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Photochemical studies of a photodissociative initiator based on a benzophenone derivative possessing a thioether moiety

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Abstract

S-(4-Benzoyl)phenylthiobenzoate (BpSBz) and 4-benzoyl-phenyl benzoate (BpOBz) in acetonitrile were photolyzed under steady-state and laser-flash conditions. Analysis of transients absorptions and final products from the photolysis of BpSBz showed that 4-benzoylphenylthiyl and 4-benzoyl radicals were formed with an initial quantum yield of 0.45. Benzaldehyde was the main final product. In contrast, photolysis of BpOBz did not yield benzaldehyde, and nanosecond laser-flash photolysis of BpOBz showed only a long-lived triplet state. These results suggest that C–O bond cleavage does not occur as a primary photochemical reaction of BpOBz. The implications for the use of BpSBz as a photoinitiator of polymerization are discussed.

Keywords: Laser-flash; BpSBz; BpOBz

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1. Introduction

An area of intense interest in organic photochemistry involves the use of visible or ultraviolet light to initiate photopolymerization. This process is traditionally initiated by the direct photolysis of a precursor that provides free radicals by bond dissociation. Recently, it has been shown that *S*-(4-benzoyl)phenylthiobenzoate is an efficient photoinitiator of methyl methacrylate polymerization in bulk [1]. The radicals, that are formed by homolytic cleavage of a sulfur–carbon bond of the photoinitiator, are believed to be responsible for the initiation of polymerization.

It is well known that chemical activity of the individual species resulting from the cleavage of different chemical bonds is dependent on its molecular structure and character [2,3]. Therefore, a replacement of one atom by another in the photoinitiator molecule might totally change the initiation ability of photoinitiator. In many cases the energy absorbed by the initiator molecule does not participate in a photochemical reaction, being re-transmitted through nonradiative or radiative processes. In order to appreciate the photochemical reactions occurring upon exposure to UV or visible light, an understanding of the fundamental photochemistry of photoinitiators is needed. Thus, in order to initiate a polymerization reaction, it is necessary that the photoinitiator, following the initial excitation, produces an initiating species. Thiyl [4] and benzoyl [5,6] radicals are known to react rapidly with olefins. While the photochemistry of the sulfur–sulfur bond has been a subject of numerous studies, little is known about the mechanism and intermediates of photolysis of the compounds possessing carbon–sulfur bonds. Fouassier and Lougnot [7] suggested that compounds possessing C–S bonds, on excitation by light, exhibit cleavage of the C–S bond via the excited triplet state, yielding benzoyl and thiyl radicals. Su et al. [8] have shown that products and their distribution of *S*-phenyl thiobenzoate photolysis strongly depend on the reaction medium. In this contribution, we present detailed study on the photochemistry of *S*-(4-benzoyl)phenylthiobenzoate, an efficient photoinitiator of free radical polymerization.

2. Experimental section

Synthesis of *S*-(4-benzoyl)phenylthiobenzoate (BpSBz) was described elsewhere [1] and 4-benzoylphenyl benzoate (BpOBz) was a gift from Dr. H. Janota (Scheme 1).

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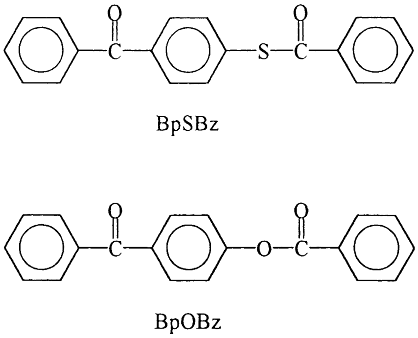


Scheme 1.

2.1. Steady-state irradiations

Steady-state photolysis experiments were carried out in 1 cm × 1 cm rectangular UV cell on a standard optical bench system. A low-pressure mercury lamp (Original Hanau TNN 15/30) was used as the excitation source for 254-nm irradiation. A high-pressure mercury lamp (HBO 200) with the combination of a BC-4 glass filter and a 313 nm interference filter (Zeiss) was used for 313-nm irradiation. Uranyl oxylate and 2-hexanone actinometries were used to measure light intensities at 254 and 313-nm, respectively [9]. The light intensities I_0 were determined to be 3.05×10^{-4} and 1.36×10^{-3} Einstein $\mathrm{dm^{-3}\,min^{-1}}$ for 254 and 313 nm irradiations, respectively. The solutions of BpSBz and BpOBz in acetonitrile ($c = 6 \times 10^{-5}$ M) were deoxygenated by bubbling high-purity argon through them and were irradiated at 254 or 313 nm. The photolytic runs were monitored by taking UV-Vis spectra and analyzed using a high-pressure liquid chromatography (hplc) method (Waters Model 616 pump system with photodiode array UV-Vis detector Waters 996, Waters Symmetry C18 column). Phosphorescence spectra were recorded on MPF-3 spectrofluorimeter (Perkin-Elmer–Hitachi).

2.2. Nanosecond laser-flash photolysis

The nanosecond laser-flash photolysis setup has been described elsewhere [10]. A XeCl excimer laser was operated at 308 nm, 8 mJ, ab. 20 ns pulse width. The transients were monitored with a pulsed 1 kW xenon lamp, with the monitoring beam perpendicular to the laser beam. All experiments were carried out in rectangular quartz cells (0.5 cm × 1 cm). The monitoring light pathlength was 0.5 cm. The acetonitrile solutions of BpSBz and BpOBz ($c = 2 \times 10^{-4}$ M) were deoxygenated by bubbling high-purity argon through them or were saturated with oxygen.

3. Results and discussion

Absorption and phosphorescence spectra of the benzophenone based photoinitiators in this study are displayed in Fig. 1. The absorption spectra are all typical for benzophenone derivatives. The long wavelength shoulders of the spectra of benzophenone and the oxygen analogue of the initiator (BpOBz) are due to n, π^* transitions, and they are well separated from the lowest π, π^* transitions. The sulfur-containing derivative possesses a more intense absorption band shifted to the red, without a significantly separated n, π^* transition.

The type of functional group that is covalently bond to a benzophenone moiety, only slightly changes its phosphorescence spectra (see Fig. 1). On the basis of the 0, 0 transitions in the phosphorescence spectra, one can estimate the triplet energies of the molecules under study. Their values are: 278.2 kJ $\mathrm{mol^{-1}}$ for BpSBz and 282.1 kJ $\mathrm{mol^{-1}}$ for BpOBz,

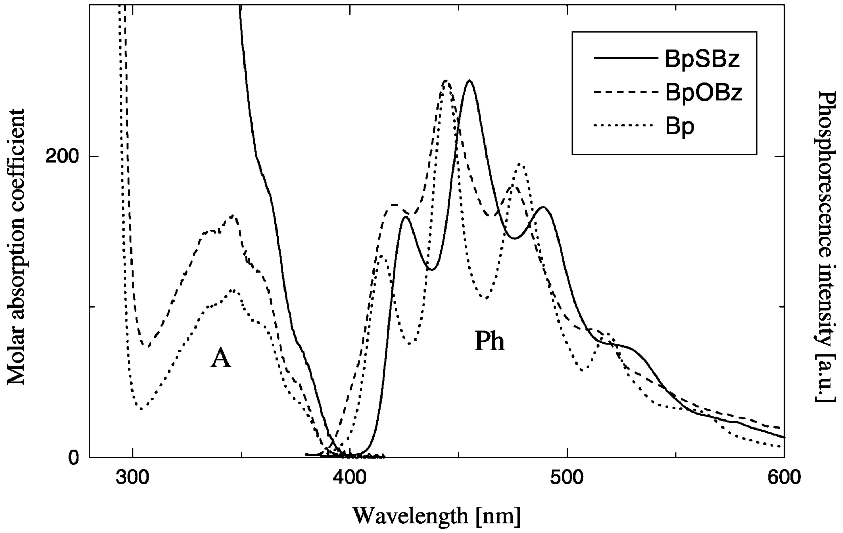


Fig. 1. Electronic absorbtion spectra (A) (in hexane) and phosphorescence emission spectra (Ph) (in EtOH–MeOH 1:1 at 77 K) of benzophenone and its derivatives.

respectively. For comparison, the benzophenone triplet 0, 0 transition was estimated to be equal to 285.5 kJ mol^{-1}. From the literature [11], it is known that the homolytic carbon–sulfur bond dissociation energy for thioethers is of the order of 293 kJ mol^{-1} and that for carbon-oxygen ethers is on the order of 323 kJ mol^{-1}. The latter value is much higher than the corresponding benzophenone triplet energies. It is worth noting that the energy of the 0, 0 transition of the lowest singlet excited state of benzophenone [9] varies between 310 and 315 kJ mol^{-1}. Taking into account all the data presented above, one can conclude that the photocleavage of the *S*-(4-benzoyl)phenyl thiobenzoate C–S bond can occur via excited singlet states or triplet states (vibronically excited), while the cleavage of C–O bond for 4-benzoylphenyl benzoate cannot occur even via benzophenone's lowest excited singlet state.

Experimental evidence, supporting the above conclusions comes from the laser-flash photolysis experiments. Fig. 2 shows the transient absorption spectra recorded for *S*-(4-benzoyl)phenyl thiobenzoate in MeCN solution.

A similar experiment performed for 4-benzoylphenyl benzoate gives quite a different picture of the process (see Fig. 3).

Comparison of the spectra in Figs. 2 and 3 reveals that *S*-(4-benzoyl)phenyl thiobenzoate behaves quite differently than 4-benzoylphenyl benzoate. In addition, it is worth noting that there is a significant difference of the effect of oxygen on the two spectra. In the case of *S*-(4-benzoyl)phenyl thiobenzoate, at short times, its spectrum in an oxygen-saturated solution is almost identical in shape to that in Fig. 2; however, at longer times, a broad band develops in the spectral region between 350 and 400 nm. From the inset of Fig. 2, the decay of the transient in argon-saturated solution is seen to be second-order, and its decay in the presence of oxygen is the same for kinetic traces monitored at 500 nm. On the other hand, for oxygen-saturated solutions of BpOBz, the transient in Fig. 3 disappears within 50 ns. This is in contrast to oxygen-free solutions of BpOBz where the decay is monoexponential with a lifetime of 10.4 μs (see inset to Fig. 3).

On the basis of the spectral characteristics and the behavior in the presence of oxygen, we assign the transient in Fig. 2 as the *p*-benzoylphenylthiyl radical (BpS$^\bullet$). The spectral characteristics of the species being assigned as the BpS$^\bullet$ radical (absorption spectrum slightly red-shifted, compared with the spectrum of phenylthiyl radical [12]) are almost identical to the features of the optical spectrum of the BpS$^\bullet$ radical found by Autrey et al. in the photolysis of bis(*p*-benzoylphenyl)disulfide (BpSSBp) [13]. In addition to the similarity in the transient's spectrum to that of BpS$^\bullet$, its second-order decay is consistent with the unknown species being a radical. Furthermore, its lack of reactivity with oxygen is consistent with the normally low reactivity of aromatic thiyl radicals with oxygen ($k < 10^4\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) [14]. The transient in Fig. 3 is assigned as the triplet state of 4-benzoylphenyl benzoate. Its spectral position and shape are reminiscent of benzophenone's triplet–triplet absorption. Its decay is monoexponential in argon-saturated solutions, and it is quenched by oxygen, both of which are consistent with the transient being a triplet state absorption. The ratio (τ_0/τ) of the unquenched lifetime $\tau_0 = 10\,\mu\mathrm{s}$ to the quenched lifetime $\tau = 50\,\mathrm{ns}$ is 200. Using these two points, the quenching rate constant (k_q) can be estimated from pseudo-first order kinetics:

$$\frac{\tau_0}{\tau} = 1 + k_\mathrm{q}\tau_0\,[\mathrm{O}_2]$$

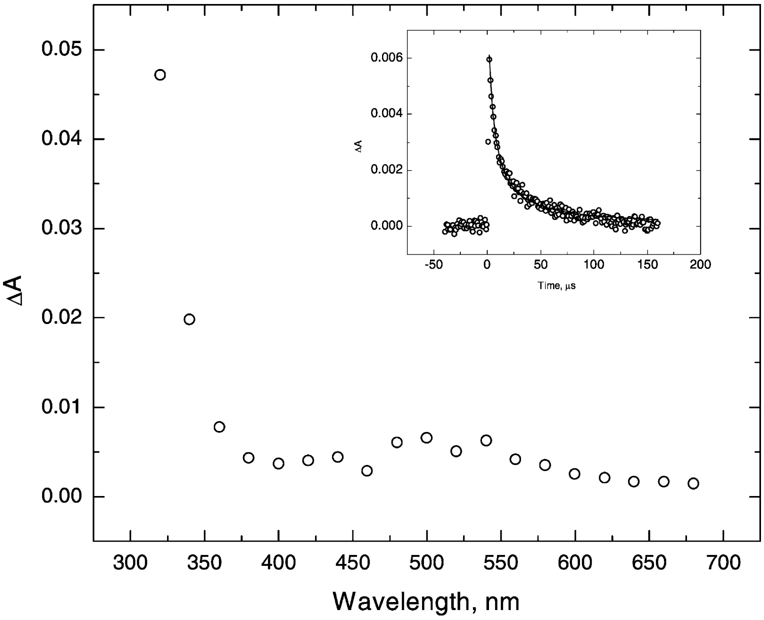


Fig. 2. Transient absorption spectrum obtained during 308-nm photolysis of *S*-(4benzoyl)phenyl thiobenzoate in MeCN (argon-saturated) solution after 450 ns delay. Inset: kinetic trace recorded at 500 nm, second-order decay with $2k/(\varepsilon l) = 2.5 \times 10^7\,\mathrm{s}^{-1}$.

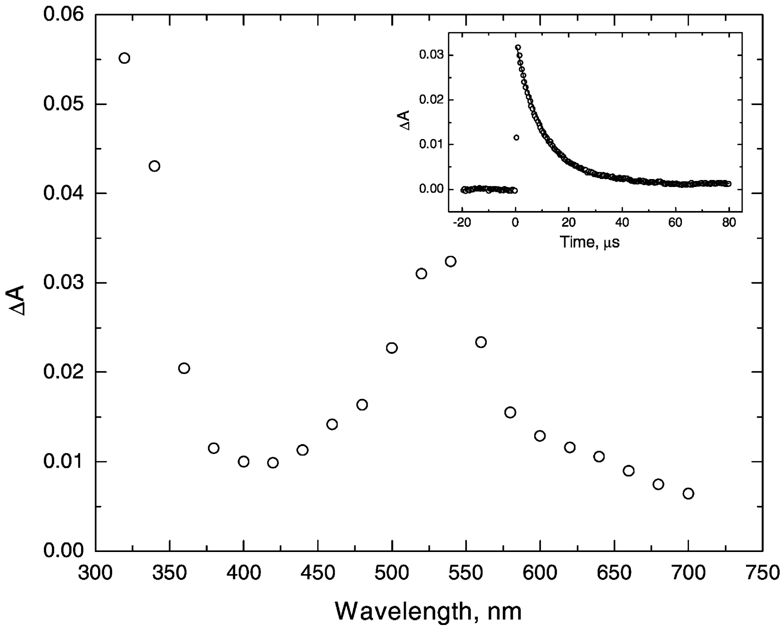


Fig. 3. Transient absorption spectrum obtained in the 308-nm photolysis of 4-benzoylphenyl benzoate in MeCN (argon-saturated) solution, recorded after 250 ns delay. Inset: kinetic trace recorded at 540 nm; monoexponential decay, $\tau = 10.4\,\mu s$.

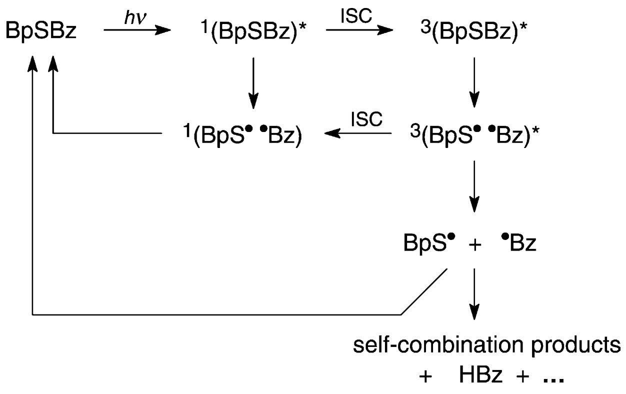
Taking the concentration of oxygen in acetonitrile at room temperature as 9×10^{-3} M [9], k_q could be calculated as $2 \times 10^9\,M^{-1}\,s^{-1}$, that is 1/9 of the diffusion-controlled rate constant in acetonitrile. This is the rate constant that is expected for the spin-statistic factor for the quenching a triplet state by the triplet ground state of oxygen.

These findings indicate that the observed transient in the photolysis of BpSBz can be assigned to the $BpS^{\bullet}$ radical that is formed from the photocleavage of the C–S bond in *S*-(4-benzoyl)phenyl thiobenzoate. On the other hand, the oxygen analog BpOBz shows no indication that it undergoes C–O bond scission during photolysis at 308 nm. These assignments are in agreement with the considerations of bond energetics discussed earlier. Photocleavage of the BpSBz C–S bond can occur via excited singlet states or triplet states (vibronically excited), while the cleavage of C–O bond for BpOBz cannot occur even via benzophenone's lowest excited singlet state.

The energetic considerations indicate the possibility of two separate pathways for photocleavage, via the singlet excited state and the triplet state (see Scheme which is in analogy to the Scheme for the photolysis of BpSSBp [13]). The singlet mechanism involves a singlet radical pair in which the radicals, $BpS^{\bullet}$ and $^{\bullet}Bz$, would likely recombine efficiently. The triplet mechanism, on the other hand, would result in a triplet radical pair that could permit substantial escape of free radicals because of spin restrictions on recombination in the solvent cage. The triplet mechanism may also be substantial since the intersystem crossing rate constant in analogous substrates, e.g. BpSMe generates triplets within 17 ps [13] (Scheme 2).

Aromatic thiyl radicals, according to the literature, show a pronounced broad and asymmetric band between 400 and 510 nm, with maximum ε values of about $2500\,M^{-1}\,cm^{-1}$, and a stronger band with absorption maximum at 295 nm (ε about $10\,000\,M^{-1}\,cm^{-1}$) [15]. More specifically, the value of the molar absorption coefficient of $BpS^{\bullet}$ radical can be estimated from the results presented in Fig. 2. From the fit of the second-order decay in the inset, $2k/(\varepsilon l) = 2.5 \times 10^7\,s^{-1}$. If the recombination rate constant is taken to be diffusion-controlled, then ε at 500 nm can be estimated to be $2000\,M^{-1}\,cm^{-1}$. This is in the range expected for other aromatic thiyl radicals.

Using 4-carboxybenzophenone in water as an actinometer, one can estimate the quantum yield of $BpS^{\bullet}$ radical formation, assuming that the molar absorption coefficient of the *p*-benzoylphenylthiyl radical is $2000\,M^{-1}\,cm^{-1}$. The result



Scheme 2.

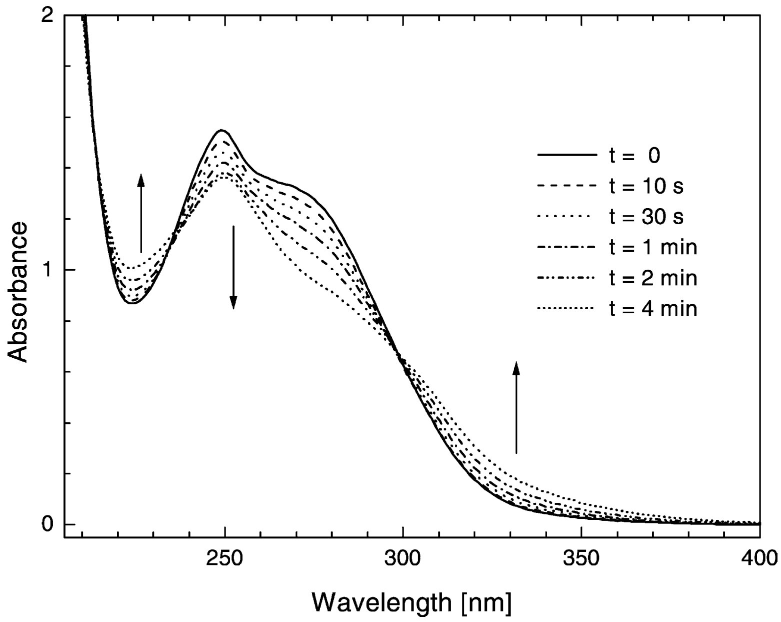


Fig. 4. Changes in the electronic absorption spectra recorded during 313-nm photolysis of *S*-(4-benzoyl)phenyl thiobenzoate in MeCN solution.

of this procedure is that the quantum yield of $BpS^{\bullet}$ formation is 0.45. This value suggests that the photochemical efficiency of C–S bond cleavage (formation of radical pairs, see Scheme) is on the order of unity, particularly if the possibility of cage recombination of the free radicals is considered [13].

As it was mentioned earlier, the 500-nm transient from BpSBz recorded during the laser-flash photolysis is not quenched by oxygen which supports the notion that the 500-nm transient was an aromatic thiyl radical ($BpS^{\bullet}$). Oxygen, on the other hand, is quite reactive with carbon-centered radicals with rate constants almost at the diffusion-controlled limit [14]. There was evidence, see above, that at times longer than a few microseconds a new absorption appeared in the 350–400 nm region of the spectrum in O_2-saturated solutions of BpSBz. This could be a product of the reaction of the benzoyl radical ($^{\bullet}Bz$) and oxygen.

It should be mentioned that, in addition to the very low reactivity of $BpS^{\bullet}$ with oxygen, these radicals also react slowly via H atom abstraction [14]. This low reactivity of aromatic thiyl radicals is important if one is concerned with chain transfer processes that might occur during free radical polymerization. Higher rate constants are reported for the addition reaction of aromatic thiyl radicals to various olefins (for example to methyl methacrylate $k_a = 3.2 \times 10^6\,M^{-1}\,s^{-1}$) [14]. Comparison of the rate constants of hydrogen atom abstraction and addition reaction to methyl methacrylate suggests that for the systems under consideration, the *p*-benzoylphenylthiyl radical will likely start polymerization by direct reaction with the monomers and avoid the secondary reactions that produce radicals able to initiate polymerization.

The continuous irradiation of *S*-(4-benzoyl)phenyl thiobenzoate in MeCN solution at 313 nm (or 254 nm) leads to subsequent changes of its electronic absorption spectra (Fig. 4). A similar picture of electronic absorption spectra modification is recorded for 4-benzoylphenyl benzoate (Fig. 5), but with more pronounced build-up, and a better separated absorption band at long-wavelengths. In the case of the 254-nm photolysis of BpOBz, the intensity of absorbed photolytic light was significantly larger than in the 313-nm photolysis of BpSBz, leading to much lower photochemical quantum yields for BpOBz than BpSBz.

Irradiation of *S*-(4-benzoyl)phenyl thiobenzoate in MeCN causes its disappearance. The quantum yield of *S*-(4-benzoyl)phenyl thiobenzoate disappearance is equal to 0.14 when irradiated at 313 nm and 0.11 at 254 nm. Benzaldehyde is the main product of the photoreaction observed with the use of hplc technique. The quantum yield of benzaldehyde formation is equal to 0.012 and 0.042 in acetonitrile and acetonitrile–isopropanol, respectively. The presence of this compound explicitly confirmed the type of bond that is cleaved during the photolysis, e.g. C–S bond. The formation of benzaldehyde, under experimental conditions, may be explained as a result of hydrogen atom abstraction from the medium by benzoyl radical. This supposition can be additionally confirmed by the data obtained during the photolysis of BpSBz in the presence of a good hydrogen atom donor, e.g. 2-propanol. The comparison of yields of benzaldehyde (HBz) measured with and without the hydrogen-atom donor showed that the efficiency of HBz formation is 3.5 times greater for the solution that contains 2-propanol ($c = 1.0\,M$). During the photolysis several other compounds are formed in addition to benzaldehyde. The measurements performed with the use of hplc with diode-array detection identified, in addition to traces of other products, bis(*p*-benzoylphenyl)disulfide (BpSSBp), which

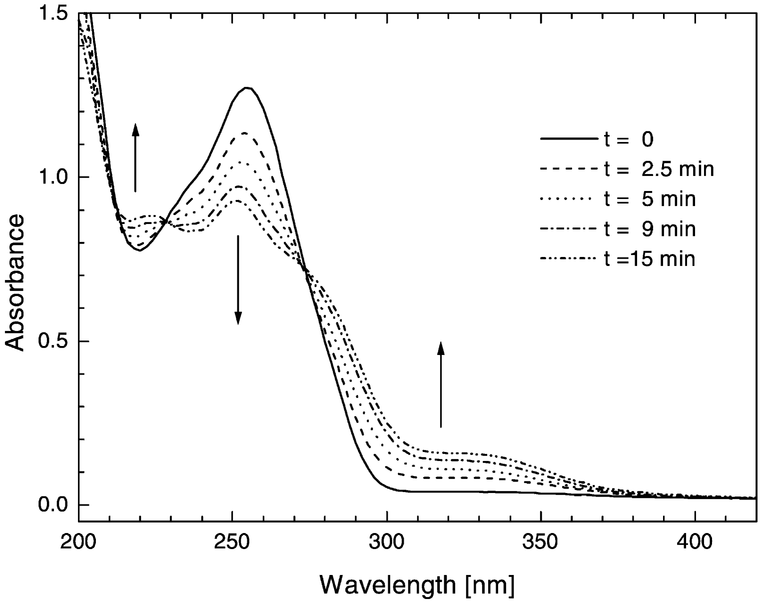


Fig. 5. Changes in the electronic absorption spectra recorded during 254-nm photolysis of 4-benzoylphenyl benzoate in MeCN solution. Numbers represent times in minutes of irradiation.

is formed by direct combination of *p*-benzoylphenylthiyl, and benzil (BzBz) formed by the combination of benzoyl radicals (see Scheme). It is necessary to add that benzoyl radicals formed also start free radical polymerization. Initiation of polymerization with benzoyl radicals can occur by two different routes. The first is through the addition of $^{\bullet}$Bz radicals to olefins (monomer), and the second pathway involves the chain transfer reaction that forms a new free radical by hydrogen atom abstraction from the monomer, yielding benzaldehyde and a new free radical able to initiate polymerization.

It is worth contrasting the low quantum yield of *S*-(4-benzoyl)phenyl thiobenzoate's disappearance (0.14) with the estimated yield of BpS$^{\bullet}$ radical formation (0.45). As was concluded earlier (see Scheme), the C–S bond scission is either a result of singlet energy transfer to that bond or is a result of rapid ISC from the excited singlet state to the triplet electronic state, followed by C–S bond scission. As mentioned above, it is likely that the singlet radical pair recombines without forming free radicals which would account for a maximum of 0.55 of the yield of reformed substrate (BpSBz). The low value for the quantum yield of BpSBz disappearance indicates that the rest of the reformed BpSBz must come from the combination of free radicals BpS$^{\bullet}$ and $^{\bullet}$Bz as shown in the Scheme.

It is necessary to add that steady-state photolysis of 4-benzoylphenyl benzoate, in spite of the observation of changes in the electronic absorption spectra, does not yield benzaldehyde as a reaction product. The quantum yield of BpOBz disappearance is equal to 0.03. The lack of benzaldehyde formation in addition to the results obtained in nanosecond laser-flash photolysis of BpOBz (long-lived triplet state), suggests that C–O bond cleavage does not occur as a primary photochemical reaction for BpOBz.

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References

[1] A. Wrzyszczyński, H. Janota, Polimery 41 (1996) 560.
[2] W. Schnabel, Application of laser flash photolysis to the study of photopolymerization reactions in nonaqueous systems, in: J.P. Fouassier, J.F. Rabek (Eds.), Lasers in Polymer Science and Technology: Applications, vol. II, CRC Press, Boca Baton, 1990, p. 95.
[3] M.S. Szymala, R.B. Nagaswer, B. Rammurthy, Tetrahedron 44 (1988) 7234.
[4] W.A. Pryor, Free Radicals, McGraw-Hill, New York, 1966.
[5] C.J. Groenenboom, H.J. Hageman, T. Overem, A.J.M. Weber, Macromol. Chem. 183 (1982) 281.
[6] H. Fischer, R. Baer, R. Hany, I. Varhoolen, M. Walbiner, J. Chem. Soc. Perkin II (1992) 787.
[7] J.P. Fouassier, D.J. Lougnot, Polymer Rep. 31 (1990) 418.
[8] J.J. Su, G.S. Dai, S.K. Wu, J. Photochem. Photobiol A: Chem. 83 (1994) 49.
[9] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, Marcel Dekker, New York 1993.
[10] M.D. Thomas, G.L. Hug, Computers Chem. 22 (1998) 491.
[11] F. Bernardi, I.G. Csizmadia, A. Mangini, Studies in Organic Chemistry 19, Organic Sulfur Chemistry, Elsevier, Amsterdam, 1985.
[12] T.J. Burkey, D. Griller, J. Am. Chem. Soc. 107 (1985) 246.

[13] T. Autrey, C. Devadoss, B. Sauerwein, J.A. Franz, G.B. Schuster, J. Phys. Chem. 99 (1995) 869.

[14] O. Ito, Reactions of Aromatic Thiyl Radicals in the Chemistry of Free Radicals: *S*-Centered Radicals, Wiley, New York, 1999, Chapter 6, p. 194.

[15] K.-D. Asmus, M. Bonifačić, Sulfur-centered reactive intermediates as studied by radiation chemical and complementary techniques, in: Z.B. Alfassi (Ed.), *S*-Centerd Radicals, Wiley, New York 1999.