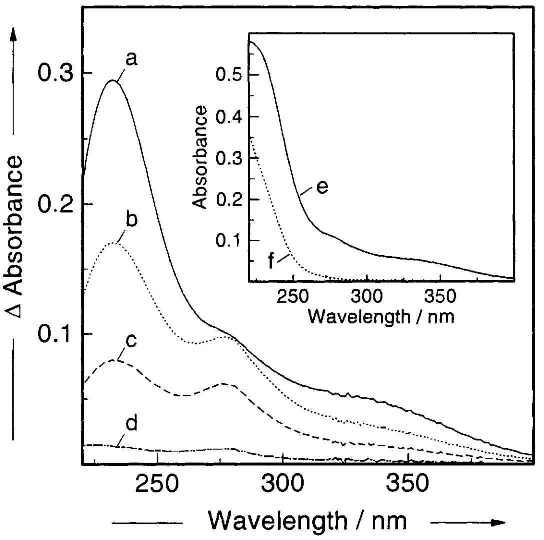


Fig. 13 γ-Radiolysis (1 min, 300 Gy) of N_2O-saturated PAA solutions (10^{-2} mol dm^{-3}), pH 10. Absorption spectra after subtraction of the final absorbance; (*a*) 1.5 min, (*b*) 15 min, (*c*) 38 min and (*d*) 105 min after irradiation. An increase at 280 nm above the value at 15 min occurs already within 4 min (spectrum omitted for clarity reasons). Inset: spectra measured against an unirradiated sample, (*e*) at 1.5 min and (*f*) final spectrum (222 min).

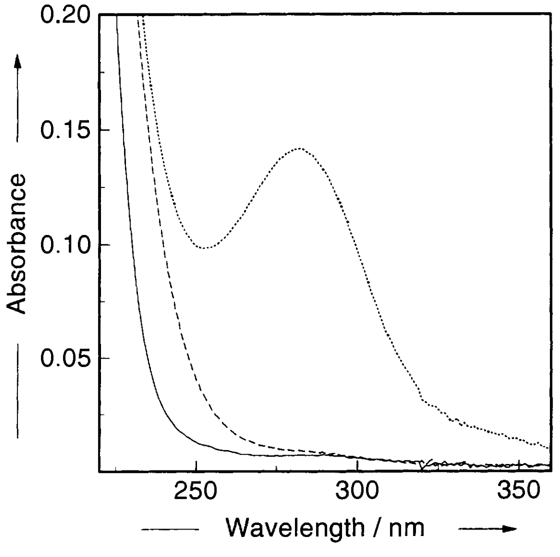


Fig. 14 γ-Radiolysis of N_2O-saturated PAA solutions (10^{-2} mol dm^{-3}), pH 10, 140 Gy. UV spectra before irradiation (——) and after irradiation: the vessel was opened shortly after irradiation (· · ·), the vessel was kept closed for 24 h (– – – –).

structures are already formed in reaction (8) and there seems to be not much room for further end groups of this type. This indicates that depolymerization reactions beyond the scission reaction (8) are inefficient or strongly reversible under our conditions. The latter is well possible for equilibrium (13/14), but whenever reaction (15) occurs, radicals **9** would decay bimolecularly within 1 s thus limiting the lifetime of the PAA radicals to a few seconds. The observed lifetime at pH 10, however, is much longer (> 15 min, see above).

Absorbance of final products

The recently reported observation[24] that under anoxic conditions the products of the decay of the PAA radicals are characterized by permanent absorbances in the 280–300 nm range could not be confirmed in our experiments. It can be seen from Fig. 13 that the UV absorbance in this range decays to zero within 200 min (the temporary relative enhancement of the absoption near 280 nm occurs in the timescale of chain breakage). It may be that in the described experiments[24] the irradiated samples were opened prematurely and oxygen has reacted with the persisting PAA radicals. In fact, when samples that had received a dose of 140 Gy were opened right after irradiation we observed the formation of such an absorbance, but it was fully absent when the samples were kept sufficiently long (overnight) for all radicals to decay (Fig. 14).

Acknowledgements

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