Stereochemistry and Pseudosymmetries in Main Chain Polymeric Free Radicals

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Abstract: Main chain free radicals produced from 248 nm photolysis of poly(alkyl acrylate)s and poly(alkyl methacrylate)s have been unambiguously characterized for the first time by time-resolved electron paramagnetic resonance (TREPR) spectroscopy. Side chain cleavage via the Norrish I process dominates, leading to an oxo-acyl radical from the ester side chain and a main chain polymeric radical, the existence of which has been previously postulated but never confirmed by direct spectroscopic observation. There is a strong stereochemical influence on the methacrylate spectra, which manifests itself through changes in the TREPR spectra as a function of polymer tacticity and temperature. There is also a strong solvent dependence. Computer simulation provides unambiguous assignment of the signal carriers for the acrylate polymers at room temperature and above, and for PMMA main chain radicals at high temperature, where the fast motion limit for the β-methylene hyperfine coupling constants is achieved. The methacrylate spectra give remarkably similar coupling constants for all tacticities at high temperature, a phenomenon explained by an unexpected (and fortuitous) pseudosymmetry relationship between the diastereotopic protons in the radicals.

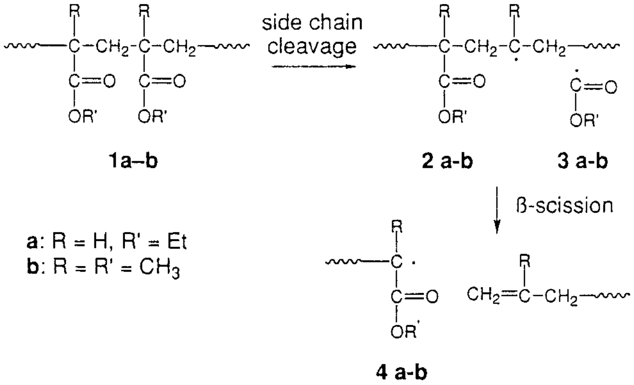
Introduction

The primary photochemical processes occurring during the photodegradation of poly(alkyl acrylate)s and poly(alkyl methacrylate)s have been a subject of interest for researchers in the fields of photochemistry and polymer photodegradation for more than 40 years.[1,2] There is definite agreement that free radical intermediates are involved in the photodestruction of these industrially important polymers. Despite some contrary interpretations[3] there is general consensus that Norrish I α-cleavage of the ester side chain is the first step in the mechanism. This process is illustrated in Scheme 1 for both acrylate (R = H) and methacrylate (R = CH_3) polymers. If indeed side chain cleavage is the first step, a main chain radical (**2**) as shown in Scheme 1 should be observed. However, this radical has a unimolecular decomposition reaction available to it, namely β-scission,[4] to give an alkene and the so-called propagating radical (**4**).[5,6] This reaction is analagous to the reverse of the free radical polymerization reaction, i.e., radical addition to the alkene monomer.[7]

Because of the rapid β-scission reaction, steady-state electron paramagnetic resonance (SSEPR) investigations carried out since 1951 on acrylate and methacrylate degradation, especially poly(methyl methacrylate) (PMMA), have been unable to confirm the chemistry shown in Scheme 1 as the first step. In fact, main chain polymeric radicals **2a** and **2b** have never been conclusively observed by any experimental technique. In 1982 Liang et al. suggested the existence of a main chain acrylate radical in a cold SSEPR experiment,[8] but their spectrum contained many overlapping lines from other radicals, so a definitive conclusion regarding its structure could not be reached. There is no evidence in the scientific literature for the EPR spectrum of main chain PMMA radical **2b**. In this paper we report the results of time-resolved electron paramagnetic resonance (TREPR) experiments that provide unambiguous spectral assignment of both radicals **2a** and **2b** for the first time, supporting the mechanism shown in Scheme 1. In addition, our results show novel features beyond the original mechanistic problem, in particular regarding the magnetic resonance properties of and symmetry relationships in these polymeric free radicals.

The advantages of TREPR spectroscopy[9] are its fast time response (60 ns vs ~10 μs for SSEPR), its high degree of

Scheme 1



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[1] Rånby, B.; Rabek, J. F. *Photodegradation, Photo-oxidation and Photostabilization of Polymers*; Wiley: London, 1975.

[2] Rånby, B.; Rabek, J. F. *ESR Spectroscopy in Polymer Research*; Springer-Verlag: Berlin, 1977.

[3] Bullock, A. T.; Sutcliffe, L. H. *Trans. Faraday Soc.* **1964**, *60*, 625.

[4] Moreau, W.; Viswanathan, N. Applications of Radiation Sensitive Polymer Systems. In *UV Light Induced Reactions in Polymers*; Gould, R. F., Ed.; ACS Symp. Ser.; American Chemical Society: Washington, DC, 1976; p 125.

[5] Fischer, H. *Polym. Lett.* **1964**, *2*, 529.

[6] Sakai, Y.; Iwasaki, M. *J. Polym. Sci. Part A-1* **1969**, *7*, 1749.

[7] Odian, G. *Principles of Polymerization*; John Wiley & Sons: New York, 1991; p 198.

[8] Liang, R. H.; Tsay, F.-D.; Gupta, A. *Macromolecules* **1982**, *15*, 974.

[9] Forbes, M. D. E. *Photochem. Photobiol.* **1997**, *65*, 73.

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structural resolution, and the possible observation of chemically induced electron spin polarization (CIDEP),[10] which allows spin information to be obtained regarding the photochemical precursors. We have previously used TREPR to study the photodegradation of alternating alkyl-CO copolymers,[11,12] and this technique has also been used by other researchers to investigate the first step of the methacrylate polymerization process.[13] The present study is the first application of TREPR to the photodegradation of these commercially important polymers, and is also the first report on solution aliphatic monoester photolysis using any time-resolved spectroscopic technique.[14]

Experimental Section

Continuous wave TREPR experiments were performed as previously described.[9] Briefly, all experiments were performed on a JEOL USA Inc. JES-RE1X X-band EPR spectrometer equipped with a fast preamplifier. Solutions of polymer (2.5 g) in solvent (60 mL) were circulated through a flat cell (0.75 or 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 an energy of 85 mJ (~15 mJ per pulse hitting the sample) and a pulse width of 17 ns. Spectra were collected in the absence of field modulation at a fixed delay time after the laser flash using a boxcar integrator (100 ns gates), while the external magnetic field was swept over 2 to 4 min.

For high-temperature TREPR experiments, the deoxygenated sample solution was circulated using a micropump (Micropump model 000-405) through Teflon PFA 1/8 in. tubing which was 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. The TEFLON joints connecting the tubing to the pump and flat cell were also insulated with polyurethane foam tape. Reported temperatures are averages of the two measurements at the top and bottom of the cell, and the maximum temperature gradient during the high temperature (140 °C) experiment was 10 °C.

Samples of poly(ethyl acrylate) and poly(*n*-butyl methacrylate) were gifts from the Rohm and Haas Company and were used as received. All solvents (Mallinckrodt), propylene carbonate (Aldrich), and atactic poly(methyl methacrylate) (Aldrich) were also used as received. Highly isotactic PMMA was synthesized via a living anionic polymerization according to the method of Zundel and co-workers.[15] Highly syndiotactic PMMA was synthesized using the method of Kitayama and co-workers.[16] Tacticities for all PMMA samples were calculated from the main chain methyl triad peaks in their ^{1}H NMR spectra ($CDCl_3$). Atactic: 6% mm, 36% mr, 58% rr. Isotactic: 91% mm, 7% mr, 2% rr. Syndiotactic: 2% mm, 12% mr, 86% rr. Values for the number-averaged (M_N) and weight-averaged (M_W) molecular weights and the polydispersity index (PDI) for each PMMA sample were determined by gel permeation chromatography. Atactic: $M_N = 5.2 \times 10^4$, $M_W = 8.0 \times 10^4$, PDI = 1.5. Isotactic: $M_N = 1.3 \times 10^5$, $M_W = 1.5 \times 10^5$, PDI = 1.2. Syndiotactic: $M_N = 7.3 \times 10^3$, $M_W = 8.$ x 10^3, PDI = 1.2.

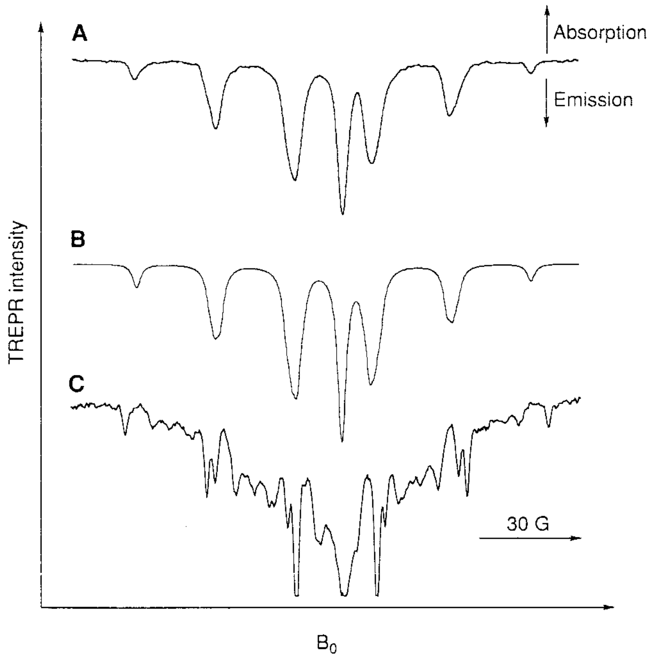

Figure 1. (A) Experimental TREPR spectrum of poly(ethyl acrylate) in methylene chloride at 0.2 μs delay time. (B) Simulation of the spectrum in A using $a_H = 22.5$ G, $a_{CH_2} = 23.8$ G, and $g = 2.0026$. (C) Experimental TREPR spectrum of poly(methyl methacrylate) in chloroform at 0.8 μs delay time. The magnetic field sweep width for all spectra is 150 G. The TREPR intensity (arbitrary units) and magnetic field (B_0, G) axes shown here are the same for all spectra and are omitted in the remaining figures. In this and all subsequent spectra, lines below the baseline are in emission while those above the baseline are in enhanced absorption.

Results and Discussion

An X-band (9.5 GHz) TREPR spectrum obtained after photolysis of poly(ethyl acrylate) (**1a**) in methylene chloride solution is shown in Figure 1A, along with a simulation in Figure 1B using hyperfine couplings and *g*-factors for the two radicals resulting from the side chain cleavage process. A six-line spectrum is present due to the main chain polymer radical (**2a**) which has, based on these simulations, two β-methylene hyperfine couplings of 23.0 G, another two β-couplings of 24.7 G, and one α-hyperfine coupling of 21.5 G. These values are comparable to those reported in the literature for radicals of similar chemical structure.[17−20] The five nearly equivalent coupling constants lead, via the $n + 1$ rule, to a six-line spectrum, with evenly spaced transitions in a 1:5:10:10:5:1 ratio. The oxo-acyl radical (**3a**), which is the other expected radical from this reaction, has no hyperfine interaction and therefore shows a singlet, but it appears at a field position slightly above the center field due to its lower *g*-factor (2.0011 vs 2.0026 for **2a**).[21] This spectrum and simulation provide the first direct spectroscopic evidence that side chain cleavage is indeed the primary photodegradation event for acrylates upon direct UV excitation in solution.

Figure 1C shows the TREPR spectrum obtained 0.8 μs after 248 nm irradiation of poly(methyl methacrylate) in chloroform.

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[10] Salikhov, K. M.; Molin, Y. N.; Sagdeev, R. Z.; Buchachenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Elsevier: Amsterdam, 1984.

[11] Forbes, M. D. E.; Barborak, J. C.; Dukes, K. E.; Ruberu, S. R. *Macromolecules* **1994**, *27*, 1020.

[12] Forbes, M. D. E.; Ruberu, S. R.; Nachtigallova, D.; Jordan, K. D.; Barborak, J. C. *J. Am. Chem. Soc.* **1995**, *117*, 3946.

[13] Karatekin, E.; O'Shaughnessy, B.; Turro, N. J. *Macromolecules* **1998**, *31*, 7992.

[14] Degradation of methacrylate copolymers with much more photochemically reactive poly(ketone) blocks have been reported: Kilp, T. G., Guillet, J. E.; Galin, J. C.; Roussel, R. *Macromolecules* **1982**, *15*, 980.

[15] Zundel, T.; Teyssié, P.; Jérôme, R. *Macromolecules* **1998**, *31*, 2433.

[16] Kitayama, T.; Shinozaki, T.; Sakamoto, T.; Yamamoto, M.; Hatada, K. *Makromol. Chem. Suppl.* **1989**, *15*, 167.

[17] Paul, H.; Fischer, H. *Helv. Chim. Acta* **1973**, *56*, 1575.

[18] Gilbert, B. C.; Holmes, R. G. G.; Laue, H. A. H.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1047.

[19] Bascetta, E.; Gunstone, F. D.; Walton, J. C. *J. Chem. Soc., Perkin Trans. 2* **1984**, 401.

[20] Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1968**, *90*, 7155.

[21] Smith, P.; Kaba, R. A.; Dominguez, L. M. *J. Phys. Chem.* **1977**, *81*, 162.

This spectrum is markedly more complex than the one above it obtained from photolysis of the acrylates, which is somewhat surprising since the major difference in the polymeric radicals, in terms of magnetic interactions, is two additional hyperfine couplings. The counter radical, also an oxo-acyl structure (**3b**, Scheme 1), is again observed in this spectrum, suggesting that the same photochemistry, ester side chain cleavage, is also taking place during photolysis of this polymer. All of the spectra shown in Figure 1 are independent of molecular weight from 10^3 to 10^6. From the complexity of the hyperfine splitting patterns in Figure 1C, it is clear that the equivalence or near equivalence of the β-hyperfine coupling constants with each other is no longer present in main chain PMMA radicals. In fact, we cannot simulate the polymer radical in Figure 1C with any standard set of magnetic parameters. Additional experiments, which will be described in detail below, were necessary to properly understand the line widths and intensities in this spectrum.

There are several other noteworthy features of the spectra in Figure 1. The first is that they represent examples of photolabile aliphatic monoesters. Apart from some reports of arc lamp photolyses in the 1950s[22,23] there has been a very limited amount of research on the photochemistry of simple aliphatic monoesters.[24−26] In the most recent papers on this topic it was noted that the familiar Norrish I cleavage and subsequent decarbonylation, recombination, and disproportionation reactions associated with triplet state photochemistry do occur, although with rather low quantum yields. In addition, one of these early papers suggested that the first excited singlet state of ester or carboxylic acid chromophores makes a significant contribution to the photochemistry.[26] This leads us to a second feature of interest to us in Figure 1, which is the strong net emissive polarization. This is due to the triplet mechanism (TM) of CIDEP.[27−29] From this we conclude that the radical-producing reaction here is predominantly from the triplet state and quite efficient, given the rather weak absorbance ($A = 0.1$ for our solutions) at 248 nm.[30]

A third feature of these spectra is most pronounced in Figure 1C, which is the presence of alternating line widths across the spectrum. This is a classic indicator of hyperfine coupling constant modulation,[31] and is in fact a clue as to why this spectrum cannot be simulated without a more sophisticated model for the hyperfine couplings. Several groups of researchers have shown that the methacrylate propagating radical (**4b**) exhibits a similar alternating line width effect,[5,6] and conformationally dependent hyperfine couplings have also been found in SSEPR experiments on small model compounds for the propagating radical.[32] In the spectra reported here the modulation effect is almost certainly due to restricted conformational motion in the more heavily substituted methacrylate polymer chain. This conformational motion alters the hyperfine interaction because the mechanism of the interaction is via hyperconjugation, leading to a dependence on the dihedral angle between the half-filled p orbital of the radical and the C−H σ bond adjacent to it.[33]

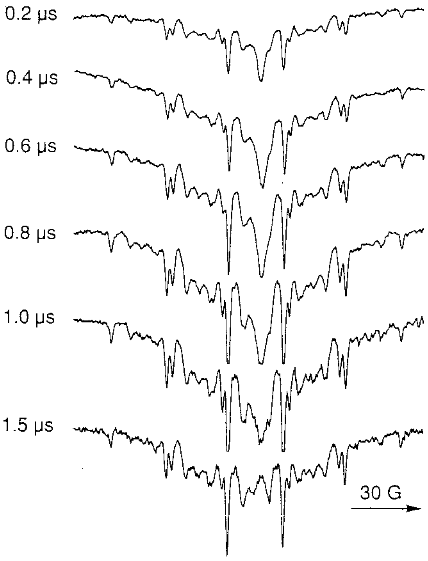

Figure 2. Time dependence of poly(methyl methacrylate) in chloroform at room temperature. Delay times are shown to the left of the spectra. The magnetic field sweep width is 150 G.

Figure 2 shows the time dependence of the spectrum from Figure 1C. The TREPR signal for each radical (**2b** and **3b**) decays over about 1 μs, and this is mostly due to spin−lattice relaxation. The triplet mechanism spin polarization is decaying and eventually the electron spin state populations will reach their Boltzmann equilibrium values. From this otherwise unremarkable time dependence we can conclude that (1) decarboxylation of the oxo-acyl radical **3b** is not taking place to any large extent, in keeping with known rates for this process from the literature,[34] and (2) the β-scission reaction shown in Scheme 1 is also not taking place on the time scale of our experiment. This is the case because the splitting patterns known to be associated with the propagating radical do not simulate this spectrum. The fact that no major changes are observed in the time dependence is a good indication that only two free radicals are observed over the time scale of our experiment, and therefore we do not need to be concerned about chemical rearrangements or secondary photochemistry in our analysis of the spectra.

Figure 3 shows TREPR spectra taken in chloroform during laser flash photolysis for three different samples of poly(methyl methacrylate) (**1b**). These samples differ in the tacticity, i.e., the stereoregularity of the polymer chain. The stereochemical relationship of the repeat units is random in Figure 3A, syndiotactic in Figure 3B, and isotactic in Figure 3C. The spectra in Figure 3 are very similar in terms of the numbers of transitions, the spectral widths, and the general appearance of the alternating line width effect. However, closer examination reveals subtle differences in line positions and intensities. Spectroscopic and other studies have shown methacrylate chain dynamics[35−37] and degradation[38] to be strong functions of

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[22] Ausloos, P. *Can. J. Chem.* **1958**, *36*, 383.

[23] Ausloos, P. *J. Am. Chem. Soc.* **1958**, *80*, 1310.

[24] Wymann, L.; Kaiser, T.; Paul, H.; Fischer, H. *Helv. Chim. Acta* **1981**, *64*, 1739.

[25] Kaiser, T.; Grossi, L.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 223.

[26] Kaiser, T.; Fischer, H. *Helv. Chim. Acta* **1979**, *62*, 1475.

[27] Our TREPR experiment operates in direct detection and relies on the non-Boltzmann populations for adequate signal-to-noise ratios. Because of the polarization we do not know the exact concentration of free radicals in our sample after each laser flash. However, the signal intensities observed here are in line with those measured previously in samples with similar absorbances known to produce radical concentrations on the order of 10^{-4} M.

[28] Atkins, P. W.; Evans, G. T. *Mol. Phys.* **1974**, *27*, 1633.

[29] Wong, S. K.; Hutchinson, D. A.; Wan, J. K. S. *J. Chem. Phys.* **1973**, *58*, 985.

[30] The phase of this polarization depends on the symmetry of the photoexcited triplet state energy levels, and this is a subject for future study.

[31] Weil, J. A.; Bolton, J. R.; Wertz, J. E. *Electron Paramagnetic Resonance: Elementary Theory and Practical Applications*; John Wiley & Sons: New York, 1994.

[32] Matsumoto, A.; Giese, B. *Macromolecules* **1996**, *29*, 3758.

[33] Kochi, J. *Adv. Free Radical Chem.* **1975**, *5*, 189.

[34] Griller, D.; Roberts, B. P. *J. Chem. Soc., Chem. Commun.* **1972**, 747.

[35] Spevacek, J.; Schneider, B. *Polymer* **1978**, *19*, 63.

[36] Inoue, Y.; Konno, T. *Makromol. Chem.* **1978**, *179*, 1311.

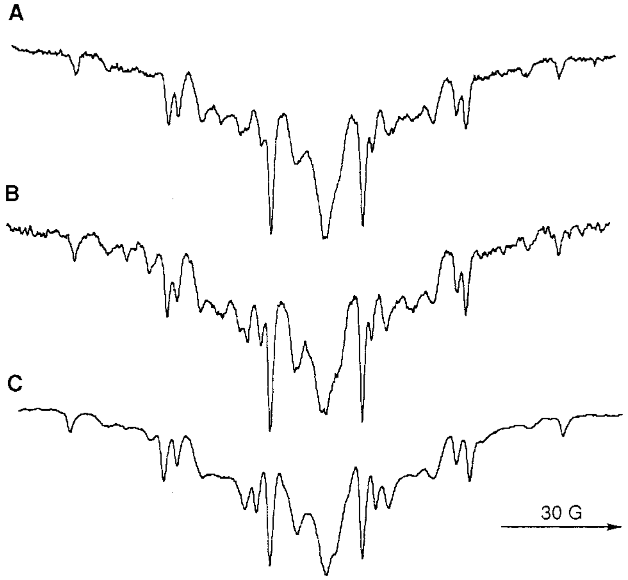


Figure 3. Tacticity dependence of poly(methyl methacrylate) TREPR spectra in chloroform at 0.6 μs. (A) Atactic PMMA: 6% mm, 36% mr, 58% rr triads. (B) Highly syndiotactic PMMA: 2% mm, 12% mr, 86% rr triads. (C) Highly isotactic PMMA: 91% mm, 7% mr, 2% rr triads. The magnetic field sweep width for all spectra is 150 G.

polymer tacticity, and we believe that the three spectra shown in Figure 3 represent a most striking example of the manifestation of such a stereochemical influence on local macromolecular chain dynamics. The spectral differences observed between the room temperature spectra in Figure 3 can be attributed to faster chain dynamics in the isotactic case (Figure 3C) relative to the slower atactic (Figure 3A) and syndiotactic (Figure 3B) polymers.[35,36]

Further support for a stereochemical influence on the TREPR spectra of these polymeric radicals comes from the fact that they are also highly temperature and solvent dependent. For example, Figure 4 shows TREPR spectra acquired during PnBMA photodegradation[39] in a variety of different solvents for the same tacticity and temperature. The spectra certainly are different in each solvent, and it should be noted that although photolysis experiments at 248 nm caused concern for solvent photochemistry or participation in the production of free radicals, scans obtained during photolysis of bulk solvent showed no TREPR signals for any of the solvents used here. Previous spectroscopic investigations of relaxation behavior in methacrylates have shown that solvent can influence local chain dynamics. For example, Horinaka and co-workers have used fluorescence depolarization data to conclude that local chain dynamics for PMMA are slower in poor solvents and faster in good solvents.[40] It is highly likely that the magnitude of such effects will differ for different tacticities. In the work presented here, it was not possible to correlate the appearance of the TREPR spectra with a single solvent parameter such as the solubility parameter, viscosity, or dielectric constant. However, the solvent dependence of the spectra clearly implies that macromolecular dynamics contribute to the observed spectral appearance.

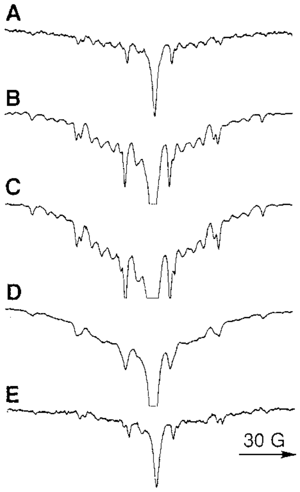
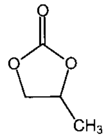


Figure 4. Solvent dependence of poly(*n*-butyl methacrylate) TREPR spectra at 0.8 μs: (A) chloroform, (B) methylene chloride, (C) dioxane, (D) cyclohexane, and (E) diethyl ether. The magnetic field sweep width for all spectra is 150 G. All spectra reflect the same sample concentration and spectrometer settings. The central peaks in spectra B−D were allowed to go off-scale to facilitate comparison of spectral patterns and intensities.

When alternating line widths are observed, it can be concluded that the nuclear spin system exists in a state between its fast and slow motion limits. At the limit of slow chain dynamics, a superposition of coupling constants from all possible conformations, weighted by their relative energies, should be observed. It is not possible to state a priori whether the slow motion spectrum will be sharp or broad; this depends on the number of available conformations and their individual spectral patterns. At the limit of fast chain dynamics, a sharp spectrum representing an average of the hyperfine coupling constants over all conformations should be observed. To successfully model the spectra shown in Figures 1−4, one would ideally like to simulate the TREPR spectra at both motional limits, and then develop a kinetic model using modified Bloch equations to simulate the transition. Therefore, a detailed temperature dependence of the TREPR spectra obtained from the photolysis of PMMA is highly desirable.

It is important to note that our photochemistry is destructive, therefore it is essential to flow or recirculate the samples. This also prevents excessive heating of the samples by the laser flashes. To obtain high-temperature TREPR spectra of radicals **2a** and **2b**, a special flow apparatus has been constructed in our laboratory, which is described in detail in the Experimental Section of this paper. This apparatus provides stable flow of liquids through the EPR resonator at temperatures up to 150 °C. The choice of solvent is critical for the success of this experiment. It must (1) dissolve the polymer up to our specified concentration, (2) have a high enough boiling point that it can withstand our reservoir temperature without evaporating or decomposing, and (3) be transparent at 248 nm. To date, we have found only one solvent, propylene carbonate, **5**, shown below, which fits all of these criteria. It is an excellent solvent for PMMA at room temperature and above, boils at 240 °C,



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(37) Ono, K.; Sasaki, T.; Yamamoto, M.; Yamasaki, Y.; Ute, K.; Hatada, K. *Macromolecules* **1995**, *28*, 5012.

(38) Moore, J. A.; Choi, J. O. Degradation of Poly(methyl methacrylate). In *Radiation Effects on Polymers*; Clough, R. L., Shalaby, S. W., Eds.; American Chemical Society: Washington, DC, 1991; p 156.

(39) A very limited number of suitable TREPR solvents were found to dissolve PMMA. The poly(*n*-butyl methacrylate) spectra are presented here because more solvents were available.

(40) Horinaka, J.; Ono, K.; Yamamoto, M. *Polym. J.* **1995**, *27*, 429.

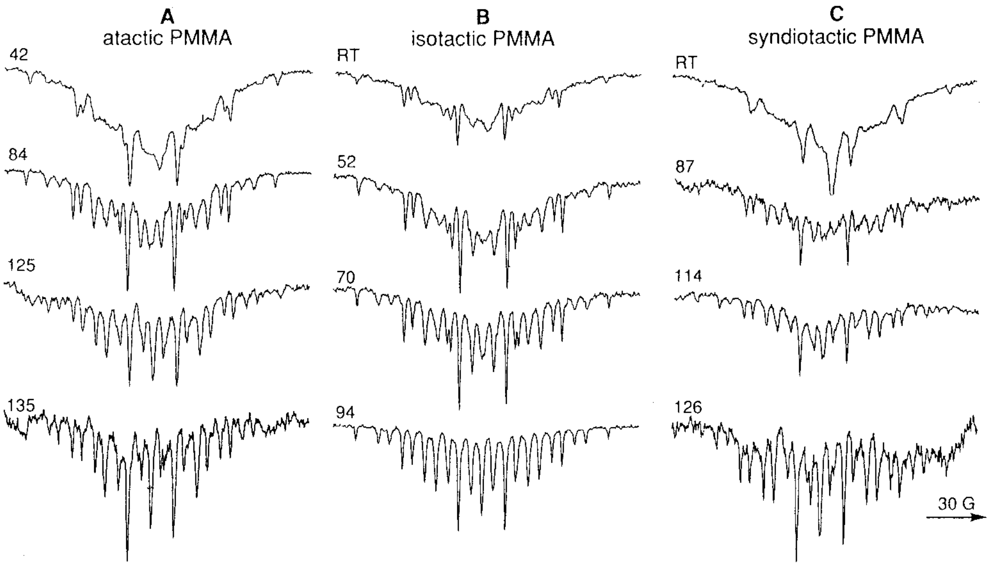


Figure 5. (A) Atactic, (B) isotactic, and (C) syndiotactic PMMA in propylene carbonate at 0.8 μs delay time. The temperature for each spectrum is shown (in °C), and the magnetic field sweep width is 150 G for all spectra.

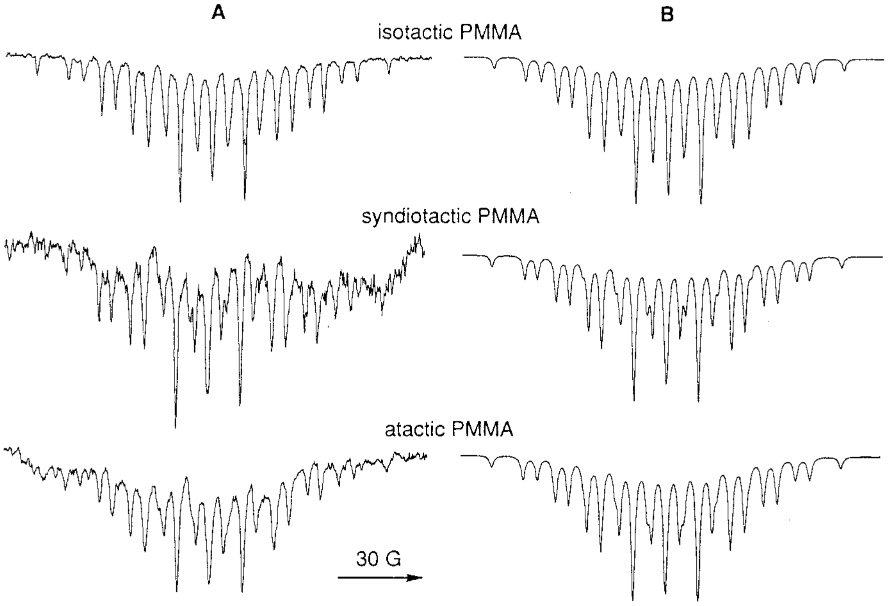


Figure 6. (A) Experimental and (B) simulated high-temperature (fast motion) PMMA TREPR spectra. The hyperfine values for the simulations are shown on the figure. The magnetic field sweep width for all spectra is 150 G. Hyperfine values for each simulation are the following: 3 $a_H(CH_3) = 22.9$ G, 2 $a_H(CH_2) = 16.4$ G, 2 $a_H(CH_2) = 11.7$ G for isotactic PMMA; 3 $a_H(CH_3) = 22.9$ G, 2 $a_H(CH_2) = 16.2$ G, 2 $a_H(CH_2) = 11.7$ G for syndiotactic PMMA; and 3 $a_H(CH_3) = 23.0$ G, 2 $a_H(CH_2) = 16.4$ G, 2 $a_H(CH_2) = 11.3$ G for atactic PMMA.

and shows no TREPR signal when run as a blank under 248 nm irradiation.

Figure 5 shows the temperature dependence of the TREPR spectra obtained upon photodegradation of all three tacticities of PMMA in propylene carbonate. Clearly, a large transformation takes place in these spectra upon heating. All three samples eventually reveal motionally narrowed spectra, simple in appearance and with very sharp line widths (<1 G). Even more remarkable is that at the highest temperature recorded for each sample, all three spectra are quite similar in appearance. It is interesting to note that convergence to the motionally narrowed spectrum takes place at a different temperature for each tacticity. Computer simulations of the fully converged, high temperature limit spectra are shown side by side with the experimental data in Figure 6. The hyperfine coupling constants used for each simulation are listed in the figure caption and are in fact nearly identical. It is of particular interest to note the near identical parameters for atactic and syndiotactic material (vide infra). In summary, all three tacticities eventually give radicals showing the following splitting pattern: a quartet from interaction of the electron with the methyl protons, each line of which is split into a triplet of triplets by interaction with the methylene protons.

At this point it is instructive to recall the experimental spectrum and simulation shown in Figure 1, spectra A and B, respectively, obtained from photolysis of an acrylate polymer. From this simulation it is clear that the line width is quite broad, which hints at the possibility that a small inequivalence of the β-hyperfine coupling constants is present and contributing to the line width, and in fact that is how the spectrum was simulated. Figure 7 shows the high-temperature spectrum for poly(ethyl acrylate) in propylene carbonate. With the narrower line width a small splitting is now observable; this is most likely to be due to the difference between the α and β coupling constants. The β-hyperfine interactions in the acrylates appear

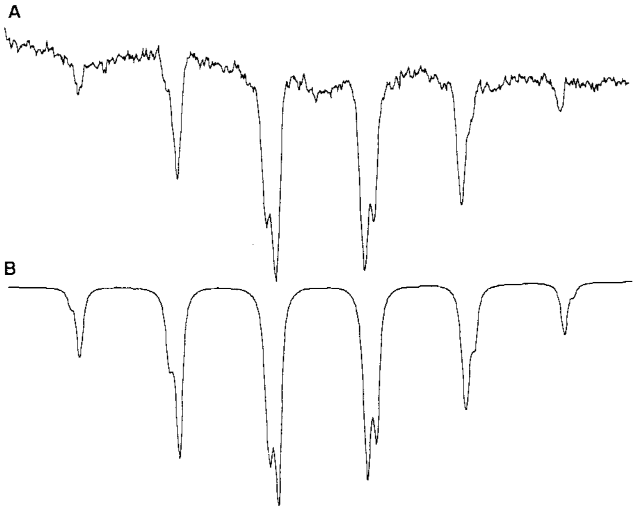
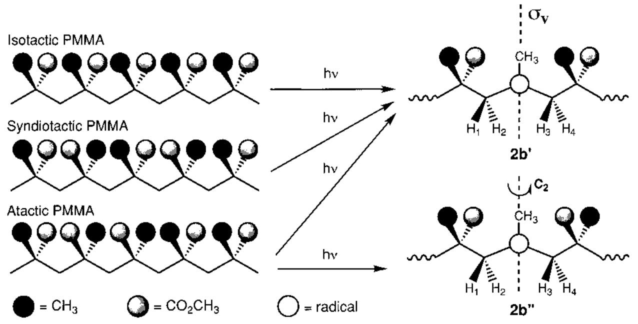


Figure 7. (A) Experimental and (B) simulated TREPR spectra for poly(ethyl acrylate) in propylene carbonate at high temperature (123 °C). Simulation parameters: $a_{\mathrm{H}}(\alpha) = 21.5$ G, 2 $a_{\mathrm{CH_2}}(\beta) = 23.5$ G, and $a_{\mathrm{CH_2}}(\beta) = 24.2$ G. The magnetic field sweep width for both spectra is 150 G.

Scheme 2



to be very similar at all temperatures, and the fast motion limit appears to be accessed at lower temperatures. This may be due to that fact that there is more conformational flexibility in this polymer. For PMMA our simulations reveal that at high temperatures two of the methylene proton coupling constants merge, as do the remaining two (but to a different value), and that all four methylene proton coupling constants differ significantly from the methyl hyperfine value at fast motion. From this large difference between PMMA and poly(ethyl acrylate), and also from the strong tacticity dependence of the PMMA spectra, we know that the final task in analyzing the high-temperature TREPR spectra of PMMA is to (1) firmly establish the connection between the stereochemical configuration closest to the radical center and any resulting proton symmetry relationships in the free radicals and (2) examine how the nature of these two parameters subsequently dictates the magnetic equivalence or inequivalence of the four β-protons.

To understand how symmetry plays a role in establishing the appearance of the fast motion methacrylate spectra, consider the structures in Scheme 2. Here the photochemistry leading to main chain PMMA radicals is again shown, but with particular attention paid to the stereochemical arrangement at the γ-carbons relative to the radical center. A hollow circle in this scheme indicates the central carbon of the radical itself, and the methyl and ester side chains are denoted by black and gray circles, respectively. By drawing the radical this way (structure **2b′**, Scheme 2) it can be seen that there exists in it a pseudomirror plane of symmetry. This mirror plane bisects the radical center and the methyl group directly attached to it. It is a pseudosymmetry element because we do not know exactly where on the polymer chain we have created the radical center. It becomes a true symmetry element for polymeric radicals only under very special circumstances: odd numbered chains with identical end groups, where the radical is created in the exact center of the polymer chain. It is unlikely that this situation arises very often, so we will retain the use of the term “pseudosymmetry” element throughout the remainder of this work.

The important pseudosymmetry elements in the radical are a direct function of polymer tacticity. The left-hand side of Scheme 2 helps to explain why. Purely isotactic (mm triads) PMMA and purely syndiotactic (rr triads) PMMA, after homolytic cleavage of one ester group anywhere in the chain, are *required* to become radical **2b′**. Photolysis of atactic material, on the other hand, may result in **2b′** only if the radical center is created from the middle of a syndiotactic (rr) or isotactic (mm) triad of repeat units. If the radical center arises from a different triad structure, the resulting polymeric radical no longer contains a pseudomirror plane, but instead has a pseudo-C_2 rotational axis of symmetry (structure **2b″**, Scheme 2).

An immediate and important consequence of retaining a pseudosymmetry element in the radicals is that magnetic equivalence is established between certain β-protons. More specifically, using the labels in Scheme 2 we see that for the mirror plane radical **2b′**, H_1 and H_3 become equivalent, as do H_2 and H_4. This leads to the conclusion that at fast motion, both isotactic and syndiotactic PMMA should exhibit TREPR spectra with three different electron−nuclear hyperfine coupling constants. First there is a quartet of lines from interaction with the protons on the methyl group, which we assume is always free to rotate at the temperatures observed. Each line of this quartet is further split into a triplet of triplets due to interaction with two sets of equivalent β-methylene protons. This splitting pattern is exactly what is observed experimentally, and confirmed by spectral simulation in Figure 6. Although theory predicts 36 lines in the spectrum, fewer are observed because of some accidental degeneracies arising from the fact that one of the coupling constants is (coincidentally) approximately half the value of another.

The fast motion spectrum of the atactic PMMA sample is expected to be somewhat more complicated because two radicals with different pseudosymmetry elements are possible. However, one of these radicals is identical to that discussed above for isotactic and syndiotactic material (the “pseudomirror plane” radical **2b′**) and whose spectrum is understood. The second possibility is the “pseudo-C_2 axis” radical **2b″**. The TREPR spectrum associated with this radical is not required to bear any resemblance to the other radical, but it does in this case. The rationale for this is as follows: To get from radical **2b′** to radical **2b″**, all that is required is to change the stereochemical configuration at the γ-carbon on the right-hand side, leaving γ-carbon on the left-hand side in its original configuration. So, using the numbering system in Scheme 2, we can see that the hyperfine coupling constants (chemical shift) of H_3 and H_4 are interchanged by this process, and that the chemical shifts of H_1 and H_2 are only mildly perturbed by it because they are so remote (three carbon atoms away). Since the pseudo-C_2 axis symmetry element now establishes magnetic equivalence for H_1 and H_4 and for H_2 and H_3 in radical **2b″**, we still have a triplet of triplets from the β-protons, with nearly the same coupling constants as radical **2b′**. Note that the “diastereotopic” β-protons in these polymeric radicals never violate the rule of inequivalence at fast motion[41] *as the equivalencies are always* *established via symmetry relationships between protons on different carbon atoms.*

An interesting additional observation is that the syndiotactic spectrum in Figure 5, at the highest possible temperature, looks more like the atactic spectrum than the isotactic spectrum, a minor contradiction to the argument presented above and according to Scheme 2. In fact, our atactic PMMA sample was determined by NMR to be significantly syndiotactic (76% total r dyads). Therefore, it is not surprising that they turned out to show similar TREPR spectra. Still, the fact that all three spectra are simulated using a triplet of triplets for the β-protons and exactly the same value for the methyl hyperfine interaction is strong evidence for the correct fast motion spectral assignment for PMMA.

While the simulations of the high-temperature spectra are satisfactory, we want to rule out any other possible radicals that could give similar spectra via different chemical routes of the polymer or solvent, or both. Although the solvent in these experiments, propylene carbonate (**5**), does not absorb at 248 nm, there was considerable concern that some of these simple TREPR spectra could be due to H-atom abstraction from the solvent by the excited triplet state of the polymer carboxyl chromophore. There are three possible abstraction sites in **5**, one leading to a primary, one to a secondary, and one to a tertiary alkyl radical. The secondary and tertiary radicals are further stabilized by their neighboring oxygen atoms. The most stable is clearly the tertiary site with the neighboring oxygen. The TREPR spectrum expected from such a structure would be either a quintet (if all the β-protons are equivalent), a quartet of triplets (equivalent methyl and methylene, but not to each other), or a quartet split into a doublet of doublets (methyl quartet split by pseudoequatorial and pseudoaxial methylenes). In all cases the number of lines in the spectrum, and their intensity ratios, would not account for the spectra we have observed in our experiments.

An additional concern is that the polymer is “unzipping”, i.e., depolymerizing at these higher temperatures. We discount this for two reasons: (1) the spectrum of the propagating radical which would result from such a reaction is known to contain no more that 16 lines (4 from the equivalent methyl protons, split into a doublet of doublets if the methylene protons are inequivalent), and (2) we are observing radicals that are produced in synchronous arrangement with the laser flash. Thermal degradation, since it is not laser induced, would lead to TREPR signals that will be sampled randomly with respect to the laser timing sequence, and therefore would be averaged to zero over the nearly 6000 shots required to produce one spectrum.

Summary and Outlook

Having ruled out other possibilities, our computer simulations, coupled with the symmetry relationships denoted in Scheme 2, lead us to the unambiguous identification of the primary photochemical events of acrylate and methacrylate degradation under direct UV irradiation. The excellent visual fit of the simulations at high temperature makes the assignment of these radicals a confident one. A major remaining challenge is to use what we have learned from the fast motion spectra to work backward to the slow motion spectra. We are pessimistic about achieving the low-temperature limit in this experiment for the following technical reasons: (1) the polymer may not remain dissolved at lower temperatures, (2) the photochemistry leading to main chain free radicals may slow or be stopped due to activation barriers, and (3) the construction of a low-temperature flow system presents technical difficulties by itself in terms of pump design, heat transfer, and the fact that no metal parts can be near or inside the EPR microwave resonator. Most importantly, however, and beyond technicalities, is reason (4), that the polymer will almost certainly assume many different conformations leading to a broad superposition of spectra. In fact, one can see this beginning to happen in some of the spectra shown for different solvents in Figure 3. Other data (not shown) on systems where we have deliberately tried to slow the chain dynamics by putting large side groups on the ester functionality have also shown broad, featureless spectra at room temperature that are not possible to simulate.

The temperature dependence of these TREPR spectra is rich in information about the conformational motion of the polymer. An important question is how much of the transition between fast and slow motion in these radicals is a function of local vs macromolecular conformational parameters. To this end, we are now undertaking molecular modeling studies to attempt to predict the conformational distributions at both low and high temperatures. If we find a model that successfully reproduces the high-temperature data, there is good reason to believe that those energetic parameters could be used to predict the low-temperature spectrum as well. Present efforts are centered around conformational dynamic models that incorporate macromolecular behavior in the most rigorous fashion.

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(41) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; John Wiley: New York, 1994; p 488ff.