Direct Measurement of Primary Radical Concentrations in Pulsed Laser Photolysis

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The pulsed laser photolysis−molecular weight distribution (PLP−MWD) technique[1] has recently emerged as the preferred method for obtaining propagation rate coefficients (k_p) in free radical polymerizations. It has the merit that k_p values can be determined independently of termination rate coefficients (k_t). The PLP−MWD method has been used successfully to obtain k_p values for the homopolymerizations of a wide range of monomers including styrene,[2−4] acrylate esters,[5] methacrylate esters[6,7] and methacrylonitrile.[8] Several theoretical and modeling studies of the PLP−MWD technique have also been undertaken.[1,3,4,6,9−11] These show that, with appropriate choice of reaction conditions and methods for data analysis, the PLP−MWD method is robust and provides accurate and reliable k_p data.

Computer simulations[1,3,4,6,9−11] also show that the shape of the MWD is largely controlled by the radical flux, which is determined by the concentration of radicals generated by each laser pulse ($[I^\bullet]$/pulse) and k_t. Deady *et al.*[4] have pointed out that it should be possible to estimate k_t and establish its dependence on chain length by analysis of the shape of the MWD if either $[I^\bullet]$/pulse or the absolute polymer concentration generated during the PLP experiment is known with sufficient precision (±10%).

This communication outlines a novel method of measuring $[I^\bullet]$/pulse during PLP experiments. The technique involves a variation on the well-known nitroxide trapping technique. Nitroxides such as 4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (NTEMPO) efficiently scavenge small carbon-centered radicals at near-diffusion-controlled rates ($\sim 10^9$ M^{-1} s^{-1} for simple alkyl radicals).[12,13] The choice of the nitroxide NTEMPO for this work is based upon another important property that this molecule exhibits; namely there is a large increase in fluorescence quantum yield for the naphthalene chromophore on the formation of the alkoxyamine R-NTEMPO by trapping a carbon-centered radical (Scheme 1).[14] Gerlock *et al.*[15] have demonstrated that the increase in fluorescence intensity observed during the thermolysis of 2,2′-azobis(isobutyronitrile) (AIBN) in the presence of NTEMPO at 60 °C is proportional to the decrease in [NTEMPO]. Other workers have reached similar conclusions with related compounds.[16] These findings suggested fluorescence measurements might be used for quantitative determination of R-NTEMPO formed (and of carbon-centered radicals generated) in a PLP experiment.

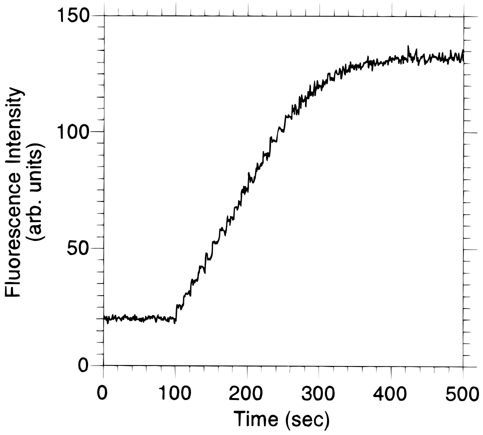
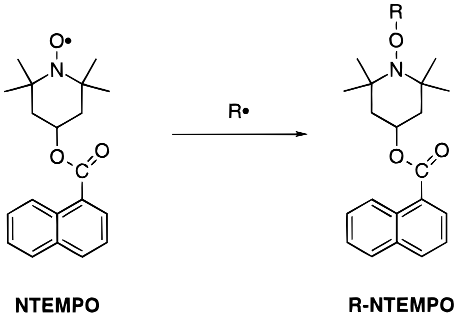


Figure 1. Change in fluorescence intensity with time during photolysis of AIBMe in the presence of NTEMPO (experiment 3 in Table 1).

Scheme 1



The fluorescence from NTEMPO and R-NTEMPO (excitation wavelength 300 nm; emission wavelength 390 nm) can be isolated from the 355 nm laser pulse.[17] Figure 1 shows an example of the "time-resolved" fluorescence observed during an 2,2′-azobis(methyl isobutyrate) (AIBMe)/NTEMPO/ benzene PLP experiment. After the initial, low value for the "background" intensity (I_i) was obtained (over the first 100 s), the sample was irradiated at a constant laser pulse repetition rate. An instantaneous rise in fluorescence intensity was observed following each laser pulse. The rate of increase in the fluorescence intensity was linear over at least the first 15 pulses. Since the total change in [AIBMe] in this period should be negligible, this is good evidence that the concentration of R-NTEMPO formed by each laser pulse is the same. This rate only levels out as the NTEMPO is depleted (after ~ 300 s). For the experiment shown in Figure 1 the laser irradiation was stopped after 400 s, whereupon the fluorescence intensity remained constant.

Fluorescence intensity was converted into concentration units by use of eq 1, where $[R^\bullet]_t$ = (cumulative)

$$[R^\bullet]_t = \frac{(I_t - I_i)[\mathrm{NTEMPO}]_i}{I_f - I_i} \qquad (1)$$

radical concentration= $[\text{R-NTEMPO}]_t$, I_t = fluorescence intensity at time t, I_i = initial fluorescence intensity, I_f = final fluorescence intensity (after complete consumption of NTEMPO), and $[\mathrm{NTEMPO}]_i$ = initial NTEMPO concentration.

This calibration method assumes quantitative conversion of NTEMPO to R-NTEMPO and has the benefit of not being reliant on absolute measurement of the fluorescence intensity. Thus, the effects on the fluores-

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Table 1. Effect on Primary Radical Concentrations ([I•]/pulse) by Changing [NTEMPO], Laser Energy and Laser Pulse Repetition Rate (All Performed in Benzene at 25 °C)

expt no.	[I•]/pulse (×10^6 M)	[AIBMe] (×10^3 M)	[NTEMPO] (×10^5 M)	laser energy (mJ/pulse)[a]	laser pulse rate (s/pulse)
1	2.58	1.74	5.15	30	1.0
2	2.81	1.74	5.15	30	5.0
3	2.63	1.74	5.15	30	10.0
4	4.75	2.95	20.0	30	5.0
5	2.63	2.95	20.0	15	1.0
6	1.43	1.00	4.12	30	5.0
7[b]	1.30	1.00	4.94	30	5.0
8[c]	1.38	1.02	10.3	30	5.0

[a] Uncertainty of ±1.0 mJ/pulse. [b] Contained [styrene] = 1.0 × 10^{-3} M. It was not possible to use higher styrene concentrations without interference with the fluorescence measurements. [c] Contained [methyl methacrylate] = 4.17 M.

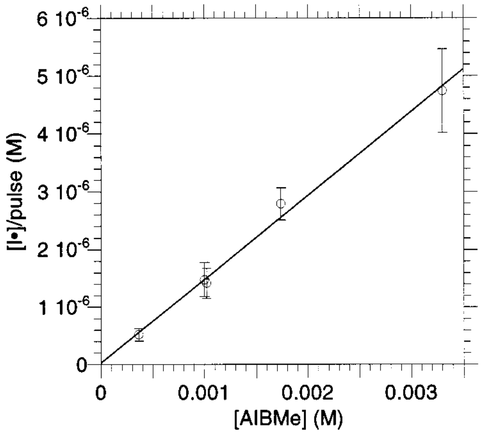

Figure 2. Dependence of primary radical concentration ([I•]/pulse) on initiator concentration (each data point is the average of three or more experiments, error bars are twice the average deviation from mean). Experimental conditions: [AIBMe] as indicated; laser energy = 30 mJ/pulse; solvent = benzene; temperature = 25 °C; $[\text{NTEMPO}]_i$ varied from 4 × 10^{-5} to 2 × 10^{-4} M.

cence intensity caused by small changes in cell position between experiments can be eliminated. Note that the fluorescence intensity for NTEMPO is <0.5% that of R-NTEMPO at the operating wavelengths in the current experiments, where [NTEMPO] < 2 × 10^{-4} M; the value of I_i is primarily due to "background" scattered light, etc. (see, for example, Figure 1). Verification of the calibration method was obtained by adding a known amount of R-NTEMPO to the AIBMe/NTEMPO/benzene solution and observing the expected increase in fluorescence intensity. Values of [I•]/pulse are then determined by fitting the linear region of the fluorescence-time curve with a straight line and multiplying the gradient by the time between each laser pulse.

Table 1 shows [I•]/pulse data for a range of experimental conditions. Importantly, there is no significant dependence of [I•]/pulse upon (a) the laser pulse repetition rate (experiments 1−3), (b) the nitroxide concentration [NTEMPO] (experiments 6−8), or (c) monomer concentration (styrene or methyl methacrylate) (experiments 7 and 8). The value of [I•]/pulse is proportional to the laser energy (experiments 4 and 5) and the initiator concentration (see Figure 2).[18] The error associated with the measurements of [I•]/pulse is estimated to be less than 10%, and appears to lie mainly with obtaining a consistent laser pulse energy.

It is known that nitroxides may abstract hydrogen if excited by low wavelength UV light.[19−21] This chemistry is unlikely to complicate the present experiments where the irradiation wavelength is 355 nm. However, several control experiments were carried out to establish the absence of side reactions. In the first experiment, a solution of NTEMPO and R-NTEMPO in benzene was irradiated under the conditions of the PLP experiment. No change in fluorescence intensity was observed. This demonstrates the stability of both R-NTEMPO and NTEMPO to the experimental conditions. In the second experiment, a reaction mixture was purged with air following completion of the irradiation period. The sample was then re-degassed and the fluorescence intensity determined. No significant change was observed. This experiment shows that NTEMPO is not converted to hydroxylamine during the irradiation period. The air purge would be expected to oxidise any hydroxylamine formed[20] resulting in a change in the fluorescence intensity.

For the [I•]/pulse data to be useful in estimating k_t, it is necessary that the same number of radicals that are trapped by NTEMPO in the above experiments initiate (or terminate) polymerization in a PLP polymerization experiment. There is extensive literature on the use of nitroxides (and other scavengers) to estimate initiator efficiencies by the inhibitor method. Examination of such data shows that initiator efficiencies obtained by the inhibitor method are often significantly higher than those estimated by analysis of polymerization kinetics or by direct measurement.[22] However, in the inhibitor method, scavenger concentrations are typically several orders of magnitude higher than those used in the present experiments. The findings that the measured [I•]/pulse is independent of [NTEMPO] and [monomer] under our experimental conditions provide supporting evidence for the validity of the assumption that [I•]/pulse is the same as in a polymerization.

A solution polymerization of styrene under PLP conditions[23] at 25 °C serves to illustrate the methodology for estimating k_t. Experimental conditions were designed such that [I•]/pulse was effectively constant for the duration of the experiment (initiator conversion was small). The MWD of the polymer formed during the PLP experiment is shown in Figure 3. A k_p value of 81 L mol^{-1} s^{-1} is obtained by analysis of the MWD according to the point of inflection method. This value is in good agreement with the literature.[2−4] Also shown in Figure 3a are simulated MWDs with a [I•]/pulse value of 4.8 × 10^{-7} mol L^{-1} (as measured with the above-mentioned technique) and three values of k_t (which, for these simulations, has been assumed to be independent of the chain-length). A k_t value of 7.5 × 10^7 L mol^{-1} s^{-1} provides the best overall fit to the experimental MWD. The relative heights of the first two peaks in the MWD are used as criteria for goodness of fit in this context. The heights of these peaks are directly related to the number of radicals that survive the laser pulses and hence to k_t. Values of k_t = 5 × 10^7 L mol^{-1} s^{-1} and k_t = 1 × 10^8 L mol^{-1} s^{-1} provide a poorer fit. Literature[24] values for k_t are between 10^7 and 10^8 L mol^{-1} s^{-1}. A value at the higher end of this range might be expected in a PLP experiment because of a higher likelihood that a very short chain radical will terminate with a longer chain radical in the period following the laser pulse.

Notwithstanding the fact that a k_t of 7.5 × 10^7 L mol^{-1} s^{-1} provides the best fit to the data according to the above-mentioned criteria, the lower k_t value (5 × 10^7 L mol^{-1} s^{-1}) gives a better fit for the longer chain-length

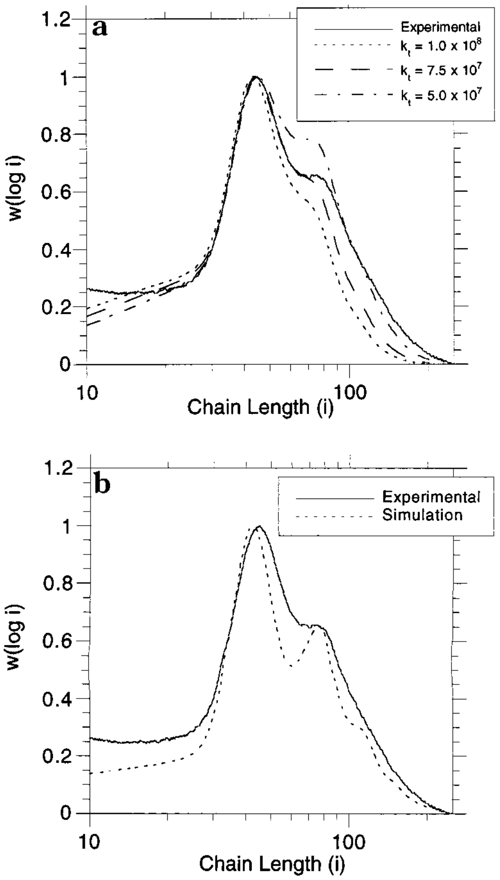

Figure 3. Comparison of experimental and simulated (normalized) MWDs. (a)Experiment: [styrene] = 4.38 M; solvent = benzene; [AIBMe] = 3.65 × 10^{-4} M; $t_f = 0.1$ s; laser pulse energy = 30 mJ/pulse; 250 pulses; temperature = 25 °C. Simulations: [styrene] = 4.38 M; [I•]/pulse = 4.8 × 10^{-7} M; k_t as indicated on figure; $k_p = 81$ mol L^{-1} s^{-1}; $k_i = 3000$ mol L^{-1} s^{-1}; % combination = 85; $t_f = 0.1$ s; number of pulses = 10. (b) Experiment as in part a. Simulation as in part a but with a chain-length dependent k_t (where[25] $k_t^{i,j} = 1.7 \times 10^8(i^{-0.487} + j^{-0.487})$).

region of the MWD. This is consistent with a view that k_t is a function of the chain-lengths (i and j) of the reacting species. Figure 3b shows a simulation assuming a chain-length dependent k_t where $k_t^{i,j}$ is determined by an expression suggested by Russell:[25] $k_t^{i,j} = 1.7 \times 10^8\ (i^{-0.487} + j^{-0.487})$. This expression provides a better overall fit to the experimental data than does a chain-length independent k_t, although the peaks are somewhat sharper in the simulation than in the experiment. A full discussion on the chain-length dependence of k_t is beyond the scope of the present communication (for leading references see refs 22, 24, and 25). The form of chain length dependence of $k_t^{i,j}$ for styrene and other monomers will be explored further in future work.

PLP experiments have been used by other workers to estimate k_t.[26-28] Olaj *et al.*[27] derived an equation which relates the product of the rate of polymerization (R_p) and the weight average degree of polymerization (P_w) with the ratio k_p^2/k_t. This enables values of an overall k_t to be obtained from the one PLP–MWD experiment wherein k_p, R_p, and P_w were also determined. This technique can be problematic because it is dependent upon the accurate determination of both R_p and P_w. Difficulties arise due to the low conversions necessary for well-designed PLP experiments, and in determining P_w by GPC (the low molecular weight end of GPC traces for polymers derived from PLP experiments can be particularly difficult to analyse accurately). Moreover, the method as defined yields no information on the chain-length dependence of k_t.

Buback *et al.*[28] estimated primary radical concentrations (derived from AIBN) and subsequently an average k_t by following monomer consumption and the formation of initiator-derived products by FT-IR. This method has limitations due to sensitivity and because it is only applicable to those few initiator systems where initiator and initiator-derived products possess resolvable IR frequencies.

In conclusion, a method of measuring the radical concentration generated per laser pulse during PLP experiments has been developed. The technique utilizes the nitroxide-trapping technique in conjunction with real-time fluorescence measurements to provide a very sensitive measure of the radicals that would initiate polymerization under PLP conditions. This knowledge allows computer modeling of polymerization kinetics to become far more powerful by enabling estimates of termination rate coefficients within PLP initiated polymerizations.

It is anticipated that the current methodology will also aid investigation of other free radical polymerization processes. In particular, the determination of initiator efficiencies, nitroxide-radical reaction rates and the study of nitroxide-mediated controlled/"living" free radical polymerization. These topics will be reported on in future communications.

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(17) The third harmonic (355 nm) of a Q-switched Nd:YAG laser (Continuum) was used as the laser source. The pulse from the laser (~8 mm diameter) was expanded and then collimated through two lenses, and passed through a square aperture (10 mm × 10 mm) immediately before entering the sample which was held in a thermostated cell holder. The samples were degassed by at least four freeze−pump−thaw cycles, and approximately 1.0 mL was placed in sealed quartz cuvettes (10 mm × 10 mm). A Perkin-Elmer LS-5 fluorimeter fitted with fiber optic light guides collected the time-resolved fluorescence. The laser, fluorimeter excitation and emission beams were orthogonal to each other. The average laser power was measured behind the sample holder (without the cell in position) with the laser pulsing at 10 Hz with the energy per pulse being calculated by dividing the average power by the repetition rate.

(18) For higher [AIBMe] (greater than $\sim 5 \times 10^{-3}$ M) it was found that the fluorescence continued to increase slowly (~5% for 5000 pulses with [AIBMe] = 5.4×10^{-3} M) under laser irradiation even after the NTEMPO was consumed and ceased only when the AIBMe was depleted. The effect can be attributed to absorption of the R-NTEMPO fluorescence by the AIBMe. The small perturbation introduced was removed by extrapolation.

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