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

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Hydroxyl radicals were generated radiolytically in N_2O–O_2 (4:1)-saturated dilute aqueous solutions of poly(acrylic acid), PAA. They react with PAA by abstracting H atoms from PAA in both the α- and β-positions to the carboxy group. The resulting PAA radicals are converted by O_2 into the corresponding peroxyl radicals ($k = 3.1 \times 10^8$ dm^3 mol^{-1} s^{-1} at pH 3.5 and $k = 1 \times 10^8$ dm^3 mol^{-1} s^{-1} at pH 10, as measured by pulse radiolysis). The lowering of the rate constant at high pH has been attributed to a diffusion barrier for O_2 exerted by the ion cloud around the charged macroradical. Although the lifetimes of the PAA peroxyl radicals (measured by EPR spectroscopy) increase with increasing pH, they still decay much faster than the very long-lived PAA radicals formed in the absence of O_2. Concomitant with an increase in the lifetime of the peroxyl radicals, O_2 uptake (in units of mol per mol PAA radicals initially formed) increases from 1.7 at pH 2.5 to 17 at pH 10 as does decarboxylation (from 1.0 at pH 3.5 to 13 at pH 10), scission (from 0.05 at pH 2 to 2.4 at pH 9) and the formation of acetylacetone-like products (from 0.35 at pH 3.5 to 1.05 at pH 10). The high yield of O_2 uptake at pH 10 is mainly the result of repetitive abstraction of α-hydrogens by PAA α-peroxyl radicals. The acetylacetone-like products are formed by intramolecular 1,5-H-transfer reactions followed by a decomposition of the ensuing hydroperoxides. The chain breaks are formed in the course of the bimolecular termination reactions as has been shown by pulse radiolysis with low-angle laser light-scattering detection.

Poly(acrylic acid), PAA, is the simplest organic polyelectrolyte, and hence has often been used to study the basic polyelectrolytic phenomena.[1-3] There also are numerous practical applications of PAA.[4-7] One of the recent directions of studies on the practical use of this polymer is the formation of hydrogels for medical applications. Treatment with ionizing radiation has proved to be a convenient method of hydrogel formation and concomitant sterilization of polymeric biomaterials (e.g. refs. 8 and 9). Under these conditions hydrogel formation is largely induced by the OH radicals generated in the radiolysis of the solvent. Flanking fundamental studies have been carried out for a better understanding of the primary processes involved in crosslinking and scission reactions in the absence of oxygen.[10-14] It will be shown that in the presence of oxygen, scission and intramolecular H-transfer reactions are the dominating processes.

Experimental

Samples of poly(acrylic acid) [PAA; Aldrich, 700 kDa weight-average molecular weight (MW)] and poly(vinyl alcohol) (Aldrich, MW = 110 kDa) were purified and dissolved in Milli-Q-filtered (Millipore) water at elevated temperature as described previously.[14,15] Poly(ethylene oxide) (Aldrich, MW ≈ 200 kDa) and poly(vinyl pyrrolidone) (K-90, Aldrich, MW ≈ 360 kDa) were used as received and their solutions were made-up by stirring at room temperature. Further experimental details are described in a preceding paper;[14] supplementary information is given here where required.

Prior to irradiation solutions were saturated with N_2O–O_2 (4:1 v/v, Messer-Griesheim) or with O_2 in the case of EPR measurements. For the experiments on the rate of oxygen addition to the carbon-centred radicals, N_2O–O_2 mixtures in

various proportions were prepared with a Brooks gas mixer. Standard saturation times were 1 h.

Rate constants for oxygen addition to the carbon-centred radicals have been obtained from the O_2 concentration dependence of the first-order rate constants of the change in absorbance [decay in the case of poly(vinyl pyrrolidone) radicals, increase in the other cases].

In the pulse radiolysis with low-angle laser light-scattering detection, the solutions were irradiated with 2.8 MeV electrons directly in the cell of a Chromatix KMX-6 apparatus equipped with an Ar-ion laser operating at 488 nm.[16] The angle of scattered-light collection was 4.5–5.5°. From the decrease of the scattered light intensity at time t (ΔU_t) molar concentrations of scissions and half-lives of their formation were calculated according to [scissions]$_t = Q\{(U_o - U_{solv} - \Delta U_t)^{-1} - (U_o - U_{solv})^{-1}\}$. U_o denotes the scattered light intensity prior to the pulse and U_{solv} is the contribution of the solvent to the light-scattering intensity. The constant Q depends on the concentration and refractive index increment of the polymer (0.30 cm^3 g^{-1} was used).[14] Dosimetry was based on measurements of the optical absorption in the same cell with N_2O-saturated solutions of KBr (10^{-2} mol dm^{-3}) and N,N,N',N'-tetramethyl-1,4-phenylenediamine dihydrochloride (TMPD), (10^{-3} mol dm^{-3} at pH 8) using the absorption coefficient of the radical cation ($\varepsilon = 3480$ dm^3 mol^{-1} cm^{-1} at 488 nm).

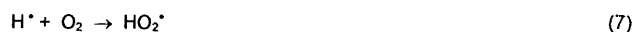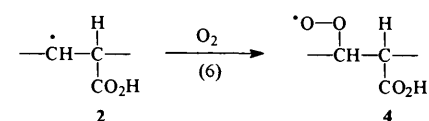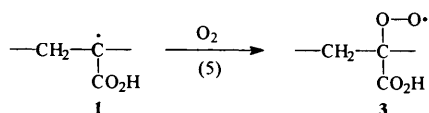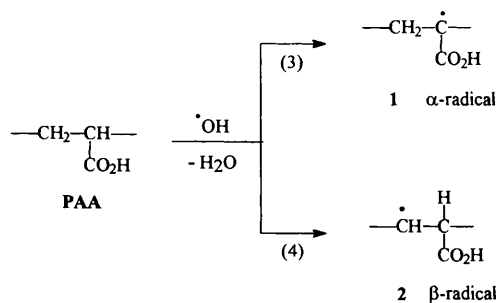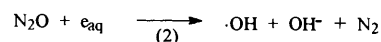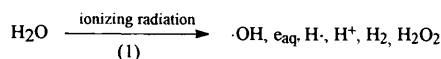EPR experiments were performed on an X-band spectrometer with 100 kHz modulation equipped with a flow system. For time-resolved measurements a stopped-flow technique was used.[17] Radicals were generated by UV irradiation in situ in the presence of 1 × 10^{-3} mol dm^{-3} hydrogen peroxide using an argon plasma light source (GAT-PB 1500, Gamma Analysentechnik).

The yield of nitroform anion was determined on the basis of its known absorption coefficient at 350 nm ($\varepsilon = 1.5 \times 10^4$ dm^3 mol^{-1} cm^{-1}),[18] while for quantifying the acetylacetone-like structures the absorption coefficient of the enolate form (pH > 12) at 294 nm was assumed to be the same as that of the acetylacetone enolate ($\varepsilon = 2.14 \times 10^4$ dm^3 mol^{-1} cm^{-1}).[19] The yield of organic hydroperoxides was determined using Allen's reagent[20] modified by an addition of N,N,N',N'-tetramethyl-1,4-phenylenediamine dihydrochloride (TMPD), as described elsewhere.[13] Carbon dioxide was quantified by GC (Porapak–T column) after on-line catalytic reduction to methane.[21] The yield of O_2 uptake was measured with a Clark electrode (OXI 530, TriOx EO 200 electrode, WTW Weilheim) in a thermostatted (20 °C) gas-tight vessel.

Results and discussion

Generation of the PAA peroxyl radicals and UV absorption spectra

Upon irradiation of dilute N_2O-O_2 (4:1)-saturated PAA solutions OH radicals are formed in reactions (1) and (2). Their radiation-chemical yield is $G = 5.8 \times 10^{-7}$ mol J^{-1}.[22] The OH radicals react with PAA by H-abstraction at both the α- and β-positions relative to the carboxylic groups [reactions (3) and (4)].[11,12,14] The H atoms react with oxygen giving rise to hydroperoxyl radicals $HO_2{}^{\bullet}$ and the conjugated super-oxide radical ions $O_2{}^{\bullet-}$ [reaction (7); $pK_a(HO_2{}^{\bullet}) = 4.8$, $G(HO_2{}^{\bullet}/O_2{}^{\bullet-}) = 0.6 \times 10^{-7}$ mol J^{-1}].

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

$$N_2O + e_{aq}^- \xrightarrow{\text{(2)}} \cdot OH + OH^- + N_2$$

[Reaction scheme: PAA $\xrightarrow{\cdot OH,\ -H_2O}$ 1 α-radical (via 3) and 2 β-radical (via 4)]

[Reaction scheme: 1 $\xrightarrow[\text{(5)}]{O_2}$ 3; 2 $\xrightarrow[\text{(6)}]{O_2}$ 4]

$$H^{\bullet} + O_2 \rightarrow HO_2{}^{\bullet} \tag{7}$$

The PAA-derived carbon-centred radicals 1 and 2, formed in a ratio of approximately 1:2.5,[14] react with oxygen to give the peroxyl radicals 3 and 4, respectively [reactions (5) and (6)]. At the oxygen concentrations used ([O_2] = 2.7×10^{-4} mol dm^{-3}) oxygen addition is much faster ($k = 3.1 \times 10^8$ dm^3 mol^{-1} s^{-1} at pH 3.5 and 1×10^8 dm^3 mol^{-1} s^{-1} at pH 10, see Table 1) than the transformation of β-radicals 2 into the α-radicals 1 ($k < 300$ s^{-1}),[14] thus peroxyl radicals 3 and 4 are also formed in an approximate 1:2.5 ratio. The absorption spectra of PAA
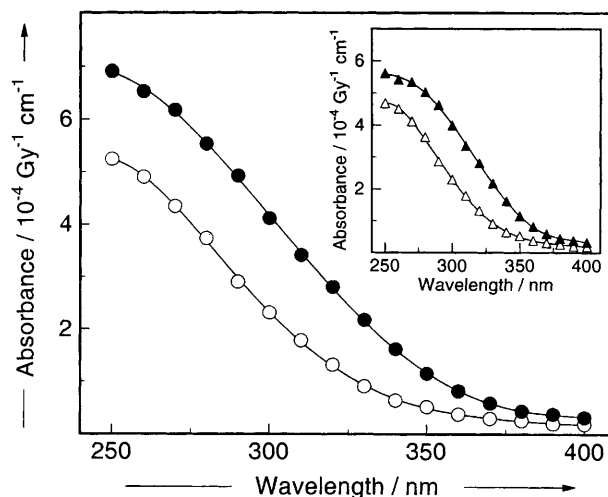
Fig. 1 Absorption spectra of PAA-derived peroxyl radicals recorded in N_2O-O_2-saturated 1×10^{-2} mol dm^{-3} PAA solutions: (○) at pH 3.5, 120–160 μs after electron pulse and (●) at pH 10, 600–800 μs after electron pulse. Dose 7 Gy. Inset: spectra (△) at pH 3.5 and (▲) at pH 10 corrected for the absorbance of $HO_2{}^{\bullet}/O_2{}^{\bullet-}$.

Table 1 Rate constants of oxygen addition to the radicals derived from PAA, 2,4-DMGA and non-ionic polymers

Compound	$k(R^{\bullet} + O_2)/10^8$ dm^3 mol^{-1} s^{-1}
Poly(acrylic acid), pH 3.5	3.1
Poly(acrylic acid), pH 10	1.0
2,4-DMGA, pH 3.5	12
2,4-DMGA, pH 10	10
Poly(ethylene oxide)	15,[a] 22[b]
Poly(vinyl alcohol)	5.2
Poly(vinyl pyrrolidone)	8.7

[a] This work (MW = 200 kDa, [PEO] = 1×10^{-2} mol dm^{-3}). [b] Ref. 23 (ferricyanide competition method, MW = 20 kDa, [PEO] = 0.45 mol dm^{-3}).

peroxyl radicals resemble the spectra obtained for the model compound radicals[13] and show rising absorbance towards shorter wavelength (Fig. 1).

The rate constant of O_2 addition to the PAA radicals 1 and 2 has been measured by pulse radiolysis following the absorption increase at 300 nm (Table 1). It is markedly lower than that of the O_2 addition reactions to the carbon-centred radicals derived from the model compound 2,4-dimethylglutaric acid (2,4-DMGA).† In the case of the reaction of 2,4-DMGA radicals with O_2 the diffusion of both reactants contribute to their approach, while in the case of the polymer radicals their diffusion can be neglected. This can, however, account only for a factor of approximately two. With PAA, there is also a pronounced pH effect, *i.e.* the reaction is slower in the case of fully dissociated carboxylic groups (pH 10) than in the partially dissociated polymer (pH 3.5, natural pH). Such a drastic pH effect is not observed with the 2,4-DMGA radicals. We hence tentatively suggest that condensation of counterions close to the polyelectrolyte chain may cause a decrease in the local solubility of oxygen and thus may contribute to the observed reduction in the rate constant of oxygen addition.

Strong polyelectrolytes are surrounded by a dense atmosphere of counterions. The ion concentration in the counterion atmosphere increases with decreasing average charge spacing. In PAA this spacing is reduced with increasing deprotonation, *i.e.* with increasing pH and at pH 10 is in the order of 2 Å. This leads to a local ion cloud concentration of *ca.* 1 mol dm^{-3}.[24] Such a high ion concentration would result in a reduction in oxygen solubility by a factor of 1.5–1.7.[25] The

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

observed ratio of the rate constants found at pH 3.5 and pH 10 is 3, *i.e.* slightly higher. The above estimate of local ion concentration is based on a value averaged for the cylindrical zone around the chain within which the ion condensation occurs. The radius of this zone is in the range of 15–20 Å.[24] It may well be that close to the centre (where the reaction with O_2 has to occur) the ion concentration is even higher and thus the barrier for O_2 diffusion may be even more effective.

A similar mechanism has been suggested to apply to polynucleotide [poly(U) and poly(A)] radicals which react significantly more slowly with O_2 than the radicals derived from the corresponding mononucleotides.[26] An even more pronounced decrease in the apparent rate constant found for double-stranded poly(A + U) may be related either to the restricted access of oxygen into the interior of the helix or by shorter average charge-spacing as compared with the single-stranded polynucleotides.

Lifetime of PAA peroxyl radicals

The PAA peroxyl radicals **3** and **4** decay bimolecularly. At pH 3.5 their decay can be followed by pulse radiolysis at 300 nm. Since under these conditions the bimolecular decay is relatively fast, there is very little interference from a strongly-absorbing stable product which is formed at low dose rates *via* a slow intramolecular reaction (see below). The decay cannot be described satisfactorily by simple second-order kinetics with a single rate constant, for the same reasons as in the case of the carbon-centred radicals **1** and **2**, *i.e.* mainly because of the non-homogeneous distribution of radicals on the polymer chains and the competition between intra- and inter-molecular termination reactions.[14] The initial rate constant of bimolecular decay is estimated as $2k = 8 \times 10^7$ dm^3 mol^{-1} s^{-1}, *i.e.* somewhat lower than the initial rate of decay of radicals **1** and **2** ($2k = 2.4 \times 10^8$ dm^3 mol^{-1} s^{-1}) under similar conditions. Also in the case of the model compound 2,4-DMGA peroxyl radicals were found to decay slower than their corresponding carbon-centred radicals.[13]

In alkaline solutions, the decay of the PAA peroxyl radicals cannot be followed as conveniently by pulse radiolysis using optical detection. Since the bimolecular termination reactions are much slower than at low pH, unimolecular reactions (see below) may take place even under pulse radiolysis conditions and as a consequence stable products are formed, whose absorbance overlaps with that of the peroxyl radicals. In order to gain some information on the pH dependence of the lifetime of the PAA peroxyl radicals, these radicals were generated photolytically in the presence of 10^{-3} mol dm^{-3} H_2O_2 within an EPR spectrometer cavity in order to follow the decay of their EPR signal. Typically, half-lives were in the order of < 1 s at pH 3 and *ca.* 10–15 s at pH 10. At still higher pH the lifetime shortens again.

The general tendency, *i.e.* an increase in the radical lifetime with increasing charge density on the macromolecules (stronger repulsive forces between the chains) and a decrease in the presence of higher concentrations of base or salt (screening effect), is similar to that of carbon-centred radicals.[14] However, here the difference in the radical lifetimes at pH 3.5 and 10 is less pronounced and the half-lives of the PAA peroxyl radicals at pH 10 are much shorter than those of the corresponding carbon-centred radicals. An explanation for this difference may be found in the difference in geometry of the two types of radicals. The distance between the polymer chains at which the combination of two peroxyl radicals can occur (five bond lengths) is significantly greater than in the case of the reaction between two carbon-centred radicals (one C–C bond length). Hence in the case of the peroxyl radicals the repulsive electrostatic forces at the point of encounter are likely to be considerably lower and could be even further weakened by a screening effect of condensed counterions. An additional
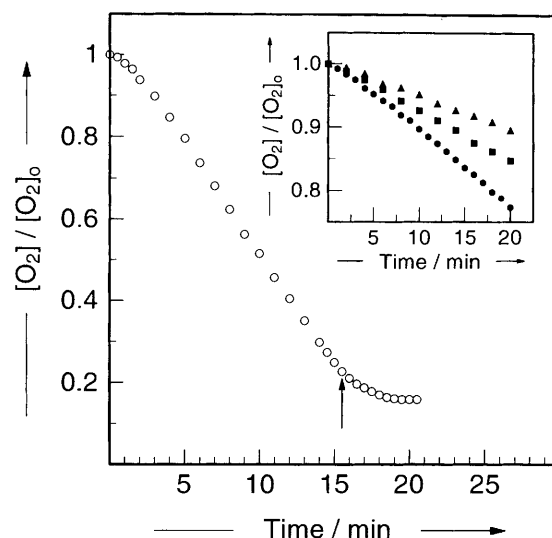

Fig. 2 Decrease in oxygen concentration in N_2O–O_2-saturated 1×10^{-2} mol dm^{-3} PAA solution upon γ-irradiation with a dose rate of 1.59 Gy min^{-1} at (○) pH 10, (●) pH 3.5, (■) pH 3.0 and (▲) pH 2.5. The arrow in the main figure denotes the end of irradiation.

shortening of the peroxyl radical life times may arise from the presence of $O_2^{\cdot-}$ generated by the photolytic ionization of PAA[14] in the EPR experiments.

### Oxygen uptake, decarboxylation and the formation of acetylacetone-like products

The O_2 uptake has been measured at the low dose rate of γ-radiolysis (0.026 Gy s^{-1}) as a function of pH. From the linear parts of the curves such as shown in Fig. 2, $G(O_2$ uptake) is calculated at $G = 10 \times 10^{-7}$ mol J^{-1} at pH 2.5, 14×10^{-7} mol J^{-1} at pH 3.0, 21×10^{-7} mol J^{-1} at pH 3.5 and 100×10^{-7} mol J^{-1} at pH 10. Addition of salt (0.1 mol dm^{-3} Na_2SO_4) at pH 10 prior to irradiation results in a decrease to 54×10^{-7} mol J^{-1}.

The yield of carbon dioxide was found to be 5.5×10^{-7} mol J^{-1} at pH 3.5. Because of experimental problems $G(CO_2)$ at pH 10 was determined after γ-irradiation of samples saturated with pure oxygen instead of the N_2O–O_2 mixture. A G value of 36×10^{-7} mol J^{-1} was obtained. Under saturation with pure oxygen the yield of primary PAA radicals is one-half of that in solutions saturated with the N_2O–O_2 mixture. Therefore, for comparison with the other results, O_2 uptake and scission data are based on the primary OH radical yield.

For straightforward bimolecular termination of peroxyl radicals $G(O_2$ uptake) may vary between 3×10^{-7} and 6×10^{-7} mol J^{-1}, depending on the termination mechanism.[27,28] In the present system at all pH values measured, $G(O_2$ uptake) is significantly higher and increases with increasing pH, *i.e.* with increasing lifetime of the PAA peroxyl radicals. Thus, besides the bimolecular termination further radical-generating reactions must occur which are kinetically of first-order. The $G(O_2$ uptake) may be regarded as a measure for the efficiency of these first-order reactions. It is noted that concomitantly with O_2 uptake the yield of CO_2 formed per primary OH radical increases with increasing pH (1 mol CO_2/mol OH radicals at pH 3.5 *vs.* 13 mol CO_2/mol OH radicals at pH 10). The formation of CO_2 is certainly connected with the formation of acetylacetone-like products.[11]

It has been suggested before that the UV absorbance which develops when PAA solutions are irradiated in the presence of O_2 is due to formation of such structures.[11,14] The suggested sequence of reactions is given by reactions (8)–(11). This suggestion has now been put on firmer ground, because in the PAA model system, 2,4-DMGA, acetylacetone has been identified unequivocally and is indeed a major product.[13]

It is suggested that peroxyl radical **3** undergoes an intramolecular H-abstraction reaction involving a six-membered transition state yielding the hydroperoxide radical **5** [reaction (8)] which adds further O_2 [reaction (9)] and the
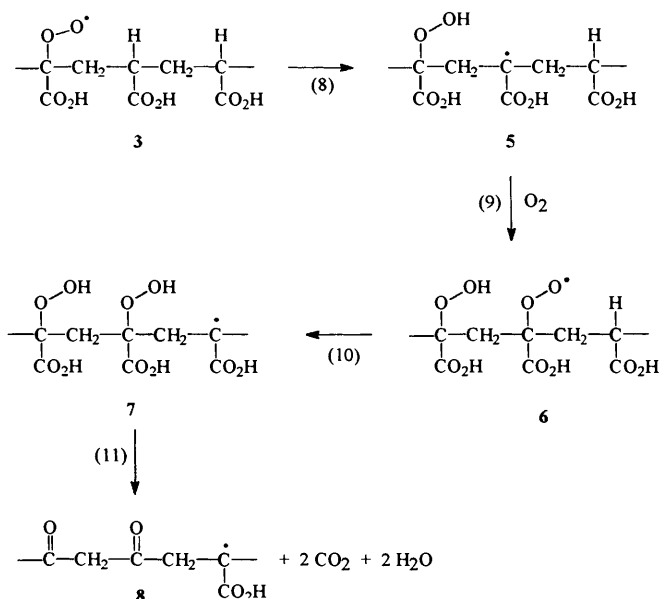
ensuing peroxyl radical **6** undergoes further H-abstraction [reaction (10)]. The chain proceeds as peroxyl radical **7** abstracts a further H-atom intramolecularly at a neighbouring position [as shown in reaction (11)] or transfers the radical site to a more distant chain segment or another macromolecule. The 1,3-dihydroperoxides such as products derived from **7** will readily decompose by a reaction reminiscent of the decarboxylation of β-keto carboxylic acids [reactions (11) and (12)].
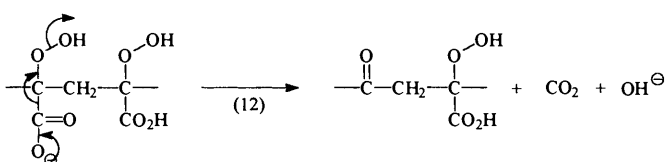
The $O_2^{\bullet-}$ radicals may contribute to the formation of the hydroperoxidic precursors of the acetylacetone-like products **8** by reducing radical **6**, but when they react with the peroxyl radicals **4** they may give rise to other more stable hydroperoxides. At pH 3.5 stable organic hydroperoxides have been found to be formed with a G value of $ca.$ 1 × 10⁻⁷ mol J⁻¹.

The acetylacetone-like structures are expected to have a pH-dependent UV spectrum, since in alkaline solutions their enolic forms deprotonate to form enolate [equilibrium (13/14)].
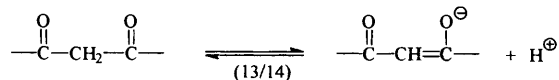
In fact, irradiation of PAA in both acidic and alkaline N_2O–O_2-saturated solutions, leads to the formation of a stable, broad absorbance band. At low and medium pH it has a maximum at 270 nm. At high pH the intensity of absorbance increases and the location of the maximum is shifted to 295 nm (Fig. 3). This resembles closely the spectral behaviour of acetylacetone. While the pK_a of acetylacetone is at 8.8–9.1,[19] the pK_a value of the corresponding PAA-derived product is found at $ca.$ 10.3. A shift to higher values is expected since in the case of PAA similar
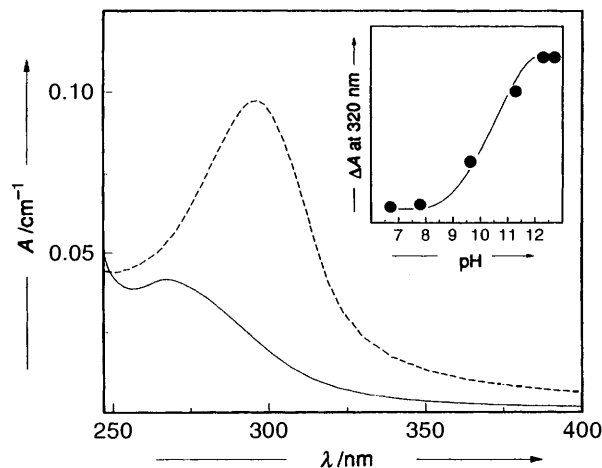
Fig. 3 Absorption spectra of N_2O–O_2-saturated 1 × 10⁻² mol dm⁻³ PAA solution after γ-irradiation with a dose of 20 Gy at pH 3.5. Spectra recorded at (—) pH 3.5 and at (– – –) pH 12.5. Inset: absorbance at 320 nm as a function of pH.

enolic structure would be more difficult to deprotonate because of the influence of neighbouring carboxylate groups. The yield of acetylacetone-like structures (based on the molar absorption coefficient of acetylacetone in basic solutions) is $G = 2.0 × 10^{-7}$ mol J⁻¹ at pH 3.5 and $G = 6.1 × 10^{-7}$ mol J⁻¹ at pH 10.

In the 2,4-DMGA system the half-life with respect to the reaction analogous to (8) has been estimated at 1.4 s. If it occurs in PAA with a similar rate, it should proceed with high efficiency since the lifetimes of the PAA-peroxyl radicals are longer, especially at high pH values. Indeed the above G values are higher than those found with 2,4-DMGA.[13] In deoxygenated PAA solutions there is a relatively efficient H-transfer from the β-radicals **2** to form the α-radicals **1**.[14] An analogous H-transfer of the [dominating, $G(4) \approx 4 × 10^{-7}$ mol J⁻¹] primary β-peroxyl radical **4** to abstract an α-hydrogen atom may be favoured thermodynamically, but the transition state would be less favoured when the reaction occurs with a hydrogen atom at one of the neighbouring α-positions. However, it could occur intramolecularly over a larger distance. Thus it is difficult to estimate at what rate the primary peroxyl radicals **4** are converted into peroxyl radicals **3**, the precursor of the acetylacetone-like product. The G value for the formation of stable hydroperoxides has been estimated at 1 × 10⁻⁷ mol J⁻¹ at pH 3.5, hence these reactions cannot be very fast and the peroxyl radicals **4** have to decay by other routes as well.

As mentioned above, the formation of acetylacetone-like structures is connected with a release of CO_2. The latter is formed with a yield of 1 mol/mol OH radicals at pH 3.5 and 13 mol/mol OH radicals at pH 10. Only a fraction of this can be accounted for by the formation of acetylacetone-like products (β-oxo-keto). Thus there must be a further source of CO_2. β,δ-Dioxo-keto and higher analogues may also be formed and account for further CO_2 formation. The products that carry multiple β-oxo structures are not expected to differ noticeably in their spectral properties from the single β-oxo-keto structures, since deprotonation beyond the single enolate form may occur only at much higher pH ($cf.$ Fig. 3, inset). In addition, the study on the low molecular weight model 2,4-DMGA suggests several conceivable termination reactions in which CO_2 is released from the peroxyl radicals in the α-position without formation of the acetylacetone-like products.[13] Besides termination reactions involving two PAA peroxyl radicals there is also a non-negligible termination by the reaction of the peroxyl radicals with $HO_2^{\bullet}/O_2^{\bullet-}$. The latter is formed with a total yield [from reaction (7) and produced in the course of bimolecular termination reactions] of 1.4 × 10⁻⁷ mol J⁻¹ at pH 3.5 and of 3.6 × 10⁻⁷ mol J⁻¹ at pH 7.5 as
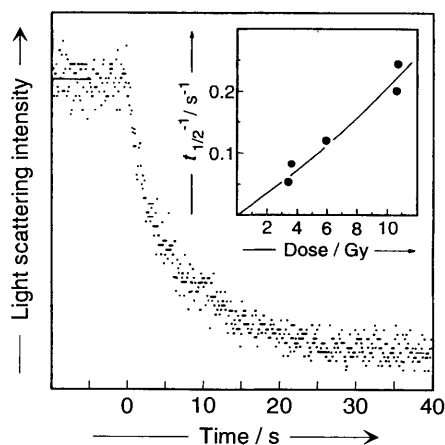
Fig. 4 Pulse radiolysis of an N_2O-O_2-saturated 10^{-3} mol dm^{-3} PAA solution containing 0.1 mol dm^{-3} Na$_2$SO$_4$, pH 10, 7 Gy/pulse. Decrease of the laser light-scattering intensity as a function of time. Inset: dependence of the reciprocal half-life of chain scission on the dose/pulse value. Incomplete OH radical scavenging by PAA has been corrected for (20% at the highest dose of 13 Gy).

monitored with tetranitromethane (formation of nitroform anions).[18]

Furthermore, in competition with the abstraction from the next-neighbour α-position [reaction (8)] the abstraction over larger distances may take place as well. Such a reaction over a distance necessarily leads to the formation of isolated α-hydroperoxides. The resulting isolated keto functions could not be assayed.

Chain scission

Direct evidence for the chain breakage reactions in our system has been gained by the low-angle laser light-scattering (LALLS) measurements of the changes in the weight-average molecular weight of PAA, both after γ-irradiation and in the time-resolved mode coupled with pulse radiolysis. (It is noted that the conductivity method applied in deoxygenated solutions is less reliable in O_2-containing solutions. Processes other than chain scission, e.g. the formation of $O_2^{\cdot-}$, formation of carbon dioxide and its decay into hydrogen carbonate/carbonate ions[29] and the deprotonation of peroxyl radicals,[30] may contribute to the conductivity change.)

In contrast to the situation in deoxygenated solutions, crosslinks between polymer chains are unlikely to occur in the presence of O_2.[28] In the absence of competing crosslinking reactions the yield of scission [G(scission)] can be calculated on the basis of molecular weight changes according to eqn. (15),

$$G(\text{scission}) = 2\,(\text{MW}^{-1} - \text{MW}_0^{-1})\,c_{\text{PAA}}\,D^{-1}\,\rho^{-1} \quad (15)$$

where MW_0 and MW (in g mol^{-1}) are the weight-average molecular weights before and after irradiation, c_{PAA} is the PAA concentration (in g dm^{-3}), D is dose in Gy and ρ is the solution density in kg dm^{-3} (cf. refs. 31–33).

Pulse radiolysis measurements with LALLS detection were performed with 1×10^{-3} mol dm^{-3} PAA at pH 10 in the presence of 0.1 mol dm^{-3} Na$_2$SO$_4$ (the aim of salt addition is to provide compact conformation of macromolecules, necessary for light-scattering measurements). A typical kinetic trace is shown in Fig. 4.

The half-lives of chain scission were calculated from such traces (see Experimental section) and found to depend on the dose per pulse (inset in Fig. 4) indicating that the breaks are formed indeed upon bimolecular peroxyl radicals reactions ($2k = 3.2 \times 10^4$ dm^3 mol^{-1} s^{-1} under these experimental conditions, i.e. in the presence of salt) and that these reactions
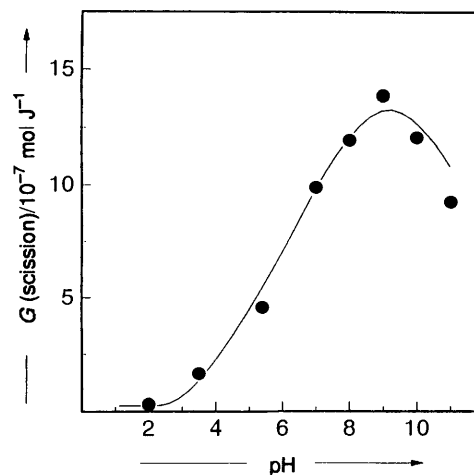

Fig. 5 γ-Irradiation of aqueous N_2O-O_2-saturated solutions of PAA. Radiation-chemical yields of chain scission as a function of pH. [PAA] = 10^{-2} mol dm^{-3}, doses up to 8 Gy (20 Gy at pH 2), dose rate 0.034 Gy s^{-1}.

are rate-limiting. The scissions occur probably by the β-scission of oxyl radicals formed bimolecularly from two peroxyl radicals by decomposition of the intermediate tetroxide. As an example the fragmentation of the α-oxyl radical is shown in reaction (16).
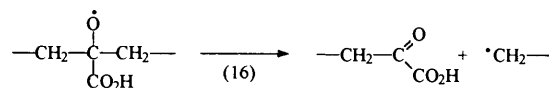
Oxyl radicals in the β-position are in principle also capable of yielding chain-scission in an analogous reaction.

The relatively low scission yield [G(scission) = 0.8×10^{-7} mol J^{-1}] provides some evidence that the cleavage observed happens mainly via the rapid bimolecular reaction of the primary peroxyl radicals rather than in the course of the chain reaction which occurs at high pH in the absence of salt (see below). Also in 2,4-DMGA splitting of the C–C bonds is not a major reaction pathway.[13]

The pH-dependence of the scission yield measured after γ-radiolysis (when no added salt was present during irradiation) is shown in Fig. 5.

At low pH the bimolecular decay of the peroxyl radicals is fast and the scission yield low, for the above reasons. However, at high pH, when the radical lifetime is longer, the terminal radicals formed in the chain-scission process [cf. reaction (16); peroxyl radicals after O_2 addition] can abstract a hydrogen atom from another chain. This starts a new sequence of events, leading to further chain breaks and an increase in O_2 uptake. Indeed at pH 9, G(scission) = 14×10^{-7} mol J^{-1} (at [PAA] = 10^{-2} mol dm^{-3}, see Fig. 5). This behaviour parallels the finding that α-peroxyl radicals at higher pH effectively abstract α-hydrogens, and thus propagate the CO_2-generating chain.

A dramatic salt effect is observed upon the addition of 0.25 mol dm^{-3} Na$_2$SO$_4$ or 0.5 mol dm^{-3} NaClO$_4$ prior to γ-irradiation of a 10^{-3} mol dm^{-3} PAA solution at pH 10. This leads to the reduction of the scission yield from G(scission) $\approx 11 \times 10^{-7}$ mol J^{-1} in the absence of salts to G(scission) $\approx 0.9 \times 10^{-7}$ mol J^{-1} in their presence. The latter value is in good agreement with the pulse radiolysis data mentioned above, which have also been obtained upon irradiation in the presence of salt.

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