Radical Addition Rate Constants to Acrylates and Oxygen: α-Hydroxy and α-Amino Radicals Produced by Photolysis of Photoinitiators

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Abstract: Laser flash photolysis of α-hydroxy and α-amino ketones, which are used as photoinitiators in free radical polymerization, lead to the generation of a series of nucleophilic α-hydroxy and α-amino radicals. Absolute addition rate constants of these radicals to *n*-butylacrylate and oxygen were measured by laser flash photolysis employing an indirect probe technique. Crystal violet and *N,N′*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,-10-perylenedicarboximide were used as selective probe molecules for these nucleophilic initiator radicals to measure the addition rate constants to *n*-butylacrylate and oxygen, respectively. High acrylate addition rate constants of some initiator radicals were found in acetonitrile solution, e.g., dimethylketyl radical ($k_{acrylate} = 1.3 \times 10^7$ M^{-1} s^{-1}) and 2-morpholino propan-2-yl radical ($k_{acrylate} = 2.9 \times 10^7$ M^{-1} s^{-1}).

Introduction

The α-hydroxy ketones 2-hydroxy-2-methyl-1-phenylpropanone (**1a**) and 1-hydroxycyclohexyl phenyl ketone (**1b**) have been used for many years as photoinitiators for free radical polymerization.[1–4] Upon irradiation, these ketones undergo classical Type I cleavage to produce benzoyl–ketyl radical pairs with high efficiency (e.g. eq 1).[5,6]
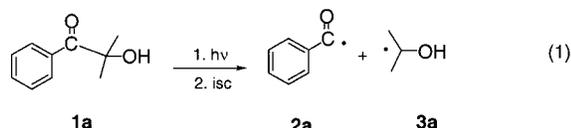
Recently, the α-amino ketones 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one (**4b**) and 2-benzyl-2-(dimethylamine)-1-[4-(4-morpholinyl)phenyl]-1-butanone (**4g**) have been successfully used to photocure pigmented coatings.[4,7] Because of their higher absorption coefficients in the 300–400 nm region, as compared to the α-hydroxy ketones **1a** and **1b**, sufficient light can be absorbed to cure pigmented coatings.

Similar to the α-hydroxy ketones **1a** and **1b**, α-amino ketones (**4**) undergo α-cleavage to produce benzoyl (**5**) and α-amino radicals (**6**) (see eq 2).[7–9]
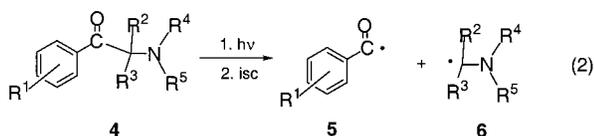
The addition of carbon-centered radicals (e.g., **2a**, **3a**, **5**, and

6) to alkenes (initiation step) is one of the most important reactions in free radical polymerization. Consequently, the factors controlling the rate constants have been the subject of much experimental and theoretical work.[10–12] Unfortunately, radicals **2a**, **3a**, **5**, and **6** have low extinction coefficients at wavelengths higher than 300 nm, and are therefore difficult to detect directly by laser flash photolysis. In addition, overlapping optical absorption of the initiator molecules (**1** or **4**), the benzoyl radicals (**2a** or **5**), and the ketyl (**3**) or α-amino radicals (**6**) causes the kinetic analysis of the transients to be problematic. Martschke et al. solved this problem by using a different precursor (2,4-dihydroxy-2,4-dimethylpentan-3-one) to produce the dimethyl ketyl radical (**3a**).[12] The benzoyl radicals (**2a** and **5**) and their kinetics can be studied without interference of other transients by time-resolved IR.[13,14] Time-resolved ESR offers another alternative method for direct detection and kinetic analysis for both radical fragments.[15] However, this method requires a strong spin polarization of the radical, which cannot be assured for most of the photoinitiators used in this work. In addition, analysis by time-resolved ESR yields the decay of the radical polarization, not the decay of the radical concentration.

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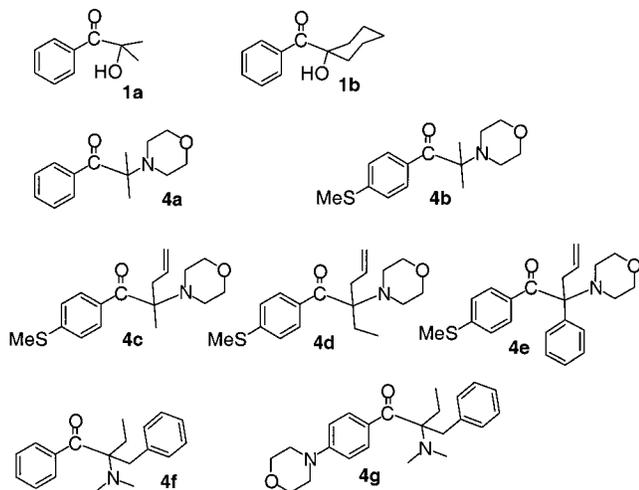
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Scheme 1. Structure of α-Hydroxy (**1a,b**) and α-Amino Ketones (**4a−g**)

Therefore, a number of corrections must be made for kinetic analysis.

Because of the problems above, we developed an indirect optical method for determination of addition rate constants of the ketyl (**3**) and α-amino radicals (**6**) to an acrylate monomer. This method is based on the use of a probe, which can react selectively and rapidly with ketyl (**3**) and α-amino radicals (**6**), leading to easy detectable intermediates by optical absorption spectroscopy.

In this paper we used a series of α-hydroxy ketones (**1a, b**) and α-amino ketones (**4a−g**) whose structures are shown in Scheme 1.
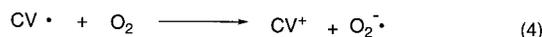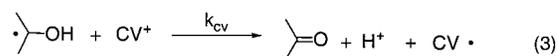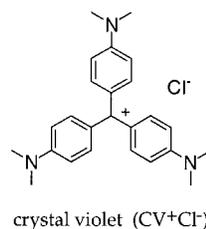
Experimental Section

Materials and Solvents. 2-Hydroxy-2-methyl-1-phenylpropanone (**1a**) (Ciba Specialty Chemicals), 1-hydroxycyclohexyl phenyl ketone (**1b**) (Ciba Specialty Chemicals), and the α-amino ketones (**4a−g**) (Ciba Specialty Chemicals) were recrystallized from ethanol. (2,4,6-Trimethylbenzoyl)diphenylphosphine oxide (BASF) was recrystallized from diethyl ether. Crystal violet (CV⁺Cl⁻) (Aldrich), *N,N′*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (DBPI) (Aldrich), *n*-butylacrylate (Polysciences, Inc.), and acetonitrile (Aldrich spectrophotometric grade) were used as received.

Laser Flash Photolysis Experiments. Laser flash photolysis experiments employed the pulses (355 nm, ca. 8 mJ/pulse, 8 ns) from a Continuum Surelite I Nd:YAG laser and a computer-controlled system that has been described elsewhere.[16] Solutions of the photoinitiators were prepared at concentrations such that the absorbance was ~0.3 at the excitation wavelength employed. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants were measured by using argon-saturated static samples contained in 1 × 1 cm Suprasil quartz cells (error limit: ±15%). Fresh solutions were prepared at each quencher concentration. Quenching rate constants with oxygen were measured as follows: Mixtures of oxygen and nitrogen of precisely known composition were prepared by using a mass flow gas controller-mixer system in connection with an Oxygen Analyzer 2566 (Illinois Instruments). A gas flow divider system diverted a small fraction of this flow through the sample in a fine stream of bubbles. Particular care was taken to keep the temperature of the sample cell constant at 24 °C during the bubbling by using a water circulator bath, to ensure a constant oxygen concentration in the sample solutions.

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Results and Discussion

Determination of the Addition Rate Constants of Ketyl (3) and α-Amino Radicals (6) to Acrylates. In the search for a probe which reacts selectively with ketyl (**3**) and α-amino radicals (**6**), we found that crystal violet (CV⁺), a triarylmethane dye, possesses the prerequisite characteristics: (i) CV⁺ possesses a strong optical absorption centered at 588 nm ($\epsilon \sim 100\,000$ M^{-1} cm^{-1} in acetonitrile) and negligible absorption at 355 nm where the photoinitiator can be excited by the third harmonic of a YAG laser, (ii) CV⁺ itself is a photostable compound, (iii) the singlet excited states of CV⁺ deactivate rapidly in nonviscous media (fluorescence lifetime: 2.3 ps in *n*-propanol[17]) as the result of rotationally induced processes, and (iv) CV⁺ is rapidly reduced by dimethyl ketyl radicals (**3a**) to CV radicals ($k_{cv} = 1.3 \times 10^9$ M^{-1} s^{-1})[18] (eq 3), which possess a strong optical absorption centered at 405 nm.[19,20]

crystal violet (CV⁺Cl⁻)

$$\cdot \!\!>\!\!-OH \ + \ CV^+ \ \xrightarrow{k_{cv}} \ >\!\!=O \ + \ H^+ \ + \ CV\cdot \qquad (3)$$

$$CV\cdot \ + \ O_2 \ \longrightarrow \ CV^+ \ + \ O_2{}^{-}\!\cdot \qquad (4)$$

The kinetics of the ketyl radical (**3**) can be monitored indirectly by monitoring the optical characteristics of the probe. In fact, two independent methods of detection of the ketyl radical reaction with the probe compound (eq 3) are possible: bleaching of the CV⁺ ground-state absorption at 550 to 630 nm or the growth of the CV radical at 405 nm.

Laser flash photolysis of **1a** ($\lambda_{ex} = 355$ nm) was performed in the presence of CV⁺ (Figure 1). During the laser flash, both benzoyl (**2a**) and ketyl radicals (**3a**) are produced (eq 1). Dimethyl ketyl radicals react with CV⁺ (eq 3) leading to ground-state bleaching of the dye (Figure 1a). Simultaneously, an optical absorption at 405 nm, assigned to the CV radical, is formed (Figure 1b) which has a growth rate equivalent to the CV⁺ decay. At longer time scales (200 μs), the CV⁺ is regenerated almost quantitatively by oxidation of CV radicals (probably by traces of oxygen) (eq 4).

The following experiment indicates that only the ketyl radical **3** (and not the benzoyl radical **2**) reacts with CV⁺. Photolysis ($\lambda_{ex} = 355$ nm) of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide leads to the generation of benzoyl and diphenylphosphinoyl radicals.[21−23] Laser flash photolysis ($\lambda_{ex} = 355$ nm) in the

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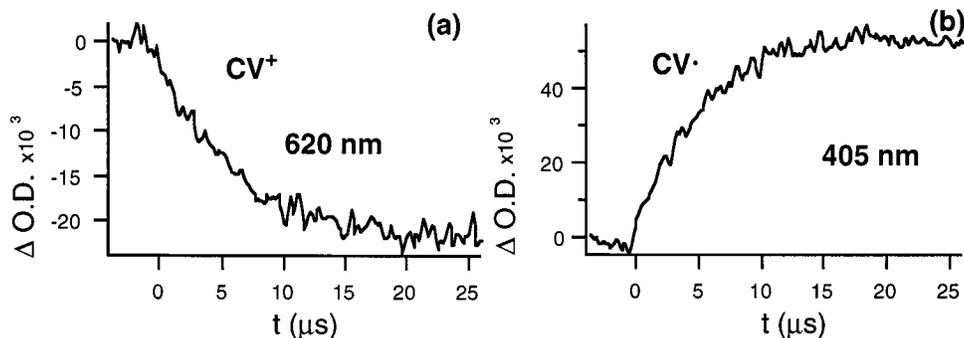
Figure 1. Kinetic traces at different wavelength following laser excitation (355 nm) of argon saturated acetonitrile solutions containing **1a** and CV$^+$ (3×10^{-5} M) at 23 °C.
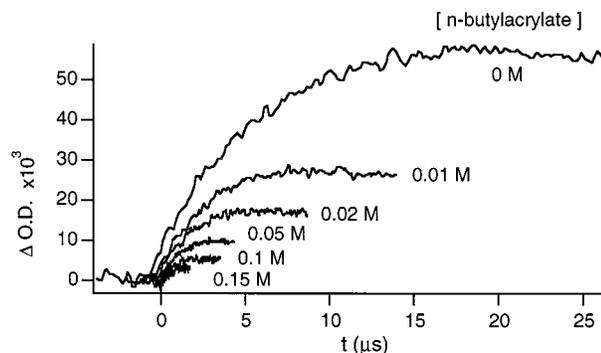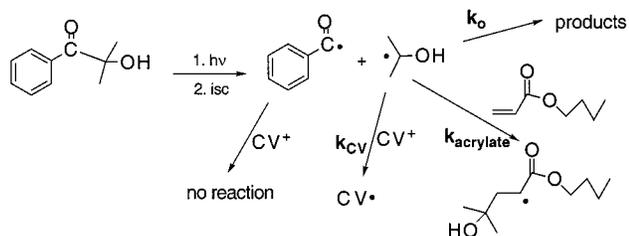
Figure 2. Kinetic traces at 405 nm following laser excitation (355 nm) of argon saturated acetonitrile solutions containing **1a** and CV$^+$ (3×10^{-5} M) and different concentrations of *n*-butylacrylate at 23 °C.

Scheme 2. Reactions of Ketyl Radicals Involved in the Indirect Method.
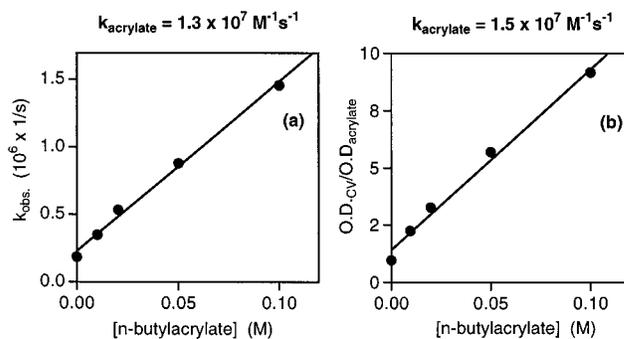
Figure 3. Pseudo-first-order rate constant of the growth of CV radicals (monitored at 405 nm) vs the *n*-butylacrylate concentration (a) and Stern−Volmer-plot (b); for experimental conditions see Figure 2.

presence of CV$^+$ showed no detectable reaction of either radicals with CV$^+$ within the first 100 μs after the laser flash, i.e., the CV$^+$ absorption was not bleached.

The selective reaction of CV$^+$ with ketyl radicals provides a specific quenching channel for ketyl radicals: the kinetics of CV$^+$ ground state bleaching and CV-radical growth indirectly is an indicator for the kinetics of ketyl radicals. This kinetic connection can be applied to determine the rate constant of the addition of ketyl radicals (**3**) to acrylates (Scheme 2). Laser flash photolysis of **1a** was performed at a fixed concentration of CV$^+$ (3×10^{-5} M) and variable concentrations of *n*-butylacrylate. As shown in Figure 2, the CV-radical growth is faster and the yield of CV-radical production decreases with increasing acrylate concentrations (see Supporting Information, p 1).

Since the growth kinetics of CV radicals (k_{obs}) reflects the decay kinetics of ketyl radicals, the addition rate constant, $k_{acrylate}$, can be determined from eq 5 and the graph shown in Figure 3 (left) ($k_{acrylate} = 1.3 \times 10^7$ M^{-1} s^{-1}). In addition, the rate constant $k_{acrylate}$ can also be extracted from a Stern−Volmer treatment of the yield of CV-radical production according eq 6, where OD$_{cv}$ is the optical density of formed CV radicals without acrylate and OD$_{acrylate}$ that with acrylate, and τ_{cv} is the observed lifetime of the CV-radical growth without acrylate

($k_{acrylate} = 1.5 \times 10^7$ M^{-1} s^{-1}). The nearly identical rate constant $k_{acrylate}$ determined from the Stern−Volmer-plot (Figure 3b) relative to the growth kinetics (Figure 3a) is striking. Furthermore, the rate constants are in good agreement with the rate constant of addition of dimethylketyl radicals to methylacrylate ($k_{methylacrylate} = 1.8 \times 10^7$ M^{-1} s^{-1}) with use of time-resolved CIDNP.[24] Employing a different precursor (2,4-dihydroxy-2,4-dimethylpentan-3-one) to produce the dimethyl ketyl radical (**3a**) and direct observation of its weak absorption at 295 nm, Martschke et al. determined a similar addition rate constant in methanol ($k_{methylacrylate} = 3.5 \times 10^7$ M^{-1} s^{-1}).[12]

$$k_{obs} = k_o + k_{CV} [CV^+] + k_{acrylate} [acrylate] \qquad (5)$$

$$\frac{O.D._{\cdot CV}}{O.D._{\cdot acrylate}} = 1 + \tau_{CV}\, k_{acrylate}\, [acrylate] \qquad (6)$$

In an earlier work by Schnabel et al.[10,11] and recently by Martschke et al.,[12] the addition of dimethylketyl radicals to acrylates was measured with styrene derivatives as competitive quenchers. The radical addition product to styrene possesses an optical absorption centered at 320 nm, which was used for kinetic analysis. Employing 2,4-dihydroxy-2,4-dimethylpentan-3-one to produce the dimethylketyl radical (**3a**), Martschke et al. determined the addition rate constant to methylacrylate in the presence of styrene in methanol solutions ($k_{methylacrylate} = 4.0 \times 10^7$ M^{-1} s^{-1}).[12] But the absorption of the styrene radical was much weaker than the CV-radical absorbance at 405 nm used in our experiments. In addition, the styrene radical absorption at 320 nm overlapped with the ground state of the initiator as well as other transient absorptions. This rendered kinetic analysis more difficult than for the CV radicals at 405 nm. Furthermore, styrene also reacts with benzoyl radicals (**2**)

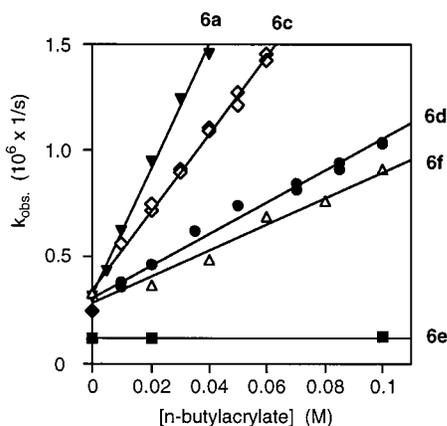(24) Batchelor, S. N.; Fischer, H. *J. Phys. Chem.* **1996**, *100*, 9794.

Figure 4. Pseudo-first-order rate constants of the growth of CV radicals (monitored at 405 nm) vs the *n*-butylacrylate concentration; laser flash photolysis of argon saturated acetonitrile solutions of **4a,c−f** ($\lambda_{ex} = 355$ nm) in the presence of CV$^+$ and different *n*-butylacrylate concentrations at 23 °C.

to form radicals, which possess the same optical absorption as the styrene radicals originating from addition of ketyl radicals (**3**) to styrene. Conversely, CV$^+$ reacts selectively with ketyl radicals (**3**) (nucleophilic radicals).

An additional requirement for the use of CV$^+$ as a probe is that the acrylate radicals, generated by addition of initiator radicals to butylacrylate, do not react with CV$^+$. This was confirmed by laser flash photolysis of (2,4,6-trimethylbenzoyl)-diphenylphosphine oxide in the presence of *n*-butylacrylate and CV$^+$, where no ground state bleaching of the dye was observed at the ms time scale (see Supporting Information, p 2), even though acrylate radicals were definitely formed.[22,25]

The use of CV$^+$ as a competitive quencher to determine addition rate constants of radicals to acrylates is not limited to photoinitiators which produce ketyl radicals (**3**). This method can also be applied to photoinitiators which produce nucleophilic radicals which then are able to reduce CV$^+$. For example, laser flash photolysis ($\lambda_{ex} = 355$ nm) of **4b** and **4g** in the presence of variable CV$^+$ concentrations showed that α-amino radicals **6b** and **6g** reduce CV$^+$ with high rate constants ($k_{cv} = 1.1 \times 10^{10}$ and 1.0×10^{10} M^{-1} s^{-1}, respectively; for experimental details see Supporting Information, p 3). These high rate constants are in agreement with the reduction of CV$^+$ by the α-amino radical of triethylamine ($k_{cv} = 1.3 \times 10^{10}$ M^{-1} s^{-1}).[19]

To determine the addition rate constants of α-amino radicals **6a−g**, laser flash experiments in the presence of CV$^+$ and *n*-butylacrylate were performed for the α-amino ketones **4a−g**. The rate constants were obtained from the growth kinetic of CV radicals at various *n*-butylacrylate concentrations by using eq 5 (see Figure 4). These results are summarized in Table 1.

The ketyl and the α-amino radicals (**3** and **6**, respectively) investigated possess a high reactivity toward unsaturated substrates and are therefore efficient initiators for free radical polymerization. Radical **6a**, generated from **4a** or **4b**, possesses the highest rate constant for acrylate addition. Introducing an allyl group (**6c**) into radical **6a** reduces the rate constant, probably due to steric effects. Increasing substitution, such as introduction of a methyl group (**6d**) or phenyl group (**6e**), further reduces the addition rate constant. In the case of the most hindered radical of our series (**6e**), no reaction with acrylates at our experimental condition was observed. Therefore, if a

Table 1. Rate Constants for Addition of Ketyl Radicals **3** and α-Amino Radicals **6** to *n*-Butylacrylate and Oxygen in Acetonitrile Solution at 23 and 24 °C, Respectively

	$k_{acrylate}$ (10^6 M^{-1}s^{-1})	k_{oxygen} (10^9 M^{-1}s^{-1})
3a	13	6.6
3b	11	5.4
6a,b	29	6.3
6c	18	4.5
6d	7.5	3.9
6e	< 0.1	2.3
6f,g	6.1	4.3

reaction were to occur, the rate constant would be $<10^5$ M^{-1} s^{-1}. In addition to steric effects, electronic effects also should cause the low reactivity of radical **6e**, which possesses a benzyl radical structure. Benzyl radicals are known to show only low reactivity toward acrylates.[31]

Determination of Oxygen Addition Rate Constants to Ketyl (3) and α-Amino Radicals (6). An important side reaction that reduces the initiation efficiency of polymerization is the addition of oxygen to radicals **3** and **6**. As mentioned above, it is difficult to obtain the rate constants by direct optical detection of radicals **3** and **6** due to their low extinction coefficients. Therefore, we used an indirect method similar to the one employed for determination of the acrylate addition rate constants. It was not possible to use CV$^+$ as an indirect probe since CV radicals react rapidly with oxygen to produce the original CV$^+$ (eq 4). Thus, a probe molecule, which possesses oxygen-stable intermediates, is necessary. We found that *N,N'*-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (DBPI) fulfills the necessary requirements. DBPI possesses strong optical absorption ranging from 450 to 540 nm, but negligible absorption at 355 nm, where the photoinitiator can be excited. DBPI itself is a photostable compound.[26] Often, because of their long lifetimes, side reactions occur from the dye triplet state. But the quantum yield of triplet formation by direct excitation is very low ($\Phi_{isc} = 0.0001$ in acetonitrile).[27]

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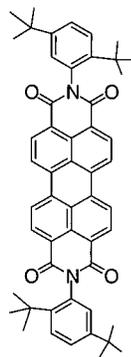
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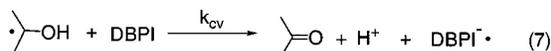
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N,N′-bis(2,5-di-*tert*-butylphenyl)-3,4,9,10-perylenedicarboximide (DBPI)

$$\cdot\!\!>\!\!-OH \; + \; DBPI \xrightarrow{\;k_{cv}\;} \; >\!\!=O \; + \; H^+ \; + \; DBPI^{-}\cdot \qquad (7)$$

DBPI is rapidly reduced by nucleophilic radicals such as dimethylketyl radicals (**3a**) to DBPI⁻ radicals ($k_{DBPI} \sim 2 \times 10^9$ M^{-1} s^{-1}) (eq 7). The DBPI⁻ radicals produced possess a strong optical absorption centered at 700 nm.[28]

Laser flash photolysis of **1a** ($\lambda_{ex} = 355$ nm) was performed in the presence of DBPI (Figure 5). During the laser flash, both benzoyl (**2a**) and ketyl radicals (**3a**) were generated (eq 1). Dimethylketyl radicals react with DBPI (eq 7) leading to ground-state bleaching of the dye at 450−540 nm (Figure 5). Concomitantly (with a growing rate that matches the DBPI decay), an optical absorption at 700 nm, assigned to the DBPI⁻ radical, was formed (Figure 5). In the presence of oxygen, the DBPI⁻ radical is stable over a longer time period (200 μs).

An additional requirement for the use of DBPI as a selective probe molecule for ketyl and α-amino radicals is the stability of DBPI against benzoyl radicals (**2**). For this experiment, we generated benzoyl radicals by laser flash photolysis of (2,4,6-trimethylbenzoyl)diphenylphosphine oxide.[21−23] Under our experimental conditions, no reaction of benzoyl radicals with DBPI was observed, i.e., the DBPI absorption was not bleached.

Laser flash photolysis of **1a** was performed at a fixed DBPI concentration (3×10^{-5} M) and variable oxygen concentrations (0 to 0.5 mM). This was achieved by saturation of the acetonitrile solution with oxygen−nitrogen mixtures with 9.1 mM as oxygen saturation concentration at 1 atm partial pressure oxygen at 24 °C.[29] The oxygen addition rate constant to the ketyl radical **3a** was obtained from the DBPI⁻ radical growth kinetic observed at 700 nm at different oxygen concentrations. Applying eq 5 to the oxygen data, the graph shown in Figure 6 with $k_{oxygen} = 6.6 \times 10^9$ M^{-1} s^{-1} was extracted. This rate constant is in good agreement with the published rate constant with acetone and 2-propanol as the ketyl radical precursor ($k_{oxygen} = 3.9 \times 10^9$ M^{-1} s^{-1}, in 2-propanol).[30] This slightly lower rate constant is expected, and attributable to the higher viscosity of 2-propanol relative to acetonitrile.

The oxygen addition rate constants to the ketyl radical **3b** and α-amino radicals **6a−g** were also measured by probing with DBPI and are summarized in Table 1. As expected, all the radicals investigated were efficiently quenched by oxygen with rate constants ranging from 2×10^9 to 7×10^9 M^{-1} s^{-1}. In the case of the α-morpholino radicals **6a−e**, a similar substituent effect was observed as for acrylate addition. Increasing substitution at the α-carbon decreases the rate constant for oxygen addition. This is probably due to steric effects.
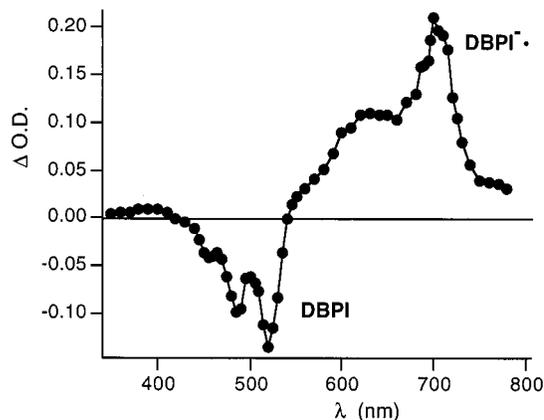

Figure 5. Transient optical absorption spectra recorded 4−9 μs following laser excitation (355 nm) of **1a** in the presence of DBPI (3 × 10⁻⁵ M) in argon-saturated acetonitrile solutions at 23 °C.
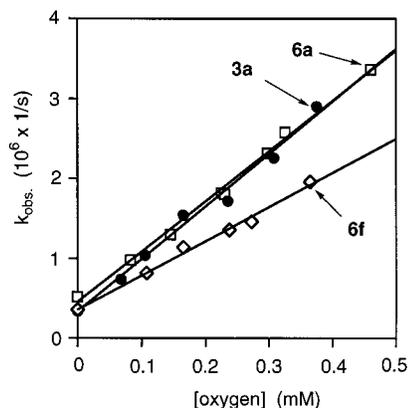

Figure 6. Pseudo-first-order growth rate constants of DBPI radicals (monitored at 700 nm) vs the oxygen concentration; laser flash photolysis of acetonitrile solutions of **1a**, **4a**, and **4f** ($\lambda_{ex} = 355$ nm) in the presence of DBPI and different oxygen concentrations at 24 °C.

Summary and Conclusion

CV⁺ and DBPI are excellent probes to determine the addition rate constants of nucleophilic radicals (**3** and **6**) to acrylates and oxygen, respectively. The α-hydroxy and α-amino radicals (**3a,b** and **6a−d,f,g**, respectively) generated by photolysis of hydroxy and amino ketones possess high rate constants of addition to acrylates. This high reactivity is the basis of their effectiveness as photoinitiators in free radical polymerization.

Supporting Information Available: Description of the experiments to ensure that benzoyl and acrylate radicals do not react with CV⁺ and laser flash photolysis results for reactions of CV⁺ with **6b,g** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.