Measurements of Primary Radical Concentrations Generated by Pulsed Laser Photolysis Using Fluorescence Detection

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Received: March 15, 1999; In Final Form: June 9, 1999

Details of a novel technique for direct real-time measurement of the primary radical concentrations generated in pulsed laser photolysis (PLP) experiments are presented. The method takes advantage of the large increase in fluorescence quantum yield that occurs when a nitroxide containing a suitable fluorophore couples with a carbon-centered radical. The technique is applied to PLP experiments which involve photolysis of azobisisobutyronitrile (AIBN) or azobis(methyl isobutyrate) (AIBMe) in the presence of 4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (NTEMPO). In these experiments, the method is shown to be capable of reliably measuring transient radical concentrations of less than 10^{-7} M. Various side reactions that might complicate the technique are considered and shown not to be of significance. The concentration of radicals generated per pulse is shown to have a linear dependence on [AIBN], [AIBMe], and laser energy per pulse (and is shown to be independent of [NTEMPO]) over a wide range of conditions encompassing those typically encountered in PLP polymerization experiments. The concentration of radicals generated per pulse increases with increasing temperature, reflecting changes in the quantum yield for radical generation. The rate of intramolecular fluorescence quenching of NTEMPO in benzene was determined to be in the range $2-4 \times 10^{10}$ s^{-1}.

Introduction

Detection and quantification of free radicals in solution is made difficult by their high reactivity (rate constants for self-reaction are usually in the range $\geq 10^7-10^9$ M^{-1} s^{-1}) and consequent low concentration (typically $<10^{-7}$ M). Conventional spectroscopic techniques (e.g., electron spin resonance spectroscopy) are generally not sufficiently sensitive to enable accurate measurement of the free radical concentrations in radical polymerization except in special circumstances.[1] Fluorescence-based spectroscopic techniques are extremely sensitive such that, given an appropriate fluorophore, very low concentrations of species can be quantified. Moreover, such methods can be applied with high spatial (e.g., microscopy), spectral, and/or temporal resolution.[2]

The present paper provides details of a novel fluorescence-based technique for quantifying free radical concentrations ($[I\bullet]_0$) generated during pulsed laser photolysis (PLP) experiments. The method takes advantage of the large increase in fluorescence quantum yield observed when a nitroxide, containing a suitable fluorophore, couples with a carbon-centered radical[3−7] to provide a direct measure of the concentration of primary radicals generated by a laser pulse. We show how potential limitations of the technique can be overcome. We also examine the spectroscopy and photophysics of one nitroxide−chromophore compound.

Our particular interest in establishing free radical concentrations formed in PLP experiments has been to apply the results in the study of free radical polymerization kinetics. A large body of work[8] has recently been carried out on the use of PLP to estimate propagation rate constants in free radical polymerization. The method was recommended by an IUPAC working party as the method of choice for obtaining these parameters.[9,10] It was proposed some time ago[11,12] that, with knowledge of the radical concentrations, it would also be possible to estimate termination rate coefficients. Previously, radical concentrations had been estimated on the basis of presumed initiator efficiencies and measured light intensities[8] or by monitoring the reaction products.[13,14] However, uncertainties inherent in such numbers are large and the need for a more direct means of establishing radical concentrations is generally recognized.[8] We recently published[15,16] two brief communications outlining the use of the present method in this application.

Fluorescence methods were previously applied in the study of polymerization to establish polymerization rates[17,18] and to indirectly determine initiator efficiencies.[19] These methods, which rely on changes in solution viscosity (and probe mobility) induced by polymer formation, cannot be applied to estimate radical concentrations in PLP experiments because of the very low conversions involved (often $\ll$1%).

Experimental Section

4-(1-naphthoyloxy)-2,2,6,6-tetramethylpiperidine-1-oxyl (NTEMPO) was synthesized and purified according to the procedure of Jones et al.[20] Azobis(methyl isobutyrate) (AIBMe) was obtained from Wako (Japan), and azobisisobutyronitrile

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10.1021/jp990892t CCC: $18.00
Published on Web 08/19/1999

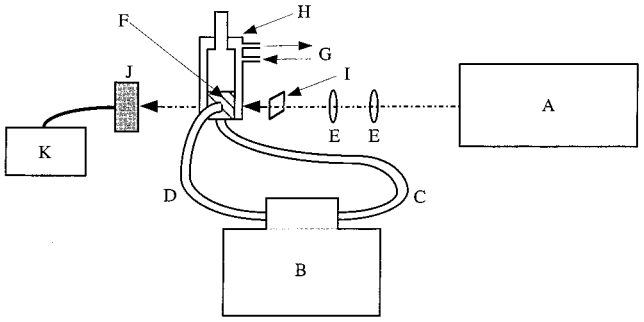
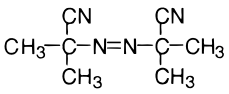
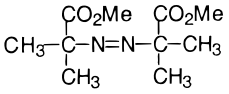


Figure 1. Schematic of apparatus used to collect fluorescence−time plots under PLP conditions. A = Nd:YAG Q-switched laser, B = fluorimeter, C = excitation fiber optic, D = emission fiber optic, E = laser beam expansion/collimating lenses, F = sample in cell, G = circulated water, H = cell holder, I = square aperture, J = beam dump/power meter, K = power meter.

(AIBN) was obtained from Schering Industrial Chemicals (U.K.).



AIBN



AIBMe

R−NTEMPO (R = $C(CH_3)_2CO_2CH_3$) was synthesized by decomposing AIBMe in the presence of NTEMPO at 60 °C for 48 h. The product was purified by column chromatography and the structure confirmed by ^{1}H NMR spectroscopy; δ_H ($CDCl_3$) 1.10 (s, 6H), 1.35 (s, 6H), 1.50 (s, 6H), 1.80 (m, 2H), 2.10 (m, 2H), 3.78 (s, 3H), 5.35 (m, 1H), 7.45−8.90 (m, 7H). R−NTEMPO (R = CH_3) was synthesized using a modified procedure of Rizzardo et al.,[21] purified by column chromatography, and the structure confirmed by ^{1}H NMR spectroscopy; δ_H (benzene-d_6) 1.18 (s, 6H), 1.22 (s, 6H), 1.60−2.05 (m, 4H), 3.50 (s, 3H), 5.45 (m, 1H), 7.2−9.50 (m, 7H). Benzene (AR grade, BDH) was distilled over sodium before use. All solutions were made up from stock solutions ($\sim 10^{-2}$ M) of NTEMPO, AIBMe, or AIBN, in benzene. Approximately 1 mL of the required solution was placed in a cell, the sample was degassed by at least four freeze−pump−thaw cycles, and 1 mL was transferred (under vacuum) to the quartz cuvette (10 × 10 mm) which was then sealed.

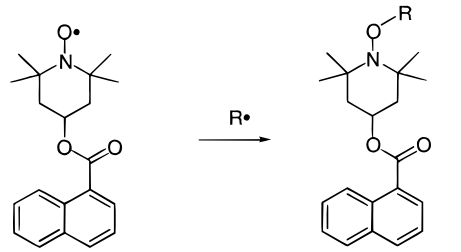
The third harmonic (355 nm) of a Q-switched Nd:YAG (Continuum, U.S.A.) was used as the laser source. The laser output (pulse frequency 0.01−10 Hz, pulse duration ~5 ns, beam diameter ~8 mm) was expanded and then collimated through two lenses, and passed through a square aperture (10 × 10 mm) immediately before entering the thermostated cell holder. A schematic of the apparatus is shown in Figure 1. Note that the fluorescence excitation and emission, and the laser beam are mutually orthogonal. The laser beam was expanded and then collimated such that the entire sample volume was uniformly irradiated, thereby minimizing radical concentration gradients.

Laser power was measured on a power meter (Ophir, Israel) placed behind the thermostated cell holder from which the laser pulse energy was then calculated. The fluorescence was collected using a Perkin-Elmer LS-5 fluorimeter with excitation and emission slits set for 10 nm band-pass. Excitation and emission wavelengths were 300 and 390 nm, respectively. The excitation beam was delivered to the sample cuvette (10 × 10 mm) in the PLP apparatus via a fiber optic placed orthogonal to the laser beam. The fluorescence was collected at right angles to both the laser and fluorescence excitation by a second fiber optic and returned to the fluorimeter.

Single photon counting detection was used to collect the fluorescence decays. A cavity-dumped picosecond dye laser (Spectra Physics, model 3500), synchronously pumped by a mode-locked argon ion laser (Spectra Physics, model 2030), was used as the excitation source. Excitation pulses [full width at half-maximum (fwhm) approximately 5 ps] at 300 nm were obtained by frequency doubling the rhodamine 6G dye laser output with a KDP angle-tuned second harmonic generating crystal. The fluorescence photons were isolated through a polarizer set at the magic angle (54.7°) and a monochromator (Jobin Yvon H-20), and were detected with a Hamamatsu (model R1564U-01) microchannel plate photomultiplier tube. The total response of the system is about 85 ps fwhm. Data were collected over 1024 channels of a Tracor-Northern multichannel analyzer. Fluorescence decays were analyzed using iterative reconvolution routines, fitting the decays using sums of exponentials functions. The success of the analysis was assessed using the usual goodness-of-fit criteria, plotted residuals, and autocorrelation functions.

Steady-state fluorescence spectra were collected using a Hitachi F-4010 spectrometer. Absorption spectra were obtained with a Hitachi 150-20 spectrophotometer.

SCHEME 1



NTEMPO
(low fluoresence)

RNTEMPO
(high fluoresence)

Results and Discussion

Technique Development. Blough et al.[3−7] demonstrated that by incorporating a suitable fluorophore and a nitroxide moiety into a single molecule, both the radical trapping and fluorescence quenching properties of the nitroxide can be turned to advantage in a technique for detecting radicals. Fluorescence from such molecules is almost fully quenched via an electron exchange mechanism which both reduces the fluorescence quantum yield and shortens the fluorescence lifetime (vide infra). However, when the nitroxide moiety in such a molecule couples with a carbon-centered radical to form an alkoxyamine, the intramolecular quenching mechanism is removed. Thus, the derived alkoxyamines exhibit fluorescence quantum yields 30−60-fold greater than the parent nitroxides.[3,6] The chemistry is exemplified in Scheme 1 which shows the reaction between the nitroxide NTEMPO and a carbon-centered radical (R•) to form an alkoxyamine R−NTEMPO.

The substantial change in fluorescence quantum yield that accompanies the trapping reaction of fluorophore−nitroxide compounds has previously been used to follow rates of alkoxyamine formation. Gerlock et al.[4] used the method to follow AIBN thermolysis in solution. Pou et al.[22] used a similar compound to observe and quantify radicals in aqueous biological systems. These studies showed that the increase in fluorescence is directly proportional to the decrease in nitroxide concentration.

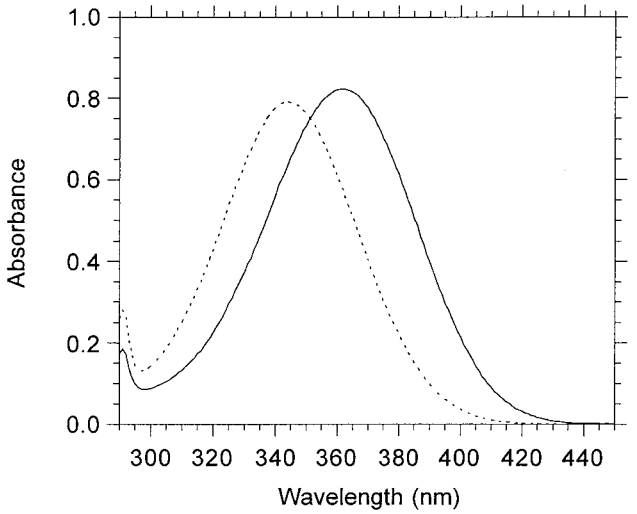


Figure 2. UV absorbance of AIBMe (—) ([AIBMe] = 3.8×10^{-2} M) and AIBN (- - - -) ([AIBN] = 5.1×10^{-2} M) in benzene.

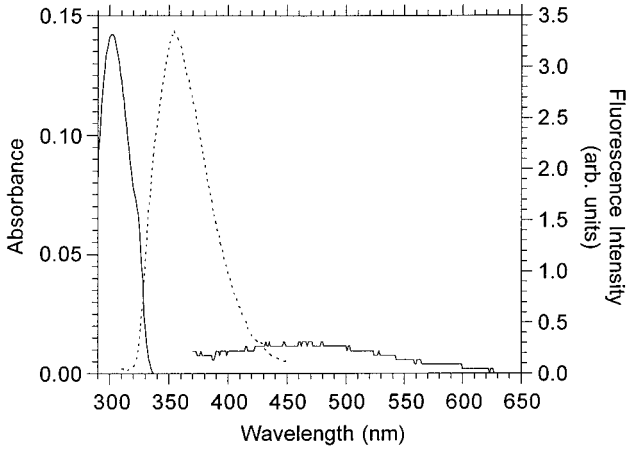


Figure 3. UV/vis absorbance of R−NTEMPO (R = $C(CH_3)_2CO_2CH_3$): naphthalene moiety (— < 370 nm) ([R−NTEMPO] = 2×10^{-4} M), nitroxide moiety (— > 370 nm) ([R−NTEMPO] = 2.1×10^{-3} M); and R−NTEMPO (R = $C(CH_3)_2CO_2CH_3$) fluorescence spectra (- - - -) ([R−NTEMPO] = 2×10^{-4} M) in benzene.

It follows that the increase in fluorescence is proportional to the increase in the concentration of alkoxyamine which, in turn, is proportional to the concentration of carbon-centered radicals generated in the experiment and which are (subsequently) trapped.

To utilize the above-mentioned chemistry to measure $[I\bullet]_0$ in PLP experiments it is necessary to carefully consider the suitability of the photoinitiators and nitroxide traps, and, in particular, the photochemistry that each compound may undergo. In the present work the wavelength of the laser used (355 nm) was chosen to be close to the absorption maxima for the azo-compound photoinitiators. Azo-initiators such as AIBN and AIBMe have absorption maxima around 350−360 nm (Figure 2). This wavelength (355 nm) also corresponds to a window of the absorption spectra of the nitroxide. Figure 3 shows the absorption and emission spectra of the nitroxide−chromophore compound NTEMPO. There is an absorption maximum at 300 nm (resulting from the naphthalene moiety) and another weaker band between 400 and 600 nm (resulting from the nitroxide moiety). Therefore, there should be minimal direct excitation of this compound by the 355 nm laser. The emission spectrum of the NTEMPO-derivatives, R−NTEMPO where R = CH_3 or $C(CH_3)_2CO_2CH_3$), span the 320−450 nm region.

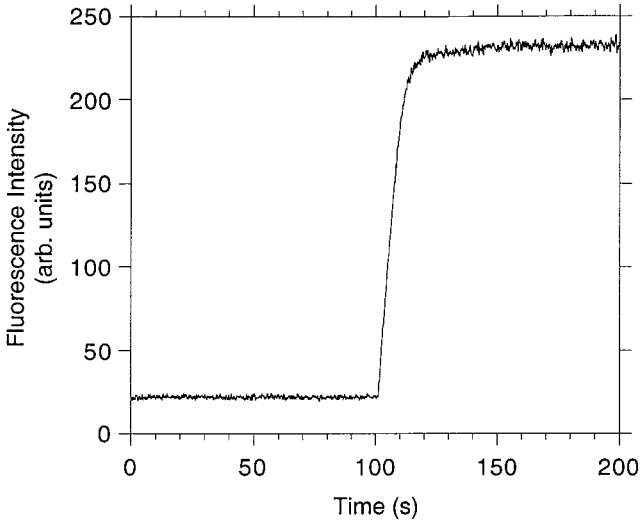


Figure 4. Fluorescence intensity−time profile for a typical PLP experiment using AIBMe as photoinitiator. [NTEMPO] = 1.656×10^{-4} M, [AIBMe] = 1.00×10^{-3} M, benzene, laser pulse rate = 10 Hz, temperature = 30 °C, laser energy = 30 mJ/pulse, laser on at 100 s, laser off at 150 s.

The increase in fluorescence that accompanies alkoxyamine formation was monitored by exciting the R−NTEMPO at 300 nm and collecting the resulting emission with a fluorimeter. It was established that excitation of the naphthalene moiety at 300 nm did not lead to a detectable change in the initiator concentration (AIBN or AIBMe) which is consistent with their absorbance at this wavelength being minimal. A wavelength of 390 nm was found to be the best choice for monitoring the emission, because at shorter wavelengths, scatter from the laser light interferes with the fluorescence measurements, whereas at longer wavelengths, the signal-to-noise ratio is too low.

Radical Concentration Measurements—AIBMe as Photoinitiator. A typical fluorescence−time plot for a PLP experiment on an AIBMe/NTEMPO/benzene mixture is shown in Figure 4. During the initial period of the experiment (0−100 s) the sample was not irradiated. This enabled a background intensity level to be recorded. In the experiment shown in Figure 4, irradiation of the sample by the laser commenced at the 100 s mark with a pulse repetition rate of 10 Hz whereupon an immediate increase in fluorescence intensity was observed. The fluorescence intensity increased steadily until ca. 110 s when the rate of increase slowed and began to asymptote at ca. 120 s. The laser irradiation was stopped at 150 s after which the fluorescence intensity remained constant.

The fluorescence intensity was observed to increase very slightly even after the point corresponding to complete consumption of NTEMPO (in the range 120−150 s). This is attributed to the AIBMe absorbing some of the NTEMPO fluorescence. Thus, as the AIBMe is consumed during the course of the experiment, the amount of reabsorption should be correspondingly lowered with a consequent increase in the fluorescence intensity. As a test of this hypothesis, a PLP experiment was performed on a AIBMe/R−NTEMPO/benzene solution (where R = $C(CH_3)_2CO_2CH_3$, [AIBMe] = 5.4×10^{-3} M, and $[R-NTEMPO]_i = 9.4 \times 10^{-5}$ M). An increase in the fluorescence intensity of approximately 5% over 5000 pulses was observed. The increase ceased once the AIBMe was depleted. The increase in fluorescence by this mechanism is quite small compared with the time scale of the PLP experiments presented here (most experiments consist of <500 pulses). This (secondary) increase can be removed by subtracting the

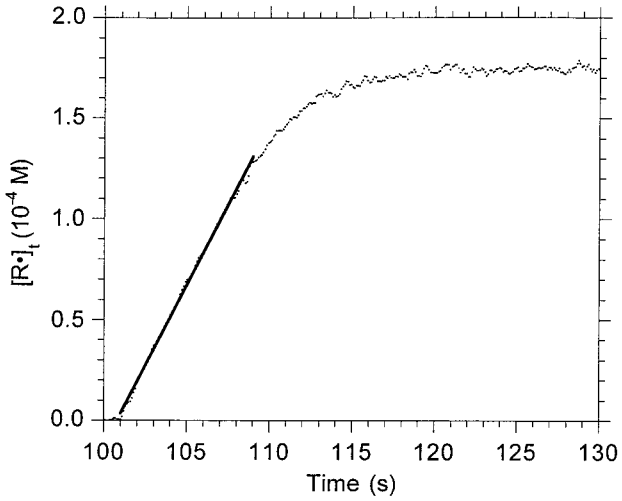


Figure 5. Cumulative radical concentration (·····; $[R\bullet]_t$) and resulting curve fit (—; $[R\bullet]_t = -0.001601 + 1.5886 \times 10^{-5} \times t$).

extrapolated straight line obtained by fitting the data in the region where the NTEMPO is depleted (between 135 and 145 s for the experiment shown in Figure 4).

A background fluorescence intensity was determined by averaging over the period prior to irradiating the sample (0−100 s). The background intensity is mostly due to scattered light with only a very small contribution from NTEMPO fluorescence. The measured fluorescence intensity was <0.5% of that of the R−NTEMPO formed in the experiments and could therefore be safely neglected during the calibration procedure (below).

The measured fluorescence intensities were converted to concentration units through eq 1.

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

where $[R\bullet]_t$ = (cumulative) radical concentration = $[R-NTEMPO]_t$, I_t = fluorescence intensity at time t, I_i = initial fluorescence intensity, I_f = final fluorescence intensity, and $[NTEMPO]_i$ = initial NTEMPO concentration.

This calibration is based on the reasonable assumption that conversion of NTEMPO to R−NTEMPO is quantitative. It has the advantage over an external calibration procedure of not being reliant on the measurement of absolute fluorescence intensities. Thus, any effects on fluorescence intensity caused by changes in cuvette position, fluorimeter lamp power, etc., are eliminated. The method also requires that there is no significant change in absorbance at the excitation wavelength (300 nm) during the course of the experiment.

Once calibration had been performed, values of $[I\bullet]_0$ were determined by fitting the linear region of the fluorescence−time plot with a straight line, and dividing the gradient by the laser repetition rate. Figure 5 shows the cumulative radical concentration−time plot for the experiment shown in Figure 4 after the background fluorescence was subtracted and the fluorescence absorption by AIBMe was accounted for. An excellent linear fit was obtained.

Values of $[I\bullet]_0$ for a range of experimental conditions are shown in Table 1. These data indicate that $[I\bullet]_0$ is not dependent upon (a) the laser repetition rate (experiments 1−3), (b) $[NTEMPO]_i$ (experiments 6−8), or (c) on changes in solvent (experiments 7 and 8). The addition of methyl methacrylate or small amounts of styrene does not affect the value of $[I\bullet]_0$. The use of larger amounts of styrene was found to interfere with the fluorescence measurements. $[I\bullet]_0$ is proportional to laser pulse energy (experiments 4 and 5, and Figure 6) and [AIBMe] (see Figure 7). Only for very high [AIBMe] ($>4 \times 10^{-3}$ M) is $[I\bullet]_0$ lower than that predicted by a simple linear relationship. The deviation for high [AIBMe] is consistent with the absorbance of the initiator causing a small but significant attenuation of the laser beam and a consequent slight lowering of $[I\bullet]_0$.

TABLE 1: Effect on Primary Radical Concentrations ($[I\bullet]_0$) of Changing $[NTEMPO]_i$, Laser Energy, Laser Pulse Repetition Rate, and Solvent (All Performed in Benzene at 25 °C)

experiment number	$[I\bullet]_0$ μM	[AIBMe] mM	$[NTEMPO]_i$ μM	laser pulse energy[a]/mJ	laser pulse rate Hz
1	2.58	1.74	51.5	30	1.0
2	2.81	1.74	51.5	30	0.2
3	2.63	1.74	51.5	30	0.01
4	4.75	2.95	200	30	0.2
5	2.63	2.95	200	15	1.0
6	1.43	1.00	41.2	30	0.2
7[b]	1.30	1.00	49.4	30	0.2
8[c]	1.38	1.02	103	30	0.2
9[d]	1.54 (1.47)	1.02	103	30	0.2

[a] Uncertainty is ±1.0 mJ. [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. [d] Contained [R−NTEMPO] = 1.01×10^{-4} M. $[I\bullet]_0$ value calculated from [R−NTEMPO] (R = $C(CH_3)_2CO_2CH_3$) given in parentheses.

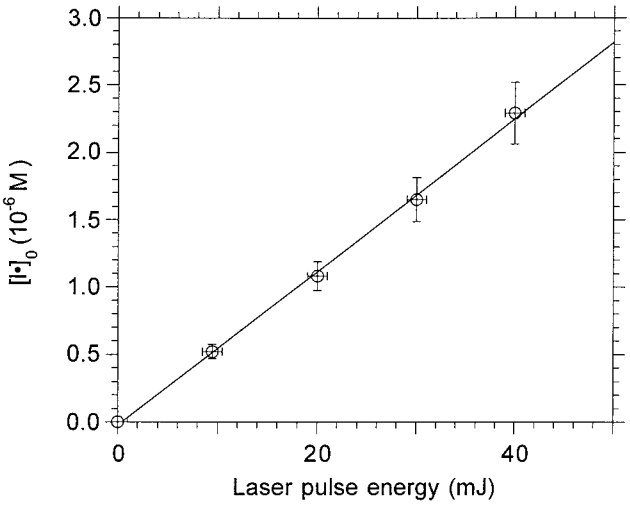


Figure 6. $[I\bullet]_0$ as a function of laser pulse energy at 25 °C, various $[NTEMPO]_i$ (error bars: abscissa ± 1 mJ, ordinate ± 10%).

Verification of the calibration method was obtained by adding a known amount of R−NTEMPO (R = $C(CH_3)_2CO_2CH_3$) to the AIBMe/NTEMPO/benzene solution and observing the fluorescence increase during the PLP experiment (experiment 9 in Table 1). There is excellent agreement between the two calibration procedures. Thus the $[I\bullet]_0$ data generated through the nitroxide−fluorescence experiments presented in this paper are behaving as expected. Error in $[I\bullet]_0$ is estimated to be <10%. The deviation from the mean in the $[I\bullet]_0$ data given in Table 1 is 5% or less for a given initiator concentration and laser energy (i.e., experiments 1−3 and also experiments 6−9). The accuracy is heavily dependent upon the initial NTEMPO concentration, which is also estimated to be within 5%.

Two further assumptions are inherent in the technique: (a) that NTEMPO traps all radicals that diffuse out of the solvent cage in which they have been generated; and (b) that NTEMPO

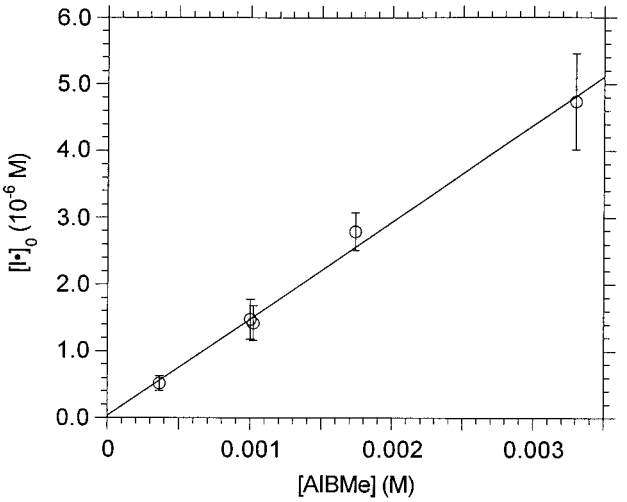


Figure 7. $[I\bullet]_0$ as a function of [AIBMe] at 25 °C (data points are the average of at least three experiments and error bars are twice the average deviation). Laser energy = 30 mJ/pulse, various $[NTEMPO]_i$.

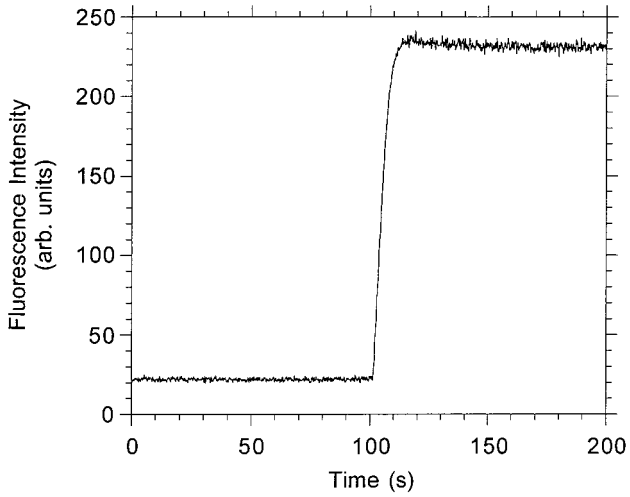


Figure 8. Fluorescence intensity time profile for a typical PLP experiment using AIBN as photoinitiator. [NTEMPO] = 8.313×10^{-5} M, [AIBN] = 9.99×10^{-4} M, benzene, laser pulse rate = 10 Hz, temperature = 30 °C, laser energy = 30 mJ/pulse, laser on at 100 s, laser off at 150 s.

does not scavenge radicals that would otherwise recombine within the solvent cage (i.e., the nitroxide does not alter the ratio of cage-to-encounter products). The validity of these assumptions can be justified in several ways. First, the rate at which nitroxides couple with carbon-centered radicals is well established[23−25] to be in the range 10^8-10^9 M^{-1} s^{-1} (the same order of magnitude as rate constants for self-reaction of small carbon-centered radicals). Thus, because the NTEMPO concentration is several orders of magnitude greater than the carbon-centered radical concentration, these radicals should react preferentially with NTEMPO. Second, our experimental findings show that radical concentrations measured with the present technique are independent of $[NTEMPO]_i$ (see Table 1). Note that the concentration of NTEMPO used in the present study is several orders of magnitude lower than that used in some studies reported in the literature[26] where it was shown that addition of nitroxide can alter the cage−encounter ratio (i.e., $<2 \times 10^{-4}$ M in this work vs $10^{-1}-10^{-2}$ M in the earlier work). Therefore, we can be confident that the nitroxide trapping technique employed here is faithfully determining the concentration of radicals that would, in the absence of nitroxide, diffuse apart to undergo reaction outside the solvent cage (for example, to initiate or terminate polymerization in the presence of added monomer).

It is known that nitroxides may abstract hydrogen if excited by low-wavelength UV (254 nm) light.[27−29] Several control experiments were carried out to establish the significance, if any, of such side reactions. In the first experiment, a solution of NTEMPO and R−NTEMPO (R = $C(CH_3)_2CO_2CH_3$) 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 redegassed and the fluorescence intensity determined. No significant change in intensity was observed. This experiment shows that NTEMPO is not converted to hydroxylamine during the irradiation period through either H-abstraction from the AIBMe or, less importantly, by disproportionation with the 1-methoxycarbonyl-1-methylethyl radicals formed from AIBMe decomposition. The air purge would be expected to oxidize any hydroxylamine formed[29] resulting in a change in the fluorescence intensity. Therefore, hydrogen abstraction is unlikely to complicate the present nitroxide trapping experiments, where the irradiation wavelength is 355 nm.

Radical Concentration Measurements−AIBN as Photoinitiator. An example of an AIBN/NTEMPO/benzene fluorescence−time curve is shown in Figure 8. The AIBN decomposes to give cyanoisopropyl radicals. A lower yield of radicals is observed in experiments with AIBN as photoinitiator with respect to similar experiments with AIBMe. This is attributed to the smaller extinction of AIBN at the wavelength used in the PLP experiments (see Figure 2). Allowing for this difference, it might be anticipated that AIBN should behave analogously to AIBMe in the experiment. However, close inspection of the data reveals that the fluorescence intensity, after the initial increase and subsequent leveling off, continues to decrease (albeit slightly) on further laser irradiation (i.e., after 120 s in Figure 8). This effect was more marked for high $[AIBN]_i$ or low $[NTEMPO]_i$.

There are at least two factors pertinent to these observations. The first relates to the lower extinction of AIBN. The absorbance of AIBN at 390 nm is ∼30% of that of AIBMe (see Figure 2), thus the reabsorption of the emitted light will be less for a given concentration of initiator. Second, the decomposition of AIBN leads to the formation of a ketenimine (Scheme 2),[30,31] which also absorbs around the 300 nm region ($\epsilon_{300\,nm} \sim 100$ M^{-1} cm^{-1}).[32] This means that as the AIBN is decomposed, not only is there an increase in fluorescence intensity because of the formation of alkoxyamine, but there is also an increase in the total absorbance at 300 nm. The amount of excitation light absorbed by the NTEMPO is therefore marginally reduced, leading to a slight lowering in fluorescence intensity. The fact that the fluorescence intensity remains constant once the laser is off (i.e., ketenimine formation is halted after 150 s) is consistent with this explanation. This complication is readily allowed for using a similar method as was used to correct for the reabsorption phenomena seen with AIBMe.

Values for $[I\bullet]_0$ again show no dependence upon $[NTEMPO]_i$ and a linear dependence upon [AIBN] for [AIBN] $<4 \times 10^{-3}$ M (see Figure 9). Thus, although the formation of ketenimine is an added complication when using AIBN as photoinitiator, error in $[I\bullet]_0$ values is negligible. We conclude that the fluorescence−nitroxide technique presented here can also be applied to reliably determine primary radical concentrations generated in PLP experiments with AIBN as the photoinitiator.

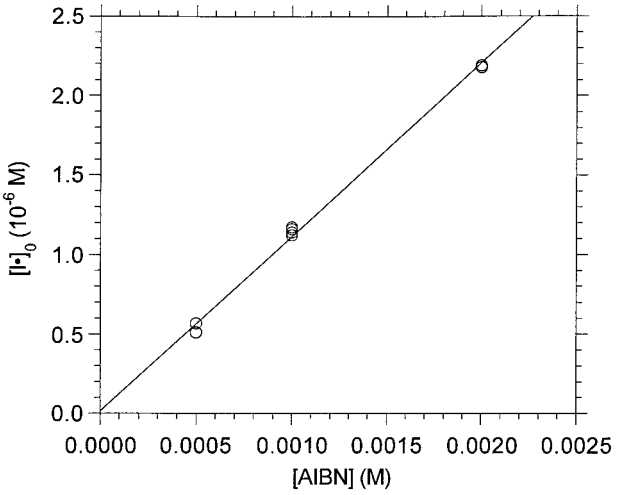


Figure 9. $[I\bullet]_0$ as a function of [AIBN] at 25 °C (data points are individual experiments). Laser energy = 30 mJ/pulse, various $[NTEMPO]_i$.

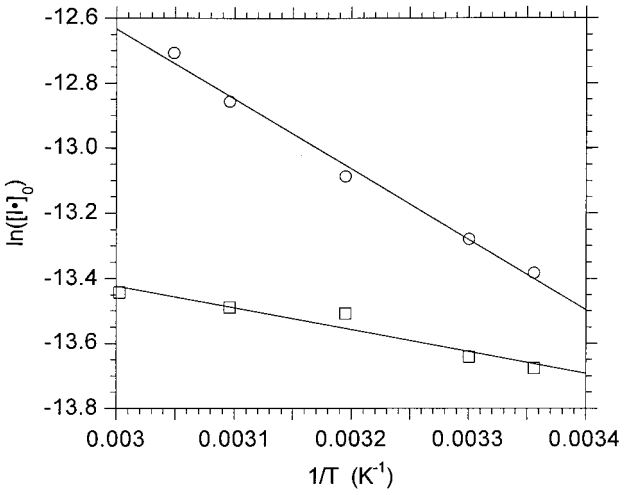
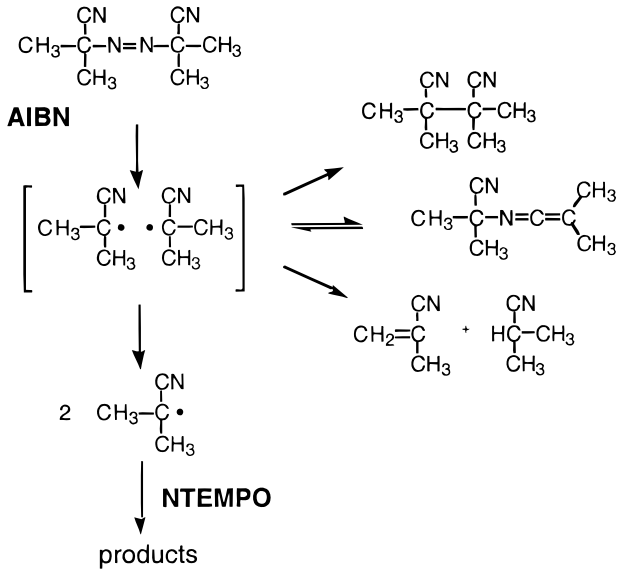


Figure 10. "Arrhenius" plot of $\ln([I\bullet]_0)$ vs temp^{-1}. ○: AIBMe; □: AIBN (data points are the average of two experiments).

SCHEME 2



Dependence of $[I\bullet]_0$ on Temperature. Figure 10 shows the variation in $[I\bullet]_0$ for AIBMe and AIBN as a function of temperature in the form of Arrhenius-type plots. The lower concentration of radicals generated from AIBN with respect to AIBMe should not be equated with a lower quantum yield for initiator decomposition (Φ) for AIBN. The lower $[I\bullet]_0$ is due, at least in part, to the smaller extinction of AIBN at the wavelength used in the PLP experiments (ϵ_{355} (AIBN) = 13.7 M^{-1} cm^{-1}; ϵ_{355} (AIBMe) = 20.9 M^{-1} cm^{-1}, see Figure 2). For both AIBMe and AIBN, an orderly increase in $[I\bullet]_0$ is observed as the temperature is increased. However, the $\ln([I\bullet]_0)$ data for AIBN has a lesser dependence on temperature than the corresponding data for AIBMe.

The dependence of $[I\bullet]_0$ on temperature is influenced by at least two parameters, (a) the quantum yield for initiator decomposition (Φ) and (b) the fraction of radicals which escape the solvent cage [the initiator efficiency (*f*)]. Both of these factors are temperature dependent. It has been reported[33] that the temperature dependence of Φ for azo-compound decomposition should not necessarily follow a simple Arrhenius relationship. This follows because the value of Φ depends not only on the rate of dissociation of the initiator into free radicals but also on the rates of other processes for deactivation of the excited state. At this stage, it is not possible to directly relate literature data for the temperature dependence of *f* to the present experiments nor is it possible to rigorously separate the individual contributions of Φ and *f* to the dependence of $[I\bullet]_0$ on temperature.

There have been many measurements of initiator efficiency (*f*) both in the context of free radical polymerization and otherwise.[26] The *f* value is usually observed to increase with increasing temperature.[13,26,34−36] However, values are dependent on the technique used (whether by analysis of polymerization kinetics, some form of radical scavenging, or other method) and even values for a given temperature vary widely.[26] It should also be noted that cage escape is a diffusion-controlled process and values of *f* are anticipated to be strongly dependent on the viscosity of reaction medium.

Time-Resolved Fluorescence on a (Sub-) Nanosecond Time Scale. To validate our method for radical concentration measurement, it is important to have some understanding of the kinetics of fluorescence quenching for molecules such as NTEMPO. Green et al.[6] previously studied the photophysics of a series of chromophore−nitroxide compounds, including NTEMPO, in several solvents (hexane, acetonitrile, methanol, and water), and concluded that the mechanism of quenching involves electron exchange enhancement of intersystem crossing. Additional discussion on the quenching mechanisms for NTEMPO and related compounds can be found in the recent paper by Herbelin and Blough.[7] In their study, Green et al.[6] found that fluorescence lifetimes for the paramagnetic compounds were difficult to measure with the instrumentation then available to them. Fluorescence lifetimes were therefore estimated from quantum yield measurements. In this way, the quenched lifetime for NTEMPO was estimated[6] to be in the range 20−100 ps, depending on the solvent. Diamagnetic analogues (Me−NTEMPO) were found to have fluorescence lifetimes in the range 0.7−7 ns. Shorter lifetimes were observed in the more nonpolar solvents.

We measured the fluorescence lifetimes of NTEMPO and a diamagnetic derivative, Me−NTEMPO (R−NTEMPO; where R = CH_3), in both methanol and benzene; a solvent not used by Green et al.[6] The fluorescence decay curves of Me−NTEMPO and NTEMPO in benzene and the resulting curve fits are shown in Figure 11. The decay of Me−NTEMPO is similar in both solvents. Decay times in methanol and benzene are ∼1.3 and ∼1.2 ns, respectively. In the case of NTEMPO, the fluorescence decay is quenched significantly in

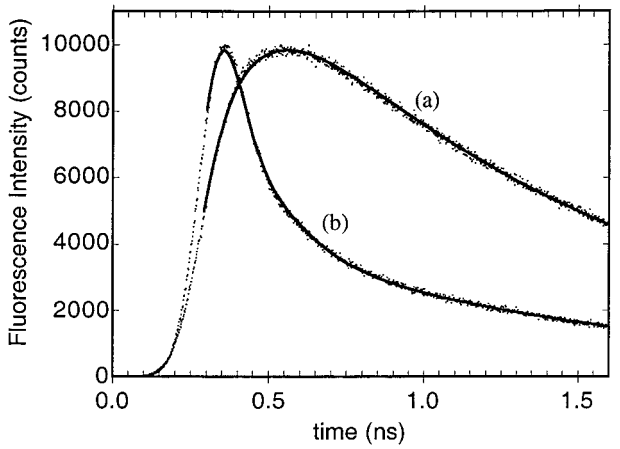


Figure 11. Fluorescence decay curves of MeNTEMPO and NTEMPO in benzene. Relevant details of the fits shown are (a) MeNTEMPO: $\tau = 1.2$ ns, (b) NTEMPO: $\tau 1 \sim 25$ ps, $\tau 2 \sim 1.2$ ns, A1 ~ 0.95, A2 ~ 0.05.

both solvents relative to the diamagnetic derivative and the decay profiles are best fitted by double exponential decay functions.

For NTEMPO in methanol the more prominent component has a lifetime of approximately 43 ps. The second, minor component has a longer lifetime of 1.34 ns which is the same (within experimental error) as the lifetime of the Me−NTEMPO in this solvent. The lifetimes in methanol compare well with the above-mentioned estimates of Green et al.[6] (54 ps and 2.8 ns, respectively). For NTEMPO in benzene, the short lifetime component decays more rapidly than in methanol (∼25 ps), whereas the long lifetime component is again similar to the lifetime of the Me−NTEMPO in this solvent (∼1.2 ns).

The longer lifetime component may therefore be attributed to a small amount of a diamagnetic impurity in the NTEMPO sample. The measured fluorescence lifetime values of NTEMPO show that the fluorescence quenching in NTEMPO is sufficiently rapid (with a quenching rate constant, $k_q \sim 2-4 \times 10^{10}$ s^{-1}) and efficient to account for the very low fluorescence quantum yield of NTEMPO.

Conclusions

This study has shown that a new technique based on the use of a radical trap containing a fluorophore (NTEMPO) and the use of fluorescence measurements can provide reliable values for primary radical concentrations generated in PLP (down to at least 10^{-7} M). The real-time measurement of radical concentrations is made feasible by the removal of the intramolecular fluorescence quenching mechanism when the nitroxide moiety traps free radicals. Primary radical concentrations generated per laser pulse were found to be proportional to both the laser energy and the photoinitiator concentration. They also increase in a predictable manner with increasing temperature. The quenching rate in benzene was found to be in the range $2-4 \times 10^{10}$ s^{-1}.

The method of determining primary radical concentrations from PLP presented herein has potential applications within the fields of free radical polymerization kinetics, initiator efficiency measurement, nitroxide/radical reaction rates and nitroxide-controlled/"living" polymerization. Certain applications will be explored in future publications. We recently published[15,16] communications outlining the use of our method in the study of free radical polymerization kinetics.

Acknowledgment. We are grateful to Dr. Ken Ghiggino (School of Chemistry, The University of Melbourne, Victoria, Australia) for the generous use of the laser equipment and helpful discussions, and to Dr. John Gerlock (Ford Motor Company, Dearborn, MI) for introducing the properties of NTEMPO to us. D.A.S also acknowledges financial support from CSIRO Molecular Science.

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