Time-Resolved EPR Studies of Main-Chain Radicals from Acrylic Polymers. Poly(acrylic acid)s

Natalia V. Lebedeva and Malcolm D. E. Forbes*

Caudill Laboratories, CB #3290, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599

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ABSTRACT: Time-resolved electron paramagnetic resonance (TREPR) spectroscopy is used to study the structure and dynamics of main chain radicals created after 248 nm laser excitation of aqueous solutions of poly(methacrylic acid) (PMAA) and poly(acrylic acid) (PAA). The polymeric radicals are created via Norrish I cleavage of the side-chain carboxyl group. The radicals are characterized by computer simulation of well-resolved, fast motion spectra acquired at high temperature (>100 °C). Hyperfine coupling constants and *g* factors are reported for both PMAA and PAA main-chain radicals. The TREPR signal intensities exhibit a strong dependence on pH, disappearing entirely at pH values >6. Similar to previously studied polymer radicals with ester side chains such as PMMA, symmetry issues play a large role in determining the magnitude of the fast motion coupling constants. Attempts to produce the polymer radicals via a photooxidative mechanism at high pH values failed, and this is discussed in terms of chromophore activity, polymer conformation, and solvent shell effects. The counter radical produced by Norrish I cleavage of the side chain is the hydroxyformyl radical, which is not observed, presumably due to fast spin relaxation. In PAA samples, at least two additional unassigned radicals are observed that may arise from impurities, defect sites, or end-group participation in the photochemistry.

Introduction

In a recent series of papers, we detailed the UV light-induced degradation processes of acrylic polymers in liquid solution using time-resolved electron paramagnetic resonance (TREPR) spectroscopy.[1] The photochemistry and ensuing free radicals from these reactions are outlined in Scheme 1. These papers, which to date have focused on poly(methyl methacrylate) (PMMA) and related polymers with ester side chains, have established the following general principles: (1) the primary photodegradation mechanism upon direct photolysis is Norrish I α-cleavage of the side-chain ester group, (2) the degradation mechanism is common to all acrylic macromolecules studied to date, (3) the TREPR method is fast enough to capture spectra from the main-chain acrylic radical before any secondary reactions take place (e.g., the *β*-scission process shown at the bottom of Scheme 1), (4) dynamic effects due to conformational motion are manifested in lower temperature spectra as an alternating hyperfine line width effect, and (5) polymer tacticity plays a strong role in both the overall spectral appearance (as determined by fast motion hyperfine coupling constants) and in the temperature-dependent line broadening processes. The TREPR experiment is unique in its ability to detect these main-chain macromolecular radicals cleanly with high resolution, on the sub-microsecond time scale, well before any rearrangements take place.

In this paper, we turn our attention to the photochemistry of the poly(acrylic acid)s and the resulting free radicals. From a structural perspective, poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) are the simplest polyelectrolytes, and they are of significant interest as biodegradable materials for wound dressings[2] and other biomedical and bioanalytical[3] applications. The main difference between the polyacrylic acids and their ester counterparts is the presence of charges on the carboxyl side chains in solution. The degree of ionization of these functional groups can influence the morphology of the polymer chains in solution (coiled vs stretched),[4] the redox properties of the carboxylate groups,[5] and the nature of the excited states involved in the photodegradation process.[6]

Quantum yields, molecular weight distributions, and product analyses from the photolysis of aqueous solutions of PMAA were reported by Baxendale and Thomas in 1958.[7] This paper outlined the basic photoreactivity (side-chain cleavage) and proposed mechanisms leading to chain scission (*β*-scission of the main-chain radical) for PMAA upon direct photolysis in water in both the absence and presence of hydrogen peroxide. In a later report, Chou and Jellinek followed up on these studies using 254 nm lamp photolysis[8] and concluded that the *β*-scission process was the dominant degradation mechanism. For several decades the degradation of both PMAA and PAA was studied by many different spectroscopic and analytical techniques, with a particular emphasis on reactivity with H_2O_2.[9] Reactions of the acrylic acids with reactive oxygen species such as hydroxyl radical are well understood and are the focus of biodegradability studies of these polymers.[10]

In regard to electron paramagnetic resonance studies, low-temperature (frozen) spectra have been reported from X-ray[11] and *γ*-radiation[12] of pure polymer samples and, in one case, a copolymer of methacrylic acid and acrylonitrile.[13] In all cases, these reports contain spectra that carry the typical burdens of low-temperature EPR spectroscopy, namely broad lines and overlapping signal carriers that make assignment and interpretation difficult and/or ambiguous. However, the main conclusion from much of this work was that the *β*-scission process was operative even in neat polymer samples at low temperatures. It is somewhat surprising to us that direct UV photolysis of pure PMAA or PAA in aqueous or other solutions at any temperature has not been studied by EPR spectroscopy in either the time-resolved or steady-state modes. There have been studies of PMAA degradation in the presence of additives such as iron salts[14] and acridine[15] and one report of TREPR experiments

* To whom correspondence should be addressed. E-mail: mdef@unc.edu.

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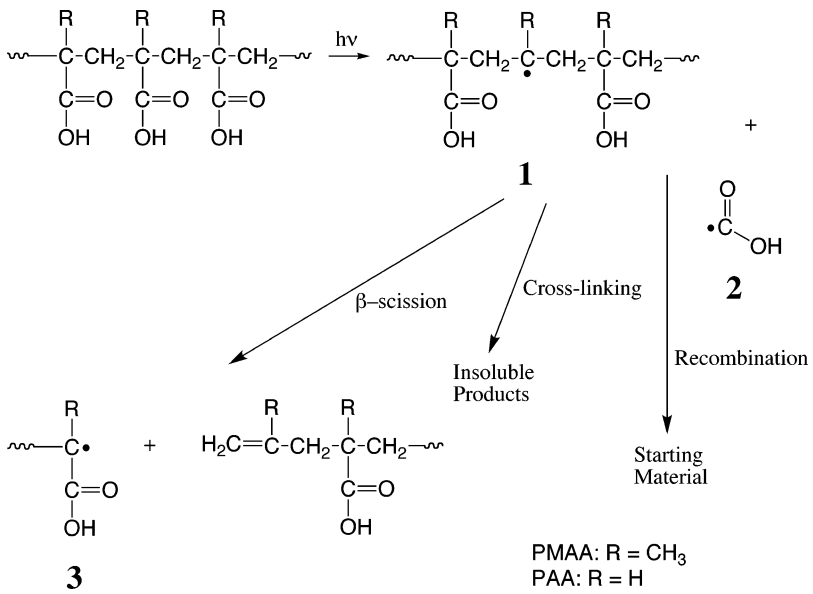
Scheme 1



during photolysis of an initiator-labeled methacrylic acid sample.[16] This latter work showed an interesting pH dependence of the signal carriers that is relevant to the results reported here, and this will be elaborated upon below.

As a natural extension of our previous work on PMMA and other methacrylates and acrylates, we report here TREPR spectra for radicals produced from direct photolysis of PAA and PMAA in aqueous solution as a function of temperature and pH, and we also compare photoredox and direct bond cleavage pathways for the production of the main-chain radicals. The results show some similarities but also some important differences in the photoinduced radical chemistry of these polymers compared to their analogues containing ester side chains.

Experimental Section

Materials. All polymers were atactic unless otherwise noted and were purchased from Sigma-Aldrich and used as received. Number-averaged molecular weights were 4.5×10^5 and 2×10^3 for PAA and 8×10^4 for PMAA. Water for all TREPR experiments was triply distilled and deionized using a Millipore water purification system.

TREPR. Continuous wave TREPR experiments were performed as previously described.[17] Briefly, all experiments were performed on a JEOL USA Inc. JES-RE1X X-band EPR spectrometer equipped with a wide bandwidth preamplifier and a low-noise GaAsFET microwave amplifier. For experiments on polymer solutions the concentrations were typically 2−3 g of polymer in 30−60 mL of solvent. Solutions were circulated through a flat cell (0.4 mm path length) positioned in the center of a Varian TE_{103} optical transmission cavity. The solutions were photolyzed using a Lambda Physik Compex 120 excimer laser (248 nm, KrF) running at 60 Hz with a pulse energy of 100 mJ (∼20 mJ per pulse hitting the sample) and a pulse width, accounting for jitter, of 25 ns. Spectra were collected in the absence of field modulation at a fixed delay time after the laser flash using a two-gate boxcar integrator (Stanford, 100 ns gates), while the external magnetic field was swept, typically over 2 or 4 min.

High-Temperature Flow System. For high-temperature experiments, the deoxygenated sample solution was circulated using a micropump (Micropump model 000-405) through Teflon PFA $^1/_8$ in. tubing insulated with polyurethane foam tape. From the pump, the sample tubing passed through a copper coil wrapped with heating tape (Omega, Inc.), which was controlled using a feedback circuit between a variable power temperature controller and thermocouples placed at the entrance and exit of the quartz flow cell. The sample was recirculated between the flat cell and the reservoir. Reported temperatures are the average of three measurements from the top and bottom of the flat cell and the reservoir. The maximum temperature gradient at the highest temperatures (∼125 °C) was 10 °C; therefore, all temperatures are reported as ±5 °C. Ethylene glycol was used as a cosolvent (about 10% by volume) for experiments above 100 °C.

Results and Discussion

PAA. TREPR spectra acquired during 248 nm photolysis of PAA in aqueous solution are shown as a function of temperature in Figure 1A. At first glance, the major signal carrier appears to be a radical exhibiting six lines from 5 equiv hyperfine couplings. In a similar fashion to acrylate polymer radicals studied previously (e.g., poly(ethyl acrylate) (PEA)), higher temperatures reveal an additional splitting in the central lines due to the magnetic inequivalence of the β-methylene protons. These inequivalencies are a function of polymer tacticity. This phenomenon was first reported and explained with regard to tacticity for acrylic main chain radicals in our 2000 paper,[1a] to which the reader is referred for further details. To briefly summarize, the two polymeric radicals shown on the right-hand side of Scheme 2 are drawn with their associated symmetry elements. The presence of stereogenic centers on each side of the main-chain radical center renders every pair of neighboring methylene protons magnetically inequivalent. However, because the hyperfine coupling constants to these protons are not perturbed greatly by the change in stereochemistry between the "meso" and "racemic" structures, the observed spectra for each type of radical are very similar. The difference in coupling constant for a methylene proton pair in either the meso or racemic radical can be quite large. In PMMA, for instance, the methylene couplings on the same carbon atom differ by about 5 G. In contrast, for an acrylic ester such as PEA, the difference is less than 1 G. The tacticity of our polymer samples is largely atactic, but it should be noted that many atactic polymer samples are siginificantly syndiotactic.

The methylene proton inequivalencies are a function of polymer stereochemistry and therefore cannot be removed by fast rotation. In fact, the differences in hyperfine coupling constants are much better resolved at higher temperatures as the fast motion limit of the couplings is reached. For PAA, these splittings are barely observed even at high temperatures,

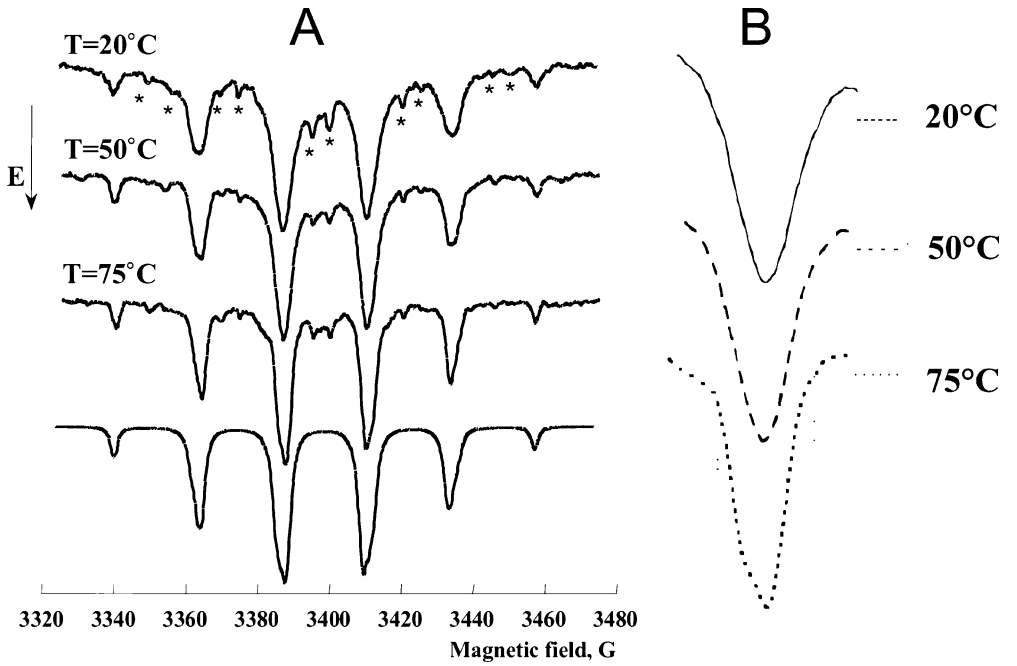
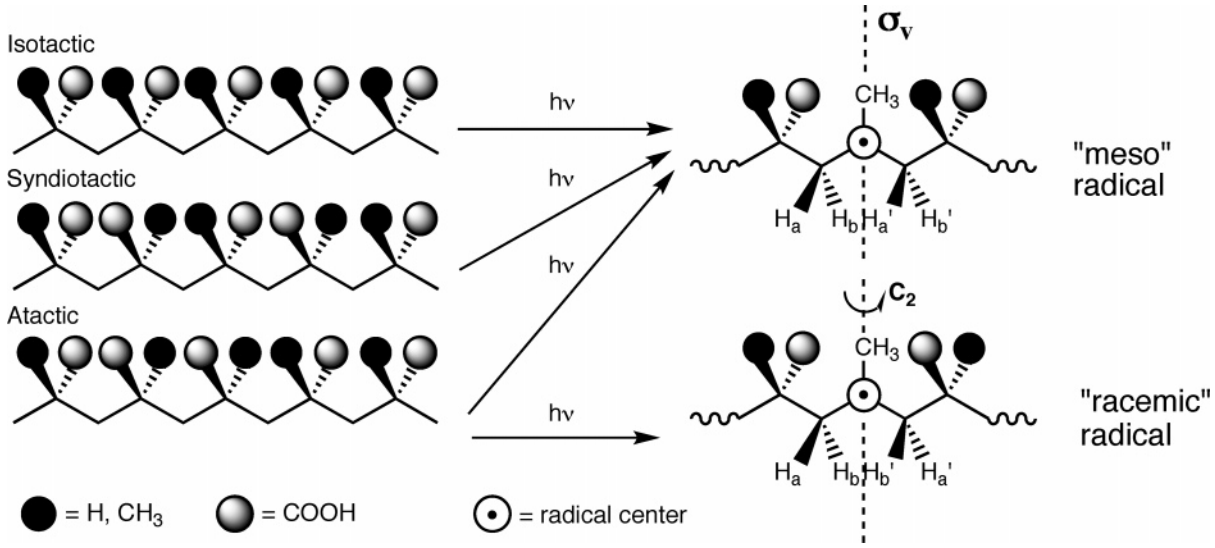


Figure 1. (A) Top: X-band TREPR spectra obtained 800 ns after 248 nm photolysis of an aqueous solution of PAA at the temperatures indicated. In this and all subsequent spectra, transitions below the baseline are emissive (indicated by E). Bottom: simulation of the spectrum acquired at 75 °C, assigned to the PAA main-chain radical. Parameters for the simulation are listed in Table 1. Asterisks in the top spectrum indicate transitions due to a different radical (see text for possible structures). (B) Expanded spectra showing the low field line of the two most intense central transitions of the PAA radical, also as a function of temperature. Note the sharpening and eventual distinction of a shoulder to the low field side of this transition in the high-temperature spectrum.

Scheme 2

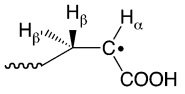
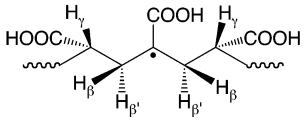
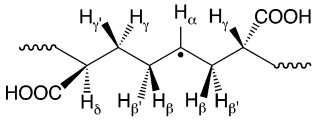
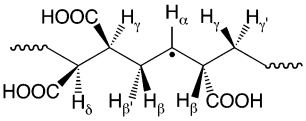
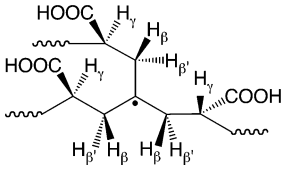


indicating that the polymer is not quite at fast motion. An expanded view of one of the most intense central lines in the spectra from Figure 1A is shown in Figure 1B for three different temperatures. From Figure 1B it is clear the lines are indeed becoming sharper with increasing temperature. In the 75 °C spectrum, a small splitting begins to be observed (it is really just a shoulder on the most intense line) that we assign to a difference in coupling constant of 0.1 G between the methylene protons on the same β-carbon atom.

The PAA radicals are easily identified as arising from direct Norrish I α-cleavage of the carboxyl group, and the chemically induced electron spin polarization[18] (CIDEP) pattern is that from the triplet mechanism (net emission), which is the same pattern observed for the acrylate analogs. The only major difference between the PAA radical spectrum here and the PEA radical spectrum from ref 1a is that we have included a small γ hyperfine coupling to better fit the PAA spectrum. This was not done for PEA earlier and so our simulation of the PEA radical in ref 1a has an anomalously large line width to compensate. Here the line width of 1.8 G is comparable to the methacrylate ester polymers studied previously.

The oxo−acyl counter radical **2** is not observed in these spectra, even at low temperatures. This is unusual: In our previous work on acrylate polymers, oxo−acyl radicals were observed at room temperature just to the high field side of the center of the polymer radical signal. Acyl radicals are known to have fast relaxation times due to spin-rotation interaction,[19] and so a lack of observation of radical **2** in our system at high temperatures is understandable. However, the absence of any signal from radical **2** at room temperature suggests that this relaxation mechanism may be much more efficient in the smaller carboxyl radical **2** than in its ester analogues from ref 1. We

Scheme 3

Radical		Source
	**3**	β–scission
	**4**	H-atom abstraction
	**5**	Tail–to–tail defect site
	**6**	Head–to–head defect site
	**7**	Branched defect site

are currently exploring methods to test this hypothesis using isotopic labeling experiments.

Another interesting feature of Figure 1 is that there is second signal carrier present, indicated by asterisks in the top spectrum. This is also a departure from the behavior of the acrylate polymers such as PEA and PMMA. In those polymers, the observed photochemistry leading to free radicals was remarkably clean in that *only* the main-chain polymeric and oxo−acyl side-chain radicals were observed at room temperature. At high temperatures, the main-chain radical was the single species observed as the side-chain oxo−acyl radical relaxes quickly in these conditions. In contrast, the TREPR signals from PAA photolysis in Figure 1 show an additional signal carrier with at least 10 lines, marked as such in the figure for the room temperature spectrum. This could be a quintet of doublets; however, the signal is rather weak, and it is not possible to tell whether there are other transitions on the perimeter that are not observed. For clarity, we will refer to this unknown radical as unknown #1.

The structure of unknown #1 and its mechanism of origin are worthy of discussion. Almost certainly it belongs to a radical with an even number of hyperfine interactions and a similar *g* factor to the main-chain radical. This is because the observed doublets are evenly spaced between the lines of radical **1** and symmetrically distributed about them. Scheme 3 lists some possible structures of unknown #1 and possible origins. It is unlikely to be the propagating radical **3** as this structure has only three hyperfine interactions, and a small doublet of ∼4 G is not expected to arise from such a structure. There is a report of a rearrangement of the radical anions of carboxylic acids and esters[20] that in the case of PAA would lead to loss of a hydrogen atom α to the carboxyl group. Such a structure is also a main-chain radical (**4** in Scheme 3), and it has an even number of hyperfine interactions. However, the splitting pattern would

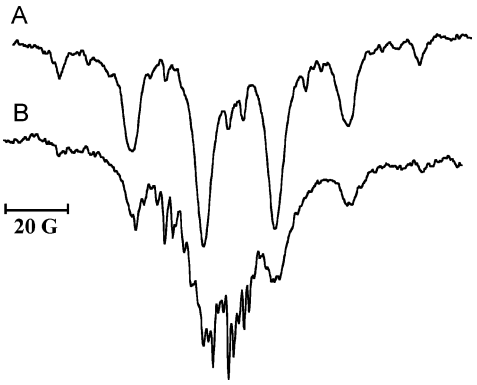


Figure 2. X-band TREPR spectra acquired 800 ns after 248 nm laser flash photolysis of PAA in aqueous solution: (A) M_w = 450 000; (B) M_w = 2000.

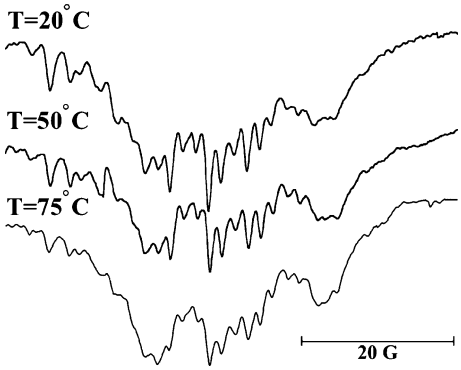


Figure 3. Central portion of Figure 2B expanded and displayed as a function of temperature. Note the large number of hyperfine lines in the center and the increase in line width of these signals with increasing temperature.

be a triplet of triplets giving a maximum of nine lines. Since we observe at least 10 lines for our unknown radical, we rule out the possibility of this rearrangement. Radicals **3** and **4** can also be eliminated as candidates by considering the fact that, as products of side reactions with appreciable activation barriers that are independent of the original polymer structure, their TREPR signals should increase in intensity with increasing temperature. This trend is clearly not observed. The ratio of the main chain signal to that from unknown #1 remains relatively constant over 50 °C.

If the synthetic method used to make our sample allowed for a significant population of either tail-to-tail or head-to-head defects, radicals **5** and **6**, respectively, could be produced by Norrish I cleavage. Radical **5** from tail-to-tail defects would show a similar hyperfine splitting pattern to the main-chain radical from nondefective sites and can be ruled out. Radical **6**, however, which arises from head-to-head defect sites, is a strong candidate for the origin of this signal because it has four hyperfine coupling constants that are all expected to be different due to stereochemical issues *and* the disruption of symmetry due to the defect. The last structure shown in Scheme 3 is radical **7,** which could arise if the photochemistry is taking place at branched sites caused by backbiting of the propagating polymer chain during the synthesis. This radical is highly substituted, has the potential to exhibit a high degree of symmetry, and cannot be ruled out as a candidate for unknown #1 at the present time.

Another interesting feature of PAA radical chemistry was observed in the molecular weight dependence study shown in Figure 2. The TREPR spectrum obtained after 248 nm photolysis of a very low molecular weight PAA sample (M_w = 2000,

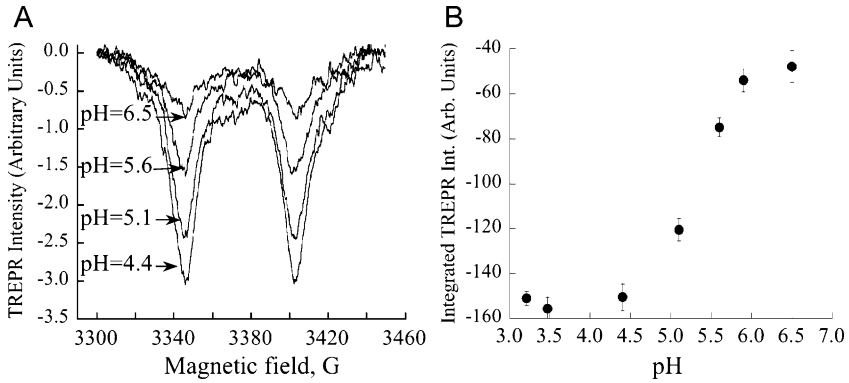


Figure 4. (A) Experimental TREPR spectra (only two centermost transitions are shown) obtained upon 248 nm photolysis at 122 °C of poly(acrylic acid) in water at the pH values indicated. (B) Integrated intensities of the two centermost transitions plotted as a function of solution pH.

Figure 2B) is shown compared to that obtained from a sample of M_w = 450 000 (Figure 2A). There is a new signal visible from a different carrier than either radical observed in Figure 1. It is of almost equal intensity to the polymer main chain radical. Some of the transitions from unknown #1 in Figure 2A (whose possible structures are delineated in Scheme 3 and surrounding text) may also be present in Figure 2B. However, there are many more hyperfine lines in Figure 2B, and we can conclude that the majority of the additional lines in the low-M_w spectrum are from a separate, distinct radical ("unknown #2") from either species observed in Figure 2A or Figure 1. This sharp, complex signal may be due to radicals from initiators that are either part of the end group of the polymer or from residual impurities.

An expansion of the central portion of the spectrum in Figure 2B is shown as a function of temperature in Figure 3. The hyperfine lines from unknown #2 are much easier to see in these spectra. There is an additional phenomenon observed in these spectra: the line widths of the transitions due to unknown #2 actually increase with temperature. This is in contrast to the main-chain radical, whose transitions become narrower with increasing temperature. The results in Figure 3 suggest two things about unknown #2: first, that it contains some very small hyperfine interactions, possibly from aromatic rings, and, second, that some of the hyperfine couplings are conformationally dependent.

The spectral resolution and overlap of the polymer radical have so far prevented a satisfactory simulation of the unknown radical in Figure 3. The polymer used in this experiment was a commercial sample and the conditions used for its synthesis are not known, and it may be difficult to make a conclusive identification without this information. This is the first reported evidence, however, for a molecular weight dependence of this photochemistry after studying more than a dozen different polymers with varying side-chain structures, main-chain structures, molecular weights, polydispersities, and solvent systems. It is also worthwhile to note that 2000 is the lowest molecular weight polymer we have examined in any of our studies of acrylic polymers. We have previously examined multiple M_w's ranging from 10^4 to 10^6, with no change in radical structure or temperature dependence at any value of M_w. It appears that very low M_w must be reached to see oligomeric, as opposed to macromolecular, behavior. In this regard, we are currently synthesizing very low M_w oligomers of PMMA ($\leq$1500) for further study.

pH Dependence. Figure 4A shows the TREPR signals from the PAA radical as a function of the pH of the solution. The spectrum of this radical completely disappears in basic solutions. This is may be due to a change in the chromophore from COOH side chains to COO^- side chains. The absorbance of the solution at 248 nm changes by only 15% across the whole range of pH values studied (2−10), but the resonance-stabilized carboxylate anions may be much less photoreactive than its conjugate acid. Figure 4B shows a plot of the integrated intensities from Figure 4A as a function of pH, showing that the most drastic changes occur at about pH = 5.5, which is close to the reported pK_a value for PAA of 4.8 reported by Mandel.[21] It is interesting to note that titration of PAA using NMR chemical shift information as a function of pH, performed by Chang et al.,[22] produces an inflection point at exactly the same pH value as we report in Figure 4B.

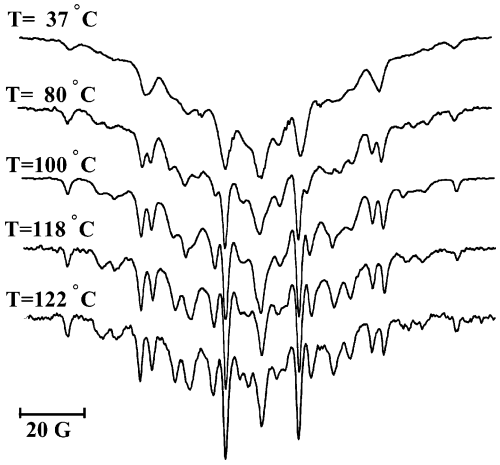


Figure 5. X-band TREPR spectra obtained 800 ns after 248 nm photolysis of an aqueous solution of PMAA at the temperatures indicated.

It is also possible that the stretched (high pH) vs coiled (low pH) polymer chains show different photophysics. This was commented on by Chou and Jellinek in their early report on PMAA photochemistry,[8] and a detailed TREPR study of pH-dependent cage effect manipulation using initiator labeled PMAA was reported by Maliakal et al.[16] It has been reported by Mittal and co-workers[6] that for small molecule analogues of PAA and PMAA the quantum yield for Norrish I cleavage drops to zero for the completely deprotonated structure. For PMAA we also observe a pH dependence in the TREPR signal intensities (data not shown). The data in Figure 4 are the first experimental evidence for such an effect in PAA radicals.

PMAA. Figure 5 shows TREPR spectra acquired during 248 nm photolysis of PMAA in aqueous solution as a function of temperature. The spectra are not well resolved at room temperature and require substantial activation to exhibit fast motion spectra. For the highest temperatures recorded in these experi-

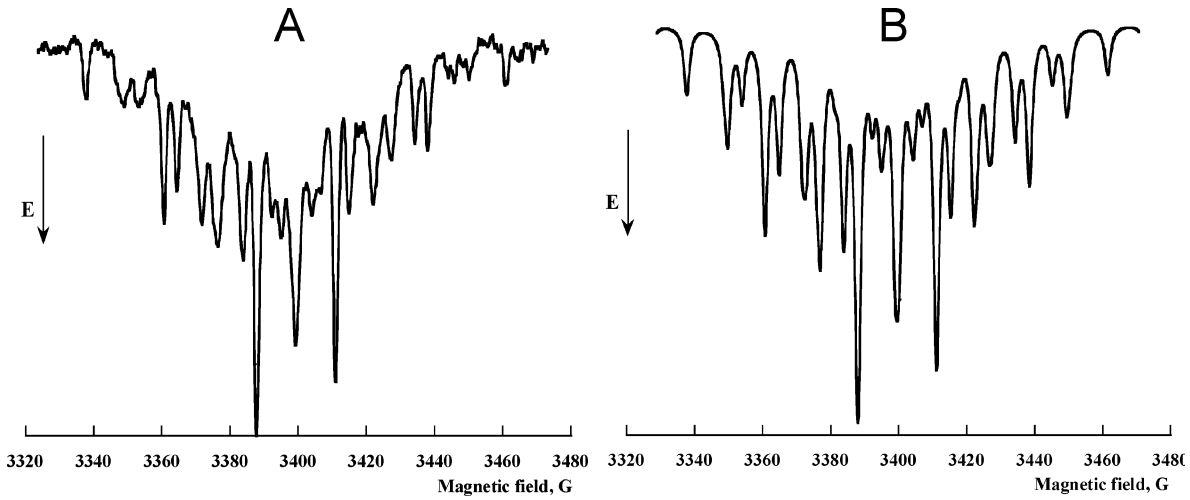
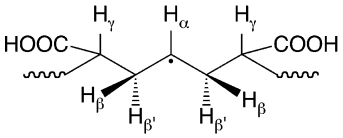


Figure 6. (A) Experimental and (B) simulated TREPR spectra of the PMAA radical at 122 °C. Parameters for the simulation are listed in Table 1.

Table 1. Radical Structures and EPR Simulation Parameters for the Bottom of Figures 1 and 6B

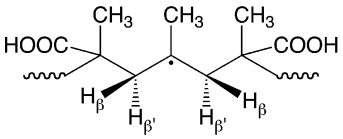


PAA Radical

H_α = 21.5 G
H_β = 23.7 G
$H_{\beta'}$ = 23.8 G
H_γ = 0.9 G

g = 2.0027

line width (FWHM) = 1.8 G



PMAA Radical

CH_3 = 23.1 G
H_β = 27.3 G
$H_{\beta'}$ = 11.0 G

g = 2.0027

line width (FWHM) = 2.1 G

ments, a small amount of ethylene glycol was added to the solutions to go over 100 °C. Also noted in our previous papers on acrylate radicals was the fact that the lower temperature spectra could not be simulated with a unique set of hyperfine coupling constants. The same is true for the PMAA radical studied here, and it is only for the highest temperature spectrum that any simulation becomes meaningful. It is notable that the observed photochemistry of PMAA is very clean, with no additional radicals present, although such radicals may be masked by the large number of transitions and by the high intensity of this signal. Similar to PAA, the oxo−acyl counter radical is not observed in TREPR spectra of PMAA at any temperature.

Figure 6B shows our best fit to the 122 °C spectrum for PMAA (Figure 6A expanded slightly on the vertical axis) using the parameters listed in Table 1. While the positions of the transitions line up quite well, it is clear that the line widths are not all equal in the experimental spectrum. In fact, it is precicely the transitions that exhibit the broadening in the alternating line width effect discussed in ref 1c that have slightly large line widths in this spectrum. We conclude that while we have confidence in the structure of the radical being created, the polymeric radical has not reached a true "fast motion" state even at the highest temperature accessible with our current apparatus. Nonetheless, each transition in the experimental spectrum does appear to be accounted for in the simulation. One striking difference between the PAA and PMAA radicals is the magnitude of the β-hyperfine interactions (Table 1). For PAA these coupling constants are almost identical, whereas for PMAA they differ by more than a factor of 2. This is a much larger difference in coupling constant than observed in PMMA and clearly reflects the asymmetry imposed on the radical conformations by the neighboring stereogenic centers. This effect may also be amplified by solvent effects and by the repulsion of charges on the carboxylate anions along the backbone.

A suitable model for the temperature dependence of the TREPR spectra in these macromolecular free radicals remains elusive. This almost certainly due to the large number of conformations accessible to the polymer chain near the radical site, and finding these minima on a polymer potential energy surface by computation from first principles is a formidable exercise. We have therefore looked for model systems with simpler conformational dynamics to guide us in this endeavor. Radicals created from model systems based on the Kemp's triacid framework look promising in this regard and will be the subject of a future publication.

We have attempted to create radicals from deprotonated PAA and PMAA by photooxidation of the carboxylate anion side chains using water-soluble quinone triplet states such as anthraquinone disulfonate (AQDS). While direct photolysis followed by α-cleavage of the neutral protonated carboxyl group is facile, all attempts to photooxidize the anionic structures failed. We can suggest several reasons for the lack of reactivity of the charged polymers. One possibility is that the oxidation potential of the carboxylate group is higher in the polymeric structure compared to the model system, although it is somewhat surprising that it would change so drastically from the model system. It is also possible that the coiled conformation of the polymeric acid in solution prevents access to the carboxylate groups, either by the polymer protecting itself or by the quinone being shielded due to a hydrophobic effect. This is also somewhat unlikely since the polymer should be uncoiled at high pH values, although clearly the model compound has no such coiling mechanism available to it and aggregation is unlikely for well solvated trianions. A third and most likely possibility is that the oxidation reaction has a higher activation energy in the polymer to due a tighter solvent shell around all of the carboxylate groups. Solvent reorganization may well be cooperative in this regard, and therefore much more difficult to reach a less well solvated transition state that is losing its charged character to a neutral radical structure. Confirmation of this point is outside the scope of the present paper but the issue is worthy

of further investigation.

Summary

The poly(acrylic acid)s show interesting and facile solution photochemistry, and the ensuing main-chain radicals, whose structural parameters have not been reported in the literature before, show very similar dynamic effects in their TREPR spectra as a function of temperature compared to the previously studied acrylates. The observed photochemical degradation mechanism is quite different from that observed in thermal degradation studies of PAA using solid-state NMR, where anhydride formation and even phenolic structures could be observed at some temperatures.[23] Interesting differences in the polyacid radical chemistry include the pH-dependent photophysics, the molecular weight dependence and associated possible end-group participation in the photochemistry, the appearance of another unknown radical with an even number of hyperfine coupling constants, and the absence of any signal from the side-chain counter radicals at any temperature. All of these effects are under further investigation, with particular attention being paid to the coiled vs stretched polymer conformations expected as a function of pH. The lack of any apparent photodegradation above pH values of 6 is perhaps underappreciated as a "photoprotective" mechanism for the poly(acrylic acid)s; this might be exploited for controlled environmental degradation in copolymers with such structures.

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