Time-Resolved EPR: A Novel Method For Studying Living Chains

Erdem Karatekin

Department of Chemistry, Columbia University, New York, New York 10027

Ben O'Shaughnessy

Department of Chemical Engineering, Columbia University, New York, New York 10027

Nicholas J. Turro*

Departments of Chemistry and Chemical Engineering, Columbia University, New York, New York 10027

Despite its great industrial importance, many aspects of free radical polymerization (FRP)[1] remain poorly understood. One of the few methods that can directly probe propagating radicals, i.e., living chains which are at the heart of FRP, is electron paramagnetic resonance (EPR), a very sensitive and nondestructive technique that provides information on the local structure and dynamics and the number density of the propagating radical centers.[2,3]

Unfortunately, in many cases the concentration of the FRP living chains is too low during the early stages (low conversions) to allow for good EPR signals. This results in poorly resolved, noisy spectra that are prone to misinterpretations. A second problem is the measurement of *many* different living chain lengths simultaneously, leading to speculations that are difficult to test.[4] The field would be significantly advanced if one could obtain spectra unambiguously corresponding to a single living chain length. In this article we demonstrate how the time-resolved EPR (TR−EPR) technique[5−7] can be used to overcome these problems. Using TR−EPR in well characterized systems, we have studied the FRP of methyl methacrylate (MMA) and its analogues and obtained well-resolved, intense spectra of monodisperse living chains. To the best of our knowledge there has been only one other study where TR−EPR was applied to study FRP.[8] The work reported here is also one of the few systematic exploitations of the transfer of "spin polarization" via chemical reactions[8−11] and the application of TR−EPR in polymer research in general.[8,10,12]

In conventional EPR, time scales for data acquisition are slow (typically seconds to minutes) compared to the time to add a monomer to a living chain, $1/(k_p [M])$ (typically milliseconds[13]). This usually limits conventional EPR measurements to steady state FRPs, where inevitably a broad distribution of living chain lengths exists. Nevertheless there has been some clever efforts to measure conventional EPR of single length living chains. Fischer and Giacometti[14] obtained well-resolved spectra of 1-mer living chains of methacrylic acid by creating a stationary concentration of these in the EPR cavity using a flow system. More recently, Matsumoto and Giese[15] succeeded in measuring 1-, 2-, and 3-mer living chains of MMA and related monomers, by reduc-

tion of the corresponding bromide precursors in an inert solvent. In contrast, TR−EPR probes submicrosecond processes, much faster than $1/(k_p[M])$; thus, *taking a "snapshot" of living chains is possible by this method.* These chains are created by very fast addition of a primary radical (created by a short laser pulse) to monomer. This first addition step is complete within 100−300 ns. Subsequent addition rates are much slower (on the order of 1 ms) due to the lower reactivity of living chains. Our TR−EPR observation times (typically 1−2 μs following the laser pulse) fall in a range well after the creation of living chains, yet well before these can react further: *only a single living chain length is monitored.* To study spectra of living chains as a function of their degree of polymerization, *N*, one can use photoinitiators which give primary radicals attached to progressively longer polymeric chains. Here we report results for the shortest living chains, $N = 1$, created using small molecule photoinitiators. Now, the matrix (consisting of monomer and pre-dissolved polymer) remains fixed during the TR−EPR observation times, allowing one to study the effect of polymer concentration on the spectra. This is not easy to do in conventional EPR in the early stages of FRP where one often needs to accumulate a large number of acquisitions to improve signals. During these times conversion (roughly equal to polymer volume fraction accumulated in the matrix) may change considerably.

The conventional EPR spectra of poly(methyl methacrylate) (PMMA) radicals in both glassy and nonglassy matrices have generated considerable controversy since the first observations in the 1950s[3] of a 9-line spectrum with an unusual intensity distribution. Studying oligomeric living chains of methacrylic acid Fischer[16] observed 16 lines in nine main groups, and interpreted these in terms of nonequivalent β-protons of the CH_2 group due to hindered rotation. More recently, Shen et al.[17] and Zhu et al.[18] observed a "13-line" EPR spectrum at low conversions (≲20%) in the bulk FRP of MMA, which gradually turned into a "9-line" spectrum that persisted as the mixture became glassy. Zhu et al.[18] suggested that the 9-line signal is due to living chains "trapped" in microscopic glassy domains. Finally, Gilbert and co-workers[4] argued, based on computer simulations, that the 13-line signal must be due to oligomeric radicals ($N ≲ 5$), which must have been abundant in the experiments of Shen et al.[17] and Zhu et al.[18] where unusually high rates of initiation were used. Resolving these various interpretations based on conventional EPR alone has clearly proven to be very difficult.

The EPR signal intensity is proportional to the difference in the populations of the energy levels involved in the observed transitions.[2,3] This difference is typically very small in conventional EPR where spin systems are in thermal equilibrium ($E_{Zeeman} \ll kT$ at room temperature). However, just after their creation, free radicals may be in a far-from-equilibrium spin state (i.e. in a "spin polarized" state) where the difference in energy level populations is far greater than that in thermal equilibrium. Hence one may observe greatly enhanced signal intensities by monitoring EPR transitions before the spin system relaxes to equilibrium, typically within microseconds. That is the essence of

* To whom correspondence should be addressed at the Department of Chemistry.

TR−EPR.[19,20,5] In this method radicals are created by a short (∼10 ns) laser pulse, and the EPR transitions are observed with nanosecond time resolution thereafter, in a fixed external magnetic field. The transient EPR signals are integrated within a set time window (which typically starts from 0.1 to a few microseconds following the laser flash, and lasts a few hundred nanoseconds) to yield a single point in the spectrum. To obtain the whole spectrum the external magnetic field is incremented and the abovementioned process is repeated many times (see footnote 21 for details). It should be noted that the TR−EPR spectra are represented in absorption form rather than the first derivative form used in conventional EPR.

In this study we chose photoinitiators that are known to give strongly polarized TR−EPR signals. The concentration of the photoinitiator is adjusted to have an optical density ≈0.3 for 0.5−1 mm thick quartz flat cells employed, ensuring uniform excitation throughout the sample. A flow system is used (typical flow rates 0.5−1 mL/min) in order to avoid photoinitiator depletion due to the large number of laser shots (≈5000) required per spectrum.

The typical aromatic ketone molecule **1** (Darocur 1173, Ciba Specialty Chemicals Corporation) shown in Figure 1, photoexcited to its first electronic singlet excited state, S_1, quickly (≲ 1 ns) decays to the first triplet excited state, T.[22] In the presence of the magnetic field of the EPR spectrometer (∼3500 G) the triplet sublevels (T_-, T_0, T_+) are nondegenerate, and one of these (T_+ for this particular molecule) is overpopulated during the $S \rightarrow T$ conversion.[19] The molecule then cleaves to give two radicals before the triplet sublevels thermally equilibrate (which requires typically 1 ns[19]). The net result is the creation of free radicals (**2** and **3**, see Figure 1) that overpopulate the upper Zeeman level, i.e., a spin-polarized system! This is the "triplet mechanism" (TM) of spin polarization and is the main one we will be concerned with here. Note that since it is the upper Zeeman level that is overpopulated, the TR−EPR spectrum of the radicals **2** and **3** shown in Figure 1a is actually in *emission*.

In an inert solvent the TR−EPR signals of the radicals **2** and **3** decay due to both radical recombination and the relaxation of the spin polarization toward thermal equilibrium. When MMA is present, it reacts with **2** and **3** and new signals, as shown in Figure 1b, appear. These new signals are assigned to radicals **4** and **5** (which give essentially the same spectrum—see caption of Figure 1). We remark that we have used a number of photoinitiators other than **1**, and obtained similar results.[23] The addition of the ketyl radical (**3**) to monomer (at concentrations of 6−9 M, or volume fractions $\phi_{mon} \approx 0.65 - 1$, in the cases studied here) is complete within a few hundred nanoseconds, consistent with addition rate constants measured previously in this laboratory and by Fischer[24] for several methacrylates ($k_{add} \approx 10^6 - 10^7$ M⁻¹ s⁻¹). The benzoyl (**2**) reactivity is about an order of magnitude smaller than that of the ketyl,[25] hence the broad singlet in parts a and b of Figure 1 marked with an arrow, assigned to benzoyl (**2**) based on previous studies,[26,27] lasts longer. Note that the *net spin polarization of the system is conserved during the addition reaction*, due to conservation of angular momentum.[7,28] This is crucial, as it allows us to observe intense, polarized signals from the adduct radicals.
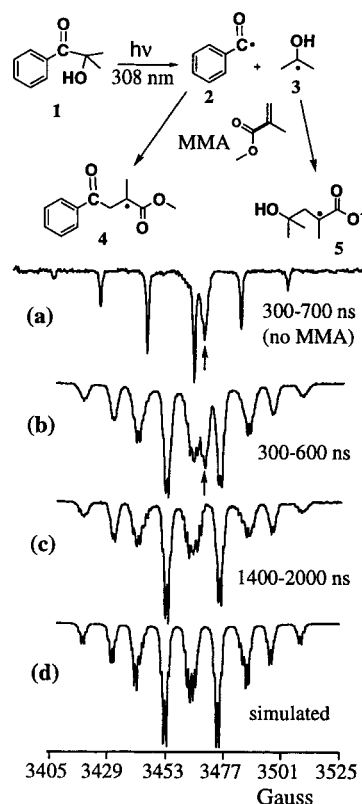

Figure 1. (a) TR−EPR spectrum observed when **1** is photolyzed in acetonitrile, an inert solvent. The transient signals for each point in the spectrum were integrated for the time window shown, following the pulse from an excimer laser (typical output power 70 mJ/pulse). The peak marked with an arrow is assigned to **2** while all the other peaks are assigned to **3**. (b and c) TR−EPR spectra observed when **1** is photolyzed in neat MMA, for the integration windows indicated. Signals from **2** are visible during earlier times (marked with an arrow) but signals from the more reactive **3** are replaced with new ones. The new signals are assigned to radicals **4** and **5**. (d) Simulated spectrum for **4** and **5**, using the following isotropic hyperfine couplings for both radicals (the two have essentially the same spectrum, due to weak couplings to the primary radical derived moieties which are ignored in the simulation): $a_H(C_\beta H_3)$=22.5 G, $a_H(C_\beta H_2)$ = 12.6 G, and $a_H(C_\delta H_3)$ = 1.16 G. In addition, a Lorentzian line shape with a width of 0.5 G was used.

The adducts ("secondary radicals") **4** and **5** are expected to have much lower reactivity toward monomer compared to the primary radicals **2** and **3**, based on the reported propagation rate constants for the FRP of MMA.[13] That is, during the later time window shown in Figure 1c, after the benzoyl (**2**) singlet has disappeared, only the secondary radicals **4** and **5** are observed, since these do not add to monomer on these time scales. Direct evidence for this claim is obtained by using the photoinitiator (2,4,6-trimethylbenzoyl)diphenylphosphine oxide (TMDPO), which yields 2,4,6-trimethylbenzoyl (**6**) and diphenylphosphonyl radicals (**7**).[8] The TR−EPR spectra of the secondary radicals formed upon the addition of the phosphorus centered radical **7** to monomer in this case exhibit a strong (≈60 G) coupling to ³¹P, derived from **7**. The magnitude of this coupling would decrease considerably if further addition occurred. This is not observed during the time scales we investigated (up to 5 μs), consistent with the results of Kajiwara et al.[8]

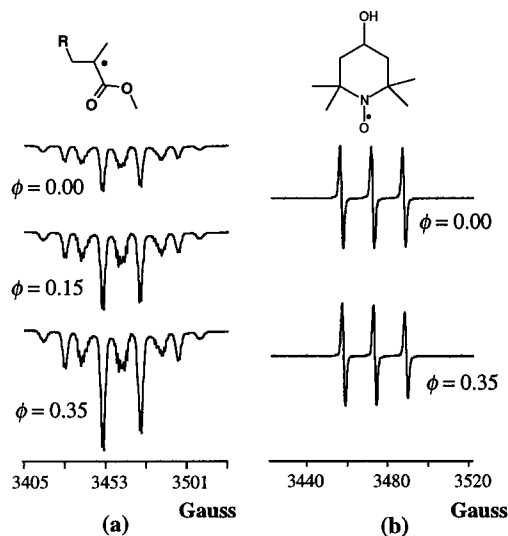In Figure 1d we show the simulated spectrum for the radicals **4** and **5**, using isotropic hyperfine couplings and

Figure 2. (a) TR−EPR spectra (integration window 1.4−2.0 μs) of $N = 1$ living chains of PMMA, in the presence of predissolved PMMA ($M_w \approx$ 15K) of different volume fractions ϕ as indicated. (b) EPR spectrum (derivative form) of the spin probe 4-hydroxy−TEMPO in 0 (top) and 35% (bottom) solutions of the same PMMA dissolved in MMA.

treating the two β-protons of the CH$_2$ group equivalently (see Figure caption). As can be seen in the Figure, the agreement between the simulated and the observed spectra is quite good,[29] suggesting that invoking more complicated models[3,15] is not required here.

Notice that the adducts **4** and **5** are in fact one-step-propagated ($N = 1$) living chains found in the conventional, steady state FRP of MMA, photoinitiated by **1**. Having thus found a way of generating 1-mer living chains in well controlled environments, we have studied the EPR behavior of these in relation to FRP. We have created $N = 1$ living chains (**4** and **5**) in solutions of MMA containing PMMA of various molecular weights ($M_w \approx$ 15 K to 200 K). The effect of the presence of polymer ($M_w \approx$ 15 K), up to 35% by volume, on the TR−EPR spectra is *minor*, as shown in Figure 2a. For comparison, we have used a spin probe, 4-hydroxy-TEMPO, shown in Figure 2b. The minor effect of the presence of polymer on the conventional EPR spectrum of this spin probe is also shown in Figure 2b. Note that these spectra are displayed in derivative form, as is common in conventional EPR.[2] The solutions used for the spin probe studies were identical to the ones used for TR−EPR experiments, except for the absence of the initiator. As the volume fraction of polymer, ϕ, is increased from 0 to 35%, the rotational correlation time[30] of the spin probe increases only about four-fold (from 0.1 to 0.4 ns) while the bulk properties are modified drastically, consistent with small molecule fluorescent probe studies.[31] Similarly, the molecular weight of the PMMA in the matrix, studied up to 200 K, has very little effect on the spectra. These spin probe studies are consistent with the observation of only *minor* changes in the TR−EPR spectra of $N = 1$ living PMMA chains as a function of ϕ.

Next, we have investigated the effect of the size of the living chains on their TR−EPR spectra. A convenient way of doing this is to use analogues of MMA, with the methyl side group replaced with longer alkyl groups. The effects of progressively going from methyl (C$_1$) to stearyl (C$_{18}$) methacrylate are shown in Figure 3. Once again we observe *minor* effects on the TR−EPR spectra.
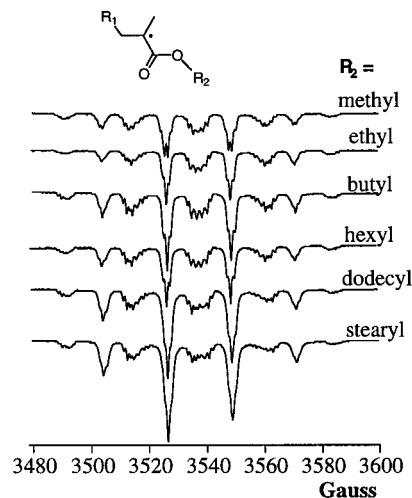

Figure 3. Effect of the size of the living chains on the TR−EPR spectra, in the absence of polymer (integration window 1.4−2.0 μs).
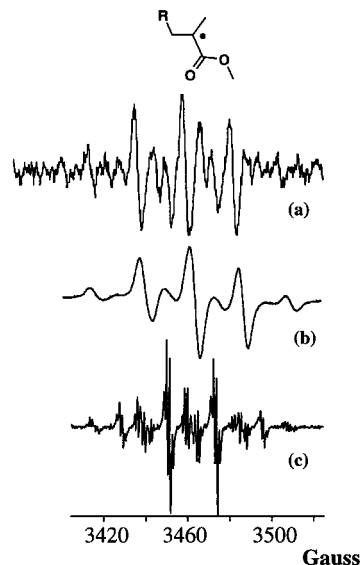

Figure 4. (a) Typical "13-line" EPR spectrum observed at low conversions ($\lesssim$ 20−25%) in FRP of MMA (in this particular case photoinitiated with 5% azobisisobutyronitrile (AIBN) at room temperature). (b). The "9-line" EPR spectrum obtained at higher conversions. (c). TR−EPR spectrum of $N = 1$ living chains of PMMA (essentially the same spectrum is observed for $\phi = 0$−35%, see Figure 2), multiplied by −1, and displayed in derivative form for ease of comparison with the conventional EPR spectra above.

The main features, the presence of nine groups of lines and the splittings of these, remain unchanged. However, a minor and expected change is observed in the hyperfine splittings within these nine groups of lines: the quartet splitting due to the methyl side group of MMA becomes a triplet splitting as the three methyl protons are replaced by two ethyl protons in going to larger alkyl side groups. These results suggest that the EPR spectrum of (oligomeric) living chains should not be modified drastically as they become progressively bigger.

Finally, in Figure 4, we compare, for MMA, the TR−EPR spectrum of $N = 1$ living chains with the conventional EPR spectra obtained in steady state FRPs. This Figure also summarizes our main findings: (i) the signal to noise ratio of the TR−EPR spectrum is far greater than what is typically observed by conventional EPR

in FRP at "low conversions", (ii) the resolution of the TR−EPR spectra is far superior, (iii) although major changes in the conventional EPR spectra are observed (13-lines → 9-lines) as more polymer builds up in FRP, no such changes in the TR−EPR spectrum are seen up to $\phi = 35$ % (Figure 2), and (iv) the TR−EPR spectrum of the $N = 1$ living chains, even in the absence of polymer, looks very similar to the 9-line EPR spectrum observed in "high conversion" FRP.

The differences between the TR−EPR spectra of $N = 1$ living chains and the conventional EPR spectra observed in FRP are quite interesting. These differences may be due to the fact that in steady state FRP typically the average living chain length $N \gg 1$, even at low conversions.[1] In this respect, we are planning to use bulkier monomers (see Figure 3) and spin probes in the presence of polymer. In addition, we are currently synthesizing photoinitiators similar to **1** that are attached to long chains. The secondary radicals generated from these should mimic $N > 1$ living chains.

In summary, TR−EPR is a novel and powerful tool to study living chains under well defined environments with excellent signal intensities and resolution. We have used this method to investigate living chains in the FRP of MMA and its analogues, and obtained new information that we hope will generate fresh discussions about the nature of PMMA living chains. Although we have not yet unambiguously identified the origin of the 13-line to 9-line transition in the conventional EPR spectra observed in FRP, our results oppose the suggestion that the 13-line signal is due to oligomeric living chains ($N \lesssim 5$) present at low conversions,[4] as we observe only 9-line signals from monodisperse $N = 1$ living chains, even in the absence of polymer. We also note that the TR−EPR as applied here is a general method that can be used in other systems. In particular, it should be of relevance to the recently developed pulsed laser polymerization methods.[13]

References and Notes

(1) Odian, G. *Principles of Polymerization*; John Wiley and Sons: New York, 1981.
(2) Ranby, B.; Rabek, J. F. *ESR Spectroscopy in Polymer Research*; Springer-Verlag: Berlin, 1977.
(3) Kamachi, M. *Adv. Polym. Sci.* **1987**, *82*, 207--275.
(4) Tonge, M. P.; Pace, R. J.; Gilbert, R. G. *Macromol. Chem. Phys.* **1994**, *195*, 3159--3172.
(5) *Time Domain Electron Spin Resonance*; Kevan, K., Schwartz, R. N., Eds.; John Wiley & Sons: New York, 1979.
(6) Salikhov, K. M.; Molin, Y. N.; Sagdeev, R. Z.; Buchanenko, A. L. *Spin Polarization and Magnetic Effects in Radical Reactions*; Studies in physical and theoretical chemistry 22; Elsevier: Amsterdam, 1984.
(7) Buckley, C. D.; McLaughlan, K. A. *Mol. Phys.* **1985**, *54* (1), 1.
(8) Kajiwara, A.; Konishi, Y.; Morishima, Y.; Schnabel, W.; Kuwata, K.; Kamachi, M. *Macromolecules* **1993**, *26*, 1656.
(9) Ohara, K.; Murai, H.; Kuwata, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1672.
(10) Kamachi, M.; Kajiwara, A.; Saegusa, K.; Morishima, Y. *Macromolecules* **1993**, *26*, 7369.
(11) Turro, N. J.; Khudyakov, I. V. *Chem. Phys. Lett.* **1992**, *193* (6), 546.
(12) Forbes, M. D. E.; Barborak, J. C.; Dukes, K. E.; Ruberu, S. R. *Macromolecules* **1994**, *27*, 1020.
(13) Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* **1993**, *26*, 6410−6415.
(14) Fischer, H.; Giacometti, G. *J. Polym. Sci.: Part C* **1967**, *16*, 2763.
(15) Matsumoto, A.; Giese, B. *Macromolecules* **1996**, *29*, 3758.
(16) Fischer, H. *Polym. Lett.* **1964**, *2*, 529.
(17) (a) Shen, J.; Tian, Y.; Wang, G.; Yang, M. *Makromol. Chem.*, **1991**, *192*, 2669. (b) Shen, J.; Tian, Y.; Wang, G.; Yang, M.; Zheng, Y. *Polym. Int.* **1992**, *28*, 75.
(18) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Macromolecules* **1990**, *23*, 1144−1150.
(19) Adrian, F. J. *Rev. Chem. Int.* **1986**, *7*, 173.
(20) McLaughlan, K. A.; Stevens, D. G. *Acc. Chem. Res.* **1988**, *21*, 54.
(21) In practice, a single point on the spectrum is the result of averaging 10 −20 decays in a fixed field to obtain better signals. To obtain the whole spectrum, it is actually easier to vary the external magnetic field continuously rather than discretely. For a sufficiently slow sweep the two methods give indistinguishable results. A typical spectrum in this work has 512 points, is 120 G wide, and is swept in 500 s, using a microwave power of 2−20 mW. Other details of the instrumental setup and the TR−EPR technique can be found elsewhere.[27,26]
(22) Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991.
(23) Using 1-hydroxycyclohexyl phenyl ketone (Irgacure 184, Ciba) and α,α-dimethoxy-α-phenylacetophenone (Irgacure 651, Ciba) gave essentially identical spectra to those obtained when **1** is used, although the addition of α,α-dimethoxy benzyl radicals derived from Irgacure 651 to MMA was rather slow and signals from both primary and secondary radicals were visible until all the polarization was lost within a few microseconds.
(24) Batchelor, S. N.; Fischer, H. *J. Phys. Chem.* **1996**, *100*, 9794.
(25) Schnabel, W. in *Lasers in Polymer Science and Technology: Applications*; Fouassier, J.-P., Rabek, J. F., Eds.; CRC Press; New York; 1991; Vol. 2, pp 95−144.
(26) Khudyakov, I. V.; McGarry, P.; Turro, N. J. *J. Phys. Chem.* **1993**, *97*, 13234.
(27) Jenks, W. S. Ph.D. Thesis Columbia University; New York, NY, 1991.
(28) Madden, K. P.; Taniguchi, H. *J. Phys. Chem.* **1996**, *100*, 7511.
(29) The minor differences between the simulated and the observed spectra arise because we ignore (i) the interactions with the primary radical derived parts of the adducts **4** and **5**, which are expected to be small ($\lesssim 1$ G), and (ii) effects of polarization mechanisms other than the TM. In particular, the radical pair mechanism[7,19] (RPM) is expected to be the cause of the less intense emission in the higher field half of the observed spectrum.
(30) *Spin Labeling II: theory and applications*; Berliner, L. J., Ed.; Academic Press: New York, 1979.
(31) Guillet, J. *Polymer Photophysics and Photochemistry*; Cambridge University Press: Cambridge, England, 1987.

MA980891J