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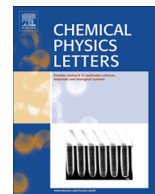
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# Laser flash photolysis of benzophenone in thin silicone films

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## ABSTRACT

The decay kinetics of benzophenone (BP) triplet state in the thin (~200 nm) films of poly(dimethylsiloxane) have been studied with a nanosecond laser flash photolysis technique. Decay kinetics of a triplet state of BP (<sup>3</sup>BP) is dispersive kinetics, and it can be well described by the kinetic law with Gaussian distribution of the activation free energy. The average rate constants of <sup>3</sup>BP decay  $k_{av}$  are 1500 and 70 s<sup>-1</sup> for air saturated and deoxygenated films, respectively. Width of distribution are 1.2 and 4.3 (dimensionless) and correspond to the first and second  $k_{av}$ , respectively presented above. The rate of hydrogen abstraction of H-atom from Si-CH<sub>3</sub> groups by <sup>3</sup>BP is low which results in long-lived <sup>3</sup>BP in silicone films.

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## 1. Introduction

Reactivity of photoexcited species in polymer films is of fundamental and of applied interest. Such research is related to study of photodegradation of polymers. Furthermore, monitoring photo-generated transients in film allows probing of polymer properties. Benzophenone (BP) is a classical object in photochemistry research with the well-documented properties [1].

We demonstrated earlier that the study of photoexcited triplet BP (<sup>3</sup>BP) can give valuable information on kinetics of reactive transients in polymer films and information on the properties of films [2].

In the present Letter we studied reactivity of the same kinetic photo probe <sup>3</sup>BP in PDMS films. Kinetics of transients in PDMS was of the main interest.

## 2. Experimental part

### 2.1. Devices

The absorption spectra and the kinetics of formation and decay of intermediates were measured with a nanosecond laser

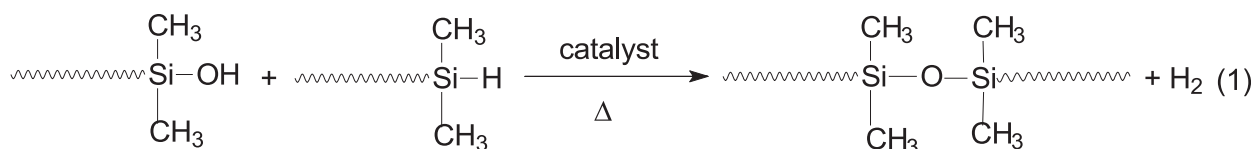
photolysis apparatus [3]. A PRA LN 1000 N<sub>2</sub> laser (with a pulse duration of 1 ns and an emission wavelength of 337 nm) operating at ≤10 Hz frequency was used as an excitation source. Acquisition and averaging of kinetic curves (at least 16 laser pulses) were performed by a UF258 high-speed digitizer (Sweden) connected with PC (Pentium 4).

Each initial kinetic curve contained 12–14 bits of points, with the time distance between the points being 4–400 ns. The data presented in this Letter are average values obtained by processing at least ten kinetic curves under the aforementioned conditions.

All kinetic measurements were made at 20 °C in a fused silica cell. Samples under investigation consisted of ten layers of thin films on a polymer support. A stack of polymer films with BP (cf. Section 2 below) was placed into the cell. The air was removed from the samples by prolonged evacuation.

### 2.2. Preparation of films

Films were prepared by the known reaction of dehydrogenative condensation of high MW silicones [4]:



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Our films were prepared with the reagents of and according to recommendation of Momentive (Waterford, New York) [5].  $\alpha,\omega$ -Dihydroxy-terminated PDMS (SS4191A [5],  $M_w = 500$  kg/mol) reacted with a lower MW silicone with hydro- and methyl groups (SS4191B [5],  $M_w = 2.3$  kg/mol). Reaction took place in hydrocarbon solvents in the presence of a catalyst (tin compound [5]). We added to the reaction mixture BP (Aldrich). Liquid coating was applied to 1 mil polyethylene terephthalate (PET) film of Toray Plastics (America) with Meyer rod. Cure of the formulation was performed in a convection oven at 140 °C during 50 s. Solvents obviously evaporate, and a solid coatings film on a PET support is produced. The coating can be named crosslinked PDMS due to the main component PDMS-silanol. Thickness of the coating was measured by Oxford 3000 XRF (UK). We got thickness of all our silicone samples of  $200 \pm 20$  nm. Concentration of BP in the cured films was 1 mol/kg. We subjected to laser flash photolysis a stack of PDMS films with their respective PET supports (cf. Section 1 above).

### 3. Results and discussion

#### 3.1. Triplet state $^3\text{BP}$

Laser excitation of BP in the films described above leads to a formation of a triplet state of BP.  $^3\text{BP}$  has a characteristic absorption spectrum (Figure 1) [1–3]. The observed spectrum in films is similar to absorption spectrum of  $^3\text{BP}$  in other media: it has  $\lambda_{\text{max}}$  525 nm and a shoulder at 600–700 nm [1–3]. The decay kinetics



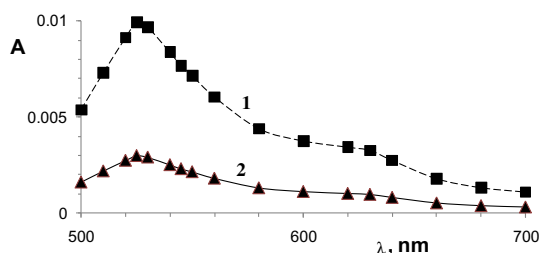
of  $^3\text{BP}$  in our experiments was not exponential (cf. Figure 2). Such exponential first order (or pseudofirst order) decay of  $^3\text{BP}$  is expected in liquid solvents – Newtonian liquids [1].

Kinetics of chemical reactions in polymers is governed by other laws than in liquids. A possible promising approach for quantitative description of kinetics in polymers was suggested in Ref. [6]. It is assumed that the first-order elementary reactions in polymers have a GAUSSIAN distribution of a logarithm of the first-order rate constants [6]. Such a suggestion leads to the following analytical expression for a kinetic curve [6]:

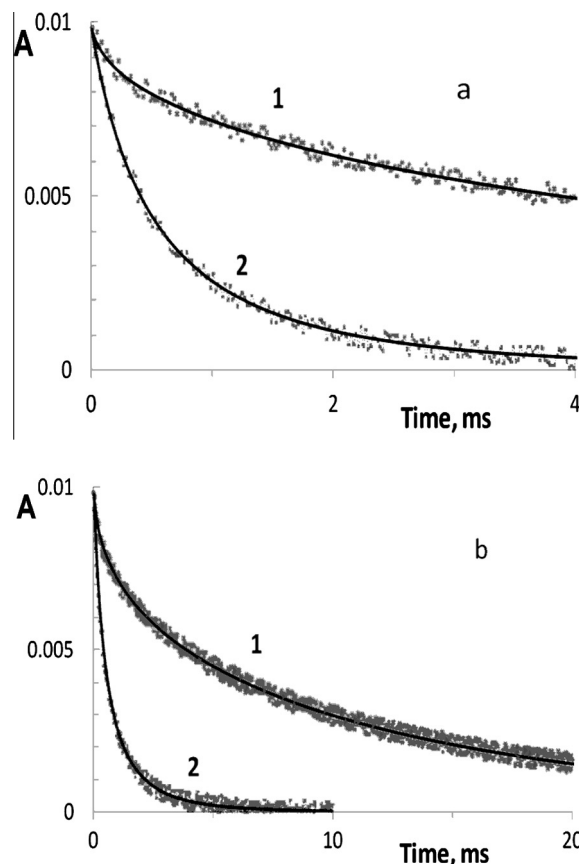
$$C(t)/C(0) = \pi^{-1/2} \int_{-\infty}^{\infty} \exp(-x^2) \exp[-k_{\text{av}} t \exp(\gamma x)] dx \quad (2)$$

where  $C(t)$  и  $C(0)$  are current and initial concentrations of reagents, respectively,  $k_{\text{av}}$  is the average value of first order rate constant, and  $\gamma$  is width of a distribution. We used Eq. (3) to simulate kinetics of  $^3\text{BP}$  decay, cf. Figure 2. The values of  $k_{\text{av}}$  and  $\gamma$  obtained as a result of the fit of experimental data (Figure 2) into Eq.(3) are presented in the Table 1:

$\gamma$ -Values obtained in this Letter are close to the same values obtained earlier for decay of  $^3\text{BP}$  other polymers [2].



**Figure 1.** Absorption spectra of transients obtained under laser flash photolysis of the film with a delay after laser flash of: 1–1 μs; 2–10 ms. Label A of ordinate axis stands for absorption (optical density) here and in Figure 2.



**Figure 2.** Decay kinetics of  $^3\text{BP}$  measured at  $\lambda$  525 nm obtained under laser flash photolysis of deoxygenated (1) and air-saturated (2) films. Solid lines are the simulation of kinetic data with Eq. (3).

One can see that in the deoxygenated solutions  $^3\text{BP}$  decays much slower than in air-saturated solutions (Table 1, Figs. 2). Life-time of  $^3\text{BP}$  in PDMS films is  $\tau = 1/62 \approx 15$  ms, cf. Table 1 and Figure 2b.  $^3\text{BP}$  lifetime in deoxygenated other common polymers like PVC [7] and PMMA [8] is much shorter ( $\tau = 1/10 \mu\text{s}$ ) than the observed  $\tau$  in the present Letter. Evidently PVC and PMMA films have abundance of C–H groups, even activated C–H groups, and  $^3\text{BP}$  reacts with a polymer matrix RH. Apparently C–H of Si–CH<sub>3</sub> groups of PDMS has poor reactivity towards  $^3\text{BP}$  which results in a relatively large  $\tau$  in PDMS.

In fact, it was demonstrated elsewhere that C–H groups of silicones are poorly reactive towards  $^3\text{BP}$  [9,10].  $^3\text{BP}$  reacts with  $(\text{CH}_3)_3\text{SiSi}(\text{CH}_3)_3$  with a very low constant of  $1.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  (benzene, room temperature) [10]. That rate constant is the lowest among many reported rate constants of  $^3\text{BP}$  reaction with different compounds [9].  $^3\text{BP}$  is quenched by triplet dioxygen  $\text{O}_2$  with a rate constant of  $\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$  in several solvents [9].

**Table 1**  
Kinetic parameters of  $^3\text{BP}$  decay (2).<sup>a</sup>

$k_{\text{av}} \text{ s}^{-1\text{b}}$	$k_{\text{av}} \text{ s}^{-1\text{c}}$	$\gamma^{\text{b}}$	$\gamma^{\text{c}}$
1500	62	1.2	4.2

<sup>a</sup> Cf. the text for definition of parameters. Determination error of the values in the Table is 10–15%.

<sup>b</sup> Air-saturated cell.

<sup>c</sup> Deoxygenated cell.

### 3.2. Radicals BPH<sup>•</sup>

Hydrogen abstraction from polymer matrix RH should lead to a formation of a triplet radical pair with benzophenone ketyl radical BPH<sup>•</sup> as the primary product [1–3]:



However, contrary to our previous work [2,3], we did not observe BPH<sup>•</sup>. The absorption spectrum of transient at 10 ms is has the same shape as that at 1 μs and should be ascribed to <sup>3</sup>BP (Figure 1) and not to a spectrum of BPH<sup>•</sup>. Due to slow reaction 4 in silicone film, a steady-state concentration of BPH<sup>•</sup> is low for the observation. Radical pair <sup>3</sup>[BPH<sup>•</sup>, R<sup>•</sup>] undergoes intersystem crossing into <sup>1</sup>[BPH<sup>•</sup>, R<sup>•</sup>], and BPH<sup>•</sup> can decay in a cage reaction with R<sup>•</sup>.

### 4. Conclusions

We found a way to prepare thin solid films of PDMS with dissolved BP. ns Laser photoexcitation of BP in PDMS leads to formation of <sup>3</sup>BP which was monitored by its absorption spectrum. Kinetics of <sup>3</sup>BP is not exponential and it can be successfully described as dispersive kinetics according to Eq. (2). <sup>3</sup>BP is long-lived in silicone polymer (τ ≈ 15 ms in the deoxygenated film), which indicates high photostability of PDMS in the presence of photoreactive additives.

Moreover, in the presence of air oxygen <sup>3</sup>BP decays much faster (τ ≈ 2–3 ms). Slow abstraction of H from silicone matrix did not allow us to observe ketyl free radicals BPH<sup>•</sup>. Most probably BPH<sup>•</sup> decays in the polymer cage.

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