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Journal of Photochemistry and Photobiology A: Chemistry 170 (2005) 195–201

Journal of Photochemistry and Photobiology A:Chemistry

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Polymerization initiation and transient spectrometric studies of water-soluble and -insoluble *tert*-butyl aroylperbenzoates☆

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Received 29 June 2004; received in revised form 28 July 2004; accepted 29 July 2004

Abstract

Similar lifetimes of the S_1 state ($\lambda_{max} \sim 590$ nm, τ_{S_1} -7.55 to 9.11 ps in acetonitrile) of the *tert*-butyl aroylperbenzoates (BAPs), water-insoluble (**1** and **2**) and water-soluble (**3**) having the perester moiety *para* (**1** and **3**) and *meta* (**2**) to the benzophenone carbonyl group, were obtained by ultrafast pump-probe techniques. The lifetime of the T_1 state of **2** ($\lambda_{max} \sim 510$ nm, $\tau_{T_1} > 1.2$ ns) was, however, found to be at least four times higher than those of **1** and **3** ($\lambda_{max} \sim 560$ nm, $\tau_{T_1} \sim 0.3$ ns). The effectiveness of **1**–**3** as photoinitiators for the polymerization of 1-vinyl-2-pyrrolidinone (NVP) and lauryl acrylate (LAC) was compared. Perester **2** is a better thermal and photoinitiator for NVP polymerization than either **1** or **3**. The photopolymerization of LAC initiated by either **1** or **2** is an efficient process.

Keywords: *tert*-Butyl aroylperbenzoates; Transient spectrometry; Photoinitiators; Polymerization

1. Introduction

tert-Butyl aroylperbenzoates (BAPs) are good candidates as initiators for photochemical vinyl polymerization because of the known direct dissociation of their weak peroxy (O–O) bond [1–4]. They initiate photopolymerization of monomers such as methyl methacrylate and styrene [1,5,6]. Recently, [4-(4′-*tert*-butyldioxycarbonylbenzoyl)benzyl]trimethylammonium chloride (a water-soluble BAP) has been shown to initiate the microemulsion polymerization of styrene [7].

The products from steady-state photolysis of BAPs indicate that homolytic dissociation of the peroxy bond leads to formation of the corresponding aroylbenzoyloxyl and aroylphenyl radicals as shown below [1,2]. The quantum yields of dissociation (ϕ_{diss}) of the O–O bond are almost unity for many of BAPs [1–3]. The absolute bimolecular rates of reactions of the aroylphenyl radicals ($\lambda_{max} \sim 550$ nm, $\tau \sim 0.4$–0.6 μs in CCl_4) with several quenchers including monomers such as methyl methacrylate, 1-vinyl-2-pyrrolidinone (NVP), and lauryl acrylate (LAC) range from 7.56×10^7 to $1.68 \times 10^9\ M^{-1}\,s^{-1}$ at room temperature [4].

$$\mathrm{ArCOPhCOOOCMe_3} + h\nu \rightarrow {}^1[\mathrm{BP}]^*$$

$${}^1[\mathrm{BP}]^* \rightarrow {}^3[\mathrm{BP}]^* \rightarrow \mathrm{ArCOPhCOO}^\bullet + {}^\bullet\mathrm{OCMe_3}$$

$$\mathrm{ArCOPhCOO}^\bullet \rightarrow \mathrm{ArCOPh}^\bullet + \mathrm{CO_2}$$

Transient spectrometry revealed that rapid intersystem crossing (ISC) of the S_1 state of BAPs ($\lambda_{max} \sim 590$ nm, $\tau_S \sim 7$–9 ps) produces the T_1 state ($\lambda_{max} \sim 540$–560 nm, $\tau_T \sim 0.6$–0.7 ns in benzene), the lifetime of which is solvent dependent [4,8,9]. The triplet excited energy initially resident on the benzophenone moiety needs to be dissipated intramolecularly in order that the O–O bond of the BAPs cleaves homolytically. It has been suggested that such an energy transfer can occur to a triplet excited repulsive state of the O–O bond [8]. However, the multi-picosecond lifetimes of the triplet states of BAPs, which have the perester moiety *para* to the benzophenone carbonyl group, indicate that such an energy transfer is not an instantaneous process [4,8].

☆ Contribution no. 529 from Center for Photochemical Sciences.

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doi:10.1016/j.jphotochem.2004.07.022

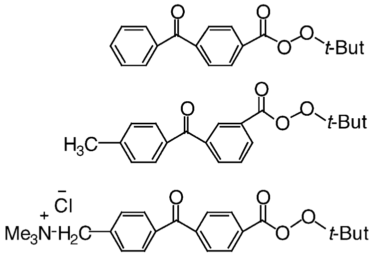


Fig. 1. Chemical structures of *tert*-butyl aroylperbenzoates.

It is known that in the excited triplet state of benzophenone, electron density on the *para* position is significantly higher than that on the *meta* position [10]. Thus, the location of the perester moiety in BAPs (either *meta* or *para* to the benzophenone carbonyl group) can affect the rates of the triplet energy transfer and, hence, dissociation of the O–O bond.

In this paper, we compare results obtained by ultrafast pump-probe investigation of *tert*-butyl (4-benzoyl)perbenzoate (**1**), *tert*-butyl 3-(4′-methylbenzoyl)perbenzoate (**2**), and [4-(4′-*tert*-butyldioxycarbonyl-benzoyl)benzyl]-trimethylammonium chloride (**3**) (Fig. 1). Results obtained from nanosecond laser flash photolysis (LFP, pulse width ∼7 ns) of **3** in different solvents are presented and compared with those of water-insoluble BAPs (**1** and **2**).

The applicability of the BAP photoinitiator system is further exemplified by its use in the polymerization of NVP, a hydrophilic, nonionic monomer and LAC, a highly hydrophobic, non-polar, bulky monomer. Polymerization data allowed us to compare the initiation activities of **1**–**3**. Monomer to polymer conversion data clearly indicate that **1** and **2** are better photoinitiators for LAC polymerization than several commercial photoinitiators.

2. Experimental

2.1. Materials

The synthesis of **1** and **2** has been reported previously [1,4]. **3** was synthesized following a literature procedure [7]. High-pressure liquid chromatography (HPLC) grade water and spectrometric grade acetonitrile and chloroform were used as solvents for LFP experiments. NVP (Antara Chemical) was distilled to remove the radical inhibitor before use. LAC (Scientific Polymer Products) containing monomethyl ether hydroquinone (MMHQ) as the radical inhibitor was used as received.

2.2. Phosphorescence

The phosphorescence spectra were recorded in EPA glass (diethyl ether:isopentane:ethanol, 5:5:2) at 77 K using a Spex 1934D3 phosphorimeter coupled to a Fluorolog®-3 spectrometer; the excitation wavelength was 350 nm. Phosphorescence quantum yields (ϕ_{Ph}) were determined according to the general procedure using benzophenone as reference [11]. The ϕ_{Ph} reported are normalized values.

2.3. Transient spectrometry

The laser system and apparatus for the ultrafast transient absorption spectroscopy experiments has been described elsewhere [8]. The output of a Ti:sapphire laser (Spectra-Physics, Hurricane) (fwhm ∼ 150 fs) was steered into an optical parametric amplifier (OPA-800C, Spectra-Physics) to obtain the 335 nm excitation wavelength. For these experiments sample solutions were prepared to have an absorbance of 0.8–1.1 at the excitation wavelength in the 2 mm flow cell and were used without degassing. Kinetic traces at appropriate wavelengths were assembled from the accumulated spectral data.

Details of the nanosecond LFP setup were provided earlier [12]. The excitation pulse (355 nm, ∼12 mJ/pulse) was the third harmonic of a Q-switched Nd:YAG laser. The excitation pulse width was ∼7 ns. The sample solutions showing an absorbance in the range of 0.17–0.24 at the excitation wavelength in 1 cm^2 quartz cuvettes were used and degassed continuously with argon throughout the experiments. Fresh samples were used for obtaining each kinetic trace.

2.4. Polymerization

Emission from a xenon short arc lamp (75 W) was used to induce the photopolymerization. The transmittance was ∼70% at 340 nm and ∼40% at 320 nm. A Galaxy Series FTIR 5000 spectrophotometer was used to record the infra-red (IR) spectra. A solution of monomer and photoinitiator was placed between two glass windows separated with a 0.75 mm spacer and the whole setup was tightly held in a mount. The incident light was focused on to this sample cell using an optical mirror. The IR absorption spectrum was recorded before irradiation. The sample was then irradiated and the IR absorption spectrum recorded again. To minimize thermal polymerization that might be induced by heating of the sample, the glass window was cooled from outside by a continuous flow of cold air. In the case of NVP, the degree of cure was determined by comparing the area of the peak at 6175 cm^{-1} (the vinylic C–H stretch) before and after irradiation using the following equation [13]:

$$\%\,\mathrm{Conversion} = \left[\frac{A_0 - A_t}{A_0}\right] \times 100$$

where A_0 is the area before irradiation and A_t the area after irradiation for time t.

The samples were irradiated without degassing. Control experiments were carried out to ensure that no photopolymerization occurred in the absence of the photoinitiator or light. The peak at 6162 cm^{-1} was monitored to follow the degree of polymerization for LAC. For bulk polymerization, the initial rate of polymerization (R_{p}) was calculated from the polymerization conversions less than 10% using the following equation:

$$R_\mathrm{p} = [M_0]\frac{\mathrm{d}\alpha}{\mathrm{d}t}$$

where M_0 is the monomer initial concentration, and α the polymerization conversion.

A slope ($\mathrm{d}\alpha/\mathrm{d}t$) was obtained from plots of polymer conversion against irradiation time, while $[M_0]$ for NVP was calculated to be 9.4017 mol l^{-1} at room temperature. The polymer conversions are average values of at least two experimental runs. All photopolymerization experiments, as well as transient absorption spectrometric experiments, were carried out at room temperature (22 ± 2 °C).

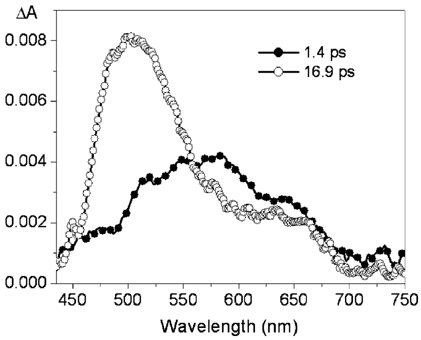


Fig. 3. Transient absorption spectra obtained from the 335 nm pump-probe experiment of **2** (6.02×10^{-3} M in acetonitrile), recorded 1.4 and 16.9 ps after the laser pulse.

3. Results and discussion

3.1. Phosphorescence

The absorption spectra of **1**–**3** recorded in acetonitrile or chloroform are similar to that of benzophenone. The phosphorescence spectra of **2** and **3** recorded in EPA are shown in Fig. 2. The phosphorescence spectra of **1**–**3** are also similar to that of benzophenone, clearly indicating that the lowest triplet transitions of **1**–**3** are n,π* in character. The phosphorescence quantum yields (ϕ_Ph) are 0.05, 0.07, and 0.22 for **1**, **2**, and **3**, respectively. The ϕ_Ph of **1** is similar to that reported [6]. The triplet energy deduced from the 0–0 band of the phosphorescence spectra was found to be higher for **2** (69 kcal/mol) than for **1** (68 kcal/mol) and **3** (66 kcal/mol) [14]. This is similar to the previous observation of higher n,π* triplet energy of *m*-cyanobenzophenone and methyl 3-benzoylbenzoate than that of *p*-cyanobenzophenone and methyl 4-benzoylbenzoate, respectively [15].

3.2. The S_1 and T_1 states

Details of the $S_1 \rightarrow S_n$ and $T_1 \rightarrow T_n$ transitions of **1** and other BAPs containing the perester moiety at the position *para* with respect to the benzophenone carbonyl group were provided previously [4,8]. The S_1 state of these BAPs absorbs (λ_max −590 nm in acetonitrile and benzene) at a higher wavelength than at which the T_1 state absorbs ($\lambda_\mathrm{max} \sim 560$ nm) [4,8]. This is similar to the behavior of the S_1 and T_1 states of benzophenone and *p*-iodobenzophenone [16]. Ultrafast pump-probe experiments of **2** in acetonitrile produced similar transient absorption spectra; the $S_1 \rightarrow S_n$ transition takes place at $\lambda_\mathrm{max} \sim 590$ nm and the $T_1 \rightarrow T_n$ transition takes place at $\lambda_\mathrm{max} \sim 510$ nm (Fig. 3). The transient spectra obtained from **3** in acetonitrile under similar experimental conditions (Fig. 4) are similar to those obtained for **1** and for *tert*-butyl 4-(4′-bromomethylbenzoyl)perbenzoate [4,8]. Thus, positioning the perester functionality *meta* causes a blue shift (~50 nm) in the λ_max of the $T_1 \rightarrow T_n$ transition of **2** as compared to that of **1** and **3**. It is noted that not only the S_0–T_1 energy gap, but also the T_1–T_n energy gap is higher for **2** than for **1** and **3**.

The lifetimes of the S_1 (τ_{S_1}) and the T_1 (τ_{T_1}) states of **1**–**3** were calculated by monitoring the rise and decay at the λ_max of the T_1 state (Table 1). There are no differences in the τ_{S_1} of **1**, **2**, or **3**. The τ_{T_1} values of **1** and **3** are also similar. Nevertheless, the τ_{T_1} of **2** (>1.2 ns) is at least four times higher than those of **1** (0.32 ns) and **3** (0.33 ns) in acetonitrile [17]. Since decay of the T_1 state of BAPs is associated with the intramolecular energy dissipation from the benzophenone moiety to the O–O bond and consequent dissociation of the later,

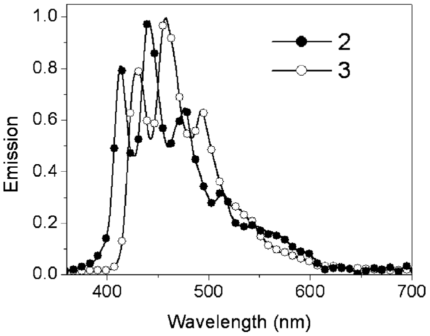


Fig. 2. Normalized phosphorescence spectra of **2** and **3** measured in EPA (5:5:2, diethyl ether:isopentane:ethanol) at 77 K; excitation wavelength −350 nm.

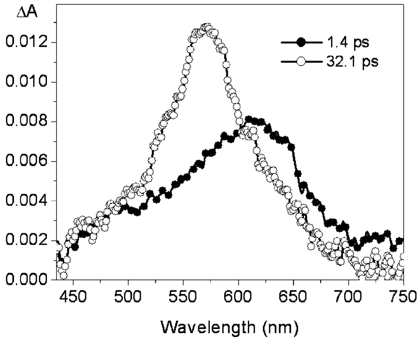
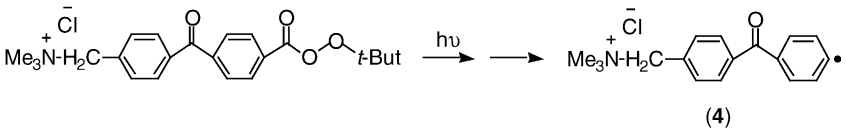


Fig. 4. Transient absorption spectra obtained from the 335 nm pump-probe experiment of **3** (1.71×10^{-2} M in acetonitrile), recorded 1.4 and 32.1 ps after the laser pulse.



Scheme 1.

Table 1
Lifetimes of the singlet (τ_{S_1}) and triplet (τ_{T_1}) states of the BAPs[a]

BAP	τ_{S_1} (ps)	τ_{T_1} (ns)
1[b]	9.11 ± 0.48	0.32 ± 0.01
2	9.09 ± 0.39	>1.2
3	7.55 ± 0.44	0.33 ± 0.02

[a] Excitation wavelength, 335 nm; solvent, acetonitrile.
[b] Ref. [8].

such energy transfer seems slower in the case of **2** than in the case of **1** or **3**. A similar intramolecular triplet energy transfer has resulted in the lower rate of cleavage of the C–I bond of *m*-iodobenzophenone than that of *p*-iodobenzophenone [18].

Decomposition of BAPs may involve a transition state that evolves as the T_1 state proceeds to radicals [8]. The lower rate of intramolecular energy dissipation in **2** relative to the cases of **1** and **3** indicates that the activation energy of the transition state of **2** may be higher than that of **1** or **3**. It may also be possible that the triplet state of **2** is more polar as compared to that of **1** or **3**. In such a case the triplet state of **2** would be more stabilized in a polar solvent like acetonitrile. Interestingly, the quantum yields of dissociation of the O–O bond of **1** and **2** are similar [3], indicating that the efficiency of energy transfer is almost the same in both BAPs irrespective of the position of the perester moiety.

3.3. *Aroylphenyl radicals*

The 4-benzoylphenyl and 3-(4′-methylbenzoyl)phenyl radicals obtained from LFP of **1** and **2**, respectively, are known to have absorption in the mid-UV-visible region (λ_{max} −550 nm) [4]. Analogous to this, a broad transient absorption having a maximum at 550 nm was obtained when **3** was laser flash photolysis (pulse width ~ 7 ns, ~15 mJ/pulse) in water (Fig. 5). Unlike the mono-exponential decay of the 550 nm transient observed in the case of LFP of **1** and **2** in different solvents, the decay monitored at 550 nm was found to be bi-exponential in the case of **3** in water. The shorter lifetime (~0.34 μs), which is similar to the lifetimes of the other aroylphenyl radicals [3,4], can be assigned to the corresponding aroylphenyl radical (**4**, Scheme 1). The origin of the longer lifetime component (~3.76 μs) is not clear.

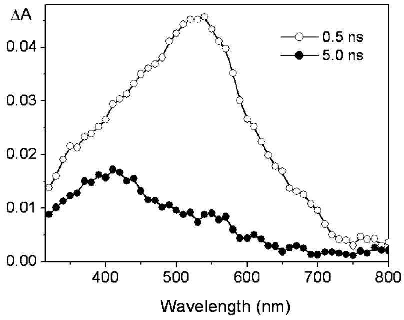


Fig. 5. Transient absorption spectra obtained from 355 nm laser flash photolysis of **3** (1.35×10^{-3} M) in water, recorded 0.5 and 5.0 ns after the laser pulse.

When chloroform or acetonitrile was used as the solvent, similar 550 nm transients were observed during LFP of **3**. The kinetics at 550 nm followed an almost mono-exponential decay in both solvents. Thus, it seems that only **4** appeared in these solvents. **4** shows solvent dependent lifetimes (Table 2) as do 4-benzoylphenyl and 3-(4′-methylbenzoyl)phenyl radicals [4]. The lifetime of **4** (τ −0.22 μs) measured in acetonitrile is comparable to that of the 4-benzoylphenyl radical (τ −0.21 μs in acetonitrile) and the 3-(4′-methylbenzoyl)phenyl radical (τ −29 μs in acetonitrile). An absorption that was almost without decay was also observed in these solvents at ~330 nm during LFP of **3**. This may be due to the light absorbing transients that are assumed to form during photolysis of benzophenones [19].

3.4. *Polymerization [20]*

1-Vinyl-2-pyrrolidinone (NVP, Fig.6) was chosen as the monomer for a comparative study of photopolymerization initiated by **1**–**3**, since both water-insoluble as well as water-soluble BAPs dissolve in it. Furthermore, NVP is an important monomer for medical use and adhesive enhance purposes and has moderate reactivity [21]. The aroylbenzoyloxyl and aroylphenyl radicals are considered to be the chain-initiating radicals in polymerization processes initiated by BAPs [22]. Results obtained from **1**- and **2**-initiated photopolymerization of lauryl acrylate (LAC Fig. 6) show that these BAPs are efficient photoinitiators for acrylate polymerization.

3.4.1. *Photopolymerization*

Each of the BAPs (**1**–**3**) initiated the photopolymerization of NVP (Fig. 7). The efficiencies of initiation of polymerization by **1** and **3** were almost similar, as reflected by similar monomer to polymer percentage conversions at different irradiation times (Table 3). The initial rates of polymerization

Table 2
Lifetimes (τ) of **4** in different solvents

Solvent	Concentration of **3** (M)	τ (μs)
H_2O	1.35×10^{-3}	0.34 ± 0.03
CH_3CN	6.32×10^{-3}	0.22 ± 0.01
$CHCl_3$	3.69×10^{-3}	0.19 ± 0.01

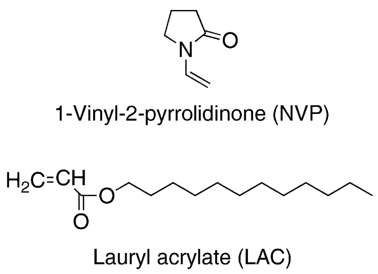


Fig. 6. Chemical structures of monomers.

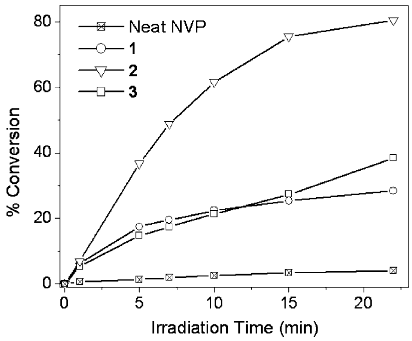


Fig. 7. Photopolymerization of NVP initiated by **1** (9.67×10^{-5} mol/g), **2** (9.06×10^{-5} mol/g), and **3** (9.76×10^{-5} mol/g).

(R_p) were also similar for **1** and **3**. Under similar conditions, the R_p for **2** was found to be only slightly higher than those of **1** and **3**. Nevertheless, the percentage polymer conversions, especially at later irradiation times, were much higher in the case of **2** than when **1** or **3** were used as photoinitiators. Thus, **2** is a better photoinitiator than **1** and **3**.

Producing higher or lower concentration of the polymerization-initiating radicals may not be the reason for the difference observed in the photoinitiation activities of **1** and **2**. The quantum yields of dissociation of the O–O bond of **1** and **2** are similar in benzene [3]. Slow but efficient production of the chain-initiating radicals as reflected by the lower rate of decay of the T_1 state of **2** than those of **1** or **3** may be the reason for its higher initiation efficiency. Nevertheless, it is possible that **1** and **2** decompose with different efficiencies in the presence of NVP. It is also possible that the secondary radicals or chain propagating radicals produced in the case of **2** and NVP are more reactive than that produced in the case of **1** and NVP or **3** and NVP.

Both **1** and **2** showed similar photoinitiator activities for the polymerization of LAC (Table 3). At similar concentrations of **1** and **2**, percentage conversions were nearly the same (**1b** and **2** in Fig. 8). This is in agreement with the similar quantum yields of dissociation of the O–O bond of these BAPs. The photopolymerization of LAC with either **1** or **2** is a rapid process. With the pyrenebutyltrimethylammonium/triethyl amine system a nearly 3.7 times higher rate of polymerization of 2-hydroxyethyl methacrylate than that of NVP has been reported [23]. This initiator exploits an electron transfer process to generate radicals. The enhancement in the efficiency of the photopolymerization of LAC than of NVP is much greater with **1** and **2**. LAC was more than 90% converted to polymer within 60 s of irradiation even at photoinitiator concentrations as low as 1.28×10^{-5} mol/g (0.004 wt%) of **1** and 1.32×10^{-5} mol/g (0.004 wt%) of **2** (Table 3). When higher concentrations of **1** (9.4×10^{-5} mol/g) were used (**1a** in Fig. 8), more than 90% conversion was achieved in less than 20 s of irradiation.

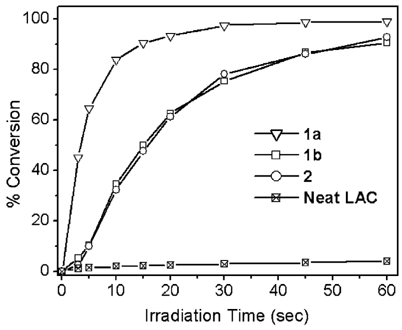


Fig. 8. Photopolymerization of LAC (containing MMHQ) initiated by **1a** (9.40×10^{-5} mol/g), **1b** (1.28×10^{-5} mol/g), and **2** (1.32×10^{-5} mol/g).

The polymer conversion data also indicate that BAPs are a better and efficient photoinitiator system for LAC than are benzoin methyl ether [24], *N*-acetyl-4-nitro-1-naphthylamine/dimethylaniline [25], and Michler's ketone/benzophenone or several other benzophenone based photoinitiators [26]. At the same time, the thermal polymerization of LAC using **1** or **2** as initiators was found to be an extremely slow process. At the 0.004 wt% concentration of **1** and **2**, for example, only 3 and 5% conversions, respectively, were observed even after 1 h of heating at 70 °C.

3.4.2. *Thermal polymerization*

The thermal polymerization of NVP was carried out at 70 °C. The efficiency of **1**–**3** as thermal initiators (Fig. 9) follows the same pattern as observed for the photopolymerization. **1** and **3** provided similar percentage conversions while

Table 3
Initial rates of BAPs-initiated NVP photopolymerization (R_p) and percentage conversions of NVP and LAC

BAP	% Conversion of NVP					% Conversion of LAC			
	Concentration (mol/g)	R_p (mol l^{-1} s^{-1})	Time of irradiation			Concentration (mol/g)	Time of irradiation		
			5 min	10 min	22 min		10 s	20 s	60 s
1	9.67×10^{-5}	8.39×10^{-3}	17.46	22.49	28.42	1.28×10^{-5}	34.49	62.61	90.53
2	9.06×10^{-5}	1.04×10^{-2}	36.77	61.63	80.55	1.32×10^{-5}	32.42	61.17	92.71
3	9.76×10^{-5}	7.09×10^{-3}	14.74	20.31	38.37	–	–	–	–

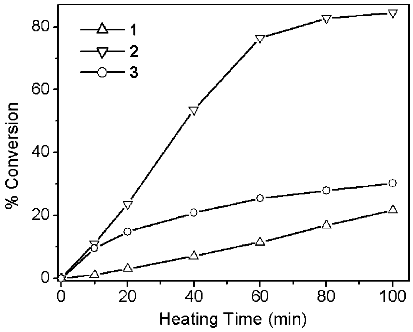


Fig. 9. Thermal polymerization of NVP initiated by **1** (9.50×10^{-5} mol/g), **2** (9.06×10^{-5} mol/g), and **3** (9.76×10^{-5} mol/g).

2 turned out to be a better thermal initiator (Table 4). After 100 min of heating, for example, the percentage conversion obtained with **2** (84.5%) was much higher than that obtained with **1** (21.8%).

The thermal polymerization data also indicate that the percentage conversions are higher only during later times of heating in the case of **2**. This again suggests that the secondary radicals or chain-propagating radicals produced in the case of **2** and NVP are more reactive than those produced in the case of NVP and the BAPs with the perester at the *para* position.

The thermal polymerization of NVP initiated by each of the BAPs seems slower than the corresponding photopolymerization under the experimental conditions used for photo and thermal processes. For example, when **2** was used as the photoinitiator, 80.5% conversion of NVP was observed after 22 min of irradiation (Table 3). To obtain similar percentage conversion during the thermal polymerization, the sample had to be heated at 70 °C for ~100 min, even though **2** is a better thermal initiator too. A similar observation of a lower rate of thermal polymerization (2.0×10^{-5} mol l^{-1} s^{-1}) than that of photopolymerization (7.0×10^{-4} mol l^{-1} s^{-1}) of methyl methacrylate has been reported for **1** [5c]. The slower thermal decomposition of BAPs than their photochemical decomposition [1] is likely the reason for the slower thermal polymerization.

3.4.3. *Effect of concentration of the photoinitiator* 1

Increasing the concentration of **1** enhanced the percentage conversion during the photopolymerization of NVP. At a concentration of 1.27×10^{-5} mol/g (0.38 wt%), the conversion was 16.6% after 22 min of irradiation (Table 5). At higher concentration of **1**, for example 1.29×10^{-4} mol/g (3.84 wt%), the conversion increased to 36.2% after the same time of irradiation. With the increase in the concentration of the photoinitiator, the chain-initiating radicals are formed in higher amounts, thereby enhancing the monomer to polymer conversion. The R_p values also increased as the concentration of **1** was increased (Table 5). A linear relationship was observed between the R_p values and the square root of the concentration of **1** with a slope of 0.5.

Table 4
Percentage conversions of NVP following thermal polymerization

BAP	Concentration (mol/g)	% Conversion		
		20 min[a]	60 min[a]	100 min[a]
1	9.50×10^{-5}	2.96	11.47	21.83
2	9.06×10^{-5}	23.65	76.53	84.55
3	9.76×10^{-5}	14.83	25.40	30.26

[a] Time of heating.

Table 5
Initial rates of photopolymerization (R_p) and percentage conversions of NVP at different concentrations of **1**

Concentration (mol/g)	R_p (mol l^{-1} s^{-1})	% Conversion		
		5 min[a]	10 min[a]	22 min[a]
1.27×10^{-5}	5.84×10^{-3}	11.84	12.74	16.60
3.61×10^{-5}	6.75×10^{-3}	14.94	17.95	21.96
6.72×10^{-5}	7.86×10^{-3}	16.26	21.15	27.15
9.67×10^{-5}	8.39×10^{-3}	17.46	22.49	28.42
1.29×10^{-4}	9.68×10^{-3}	21.24	25.92	36.20

[a] Time of irradiation.

4. Conclusions

Ultrafast pump-probe (pulse width ~ 150 fs) experiments yielded similar rates of $S_1 \rightarrow T_1$ ISC of **1**–**3** in acetonitrile ($k_{S_1 \rightarrow T_1} \sim 1.1 \times 10^{11}$ s^{-1}). The $T_1 \rightarrow T_n$ transition of **2** (λ_{max} −510 nm) was observed to be blue shifted compared to that of **1** and **3** ($\lambda_{max} \sim 560$ nm). The rate of decay of the T_1 state of **2** ($\tau_{T_1} > 1.2$ ns) was observed to be at least four times lower than that of **1** (τ_{T_1} −0.32 ns) and **3** (τ_{T_1} −0.33 ns). Dissociation of the O–O bond produces the aroylbenzoyloxyl and aroylphenyl radicals that are capable of inducing the polymerization of NVP and LAC. The corresponding aroylphenyl radical (**4**, λ_{max} −550 nm) obtained from LFP (pulse width ~ 7 ns) of **3** showed solvent dependant lifetimes, in agreement with the behavior of the 4-benzoylphenyl and the 3-(4′-methylbenzoyl)phenyl radicals obtained from LFP of **1** and **2**, respectively.

The rates of the photopolymerization of NVP initiated by **1**–**3** were similar (7.09×10^{-3} to 1.04×10^{-2} mol l^{-1} s^{-1}). Nevertheless, polymer conversion data indicate that **2** is a better thermal and photoinitiator for the polymerization of NVP than either **1** or **3**. Rapid polymerization of LAC was observed with **1** and **2** as photoinitiators. At the same time, the thermal polymerization of NVP and LAC was much slower than the corresponding photopolymerization when BAPs were used as initiators.

Acknowledgements

B.K.S. thanks the McMaster Endowment for financial support. The laser flash photolysis experiments were carried out at the Ohio Laboratory for Kinetic Spectrometry and help of Dr. Alex Gusev is highly appreciated. We also thank Jianwen Yang for his help in polymerization experiments.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2004.07.022.

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