Benzophenone as a photoprobe of polymer films

Peter P. Levin [a,b], Alexei F. Efremkin [b], Igor V. Khudyakov [c,*]

[a] Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Moscow 11933, Russia
[b] Semenov Institute of Chemical Physics, Russian Academy of Sciences, Moscow 119334, Russia
[c] Department of Chemistry, Columbia University, New York, NY 10027, USA

A R T I C L E   I N F O

A B S T R A C T

The review article is devoted to kinetics of fast reactions following photoexcitation of benzophenone in polymer films. We observed three processes by ns laser flash photolysis in elastomers: (i) decay of a triple state of benzophenone with hydrogen abstraction from polymer matrix, (ii) formation and decay of geminate radical pairs, (iii) cross-termination of the formed radicals in the polymer bulk. Application of external magnetic field (MF) of $B = 0.2$ T essentially affects recombination of geminate (G-) and a bimolecular recombination of free radicals, which escaped polymer cage (F-pairs). Theoretical calculation of MF effects on G- and F-pairs is in agreement with corresponding experimental data. Elongation of elastomer leads to an unexpected observation: recombination in the bulk becomes slower. An explanation of this phenomenon based on elastomer free volume V_f approach was suggested.

1. Introduction

Diffusivity and reactivity of free radicals in polymers is of considerable practical and theoretical importance, see e.g., Refs. [1–5]. Low and high MW free radicals are formed during photodegradation of polymers. Polymers may have different additives (residual photoinitiator, antioxidant, etc.), which are capable to form free radicals. It is well-known that free radicals formed under UV-irradiation of polymers [6]. In this brief review article based on the authors' results [7–11], we will describe reactivity of free radicals formed in polymer films under photoexcitation of benzophenone (**B**). **B** itself is an intensively studied object in photochemistry; it is even recommended as a photoprobe in surface and polymer chemistry [12]. (Another useful photoprobe studied in polymers is dibenzyl ketone and its derivatives [13].)

Thin polymer films are widely used in industry and in ordinary life. Polymer films often used under applied stress (elongated), and at a temperatures different form the room temperature. Variation of the load and of temperature should affect properties of films and kinetics of reactions in the films. The third new way to affect reactivity of free radicals in polymer films is an application of permanent moderate magnetic field (MF, several tenths of a tesla or several kilogauss). Observation of MF effects (MFE) often requires viscous media [14,15] and polymer films present such media.

Usually radicals are generated as *pairs* upon photodissociation of a chemical bond or under photoabstraction of hydrogen atom from a donor. Reactivity of photogenerated radical pairs (so called G-pairs) and reactivity of the same pairs in the polymer bulk (so-called F-pairs) is important for verification of the theory of fast reactions and the theory of MFE.

In this article we do not aim to review all approaches to reactivity/diffusivity of radicals in polymer films or to present studies of the most types of polymers. We studied fast reactions of photoexcited **B** in a number of polymer films, both commercially available and prepared by photopolymerization as coatings [7–11]. We studied soft and hard films with different T_g [7–11]. We present below most of the data on elastomer poly(ethylene-*co*-butylene) as an exemplar. This elastomer got an abbreviated name **E**.

In this paper we addressed the following specific questions:

What kinetic law recombination of low MW and high MW radicals follows?

Abbreviations: **B**, benzophenone; **³B***, benzophenone in a triplet state; **BH·**, ketyl free radical of benzophenone; **E**, film of poly(ethylene-*co*-butylene), an elastomer; l_o, initial thickness of a film **E** prior elongation; **l**, the measured thickness of an elongated **E** film; **O.D.**, optical density; D_{BH}, diffusion coefficient of **BH·** in a polymer film; G-pair, A pair of free radicals formed as a result of photochemical reaction. Here a reaction is a hydrogen atom abstraction; F-pair, A pair of free radicals encountered each other as a result of random wandering in the solvent bulk. Here solvent is polymer; MF, external magnetic field. In this paper $B = 0.2$ T; MFE, magnetic field effect; p, probability of recombination of F-pairs RP RP, radical pair; V_f, free volume of polymer; φ, cage effect value, or probability of recombination of G-pairs.

* Corresponding author at: Performance Coatings International, LLC, Bangor, PA 18013, USA.

E-mail address: ivk@pcoatingsintl.com (I.V. Khudyakov).

What is a difference in reactivity of G- and F-pairs constituted of the same radicals? Can MF affect reactivity of radicals in polymer films?

What is the effect of elongation of a polymer film on reactivity of radicals?

2. Photoexcitation of B

B was dissolved in different polymer films, see for details Refs. [8–11]. **B** was excited by N_2 laser (with pulse duration of 1 ns and emission wavelength of 337.1 nm), operating at frequency $\leq$10 Hz. Obtained data, some of which are presented below, were averaged over many independent experiments [7–11]. Special arrangements were made in order to study transient kinetics and spectra of thin films and in elongated thin films. Thickness of films l was measured, extinction coefficients of **B** in a triplet state $^3B^*$ and of the ketyl free radical **BH**$^{\cdot}$ of **B** at its absorption maximum in non-polar media (λ_{max} 545 nm) are known [16,18].

Films with the initial thickness l_o = 0.007–0.06 cm were elongated several times; the thickness of elongated films is denoted as l.

Photoexcitation of **B** leads to the formation of triplet state $^3B^*$ [6,12,16–18]. ns Photoexcitation of **B** in viscous liquid media and in solid polymers leads to three processes: (i) decay kinetics of $^3B^*$ which occurs apparently by hydrogen abstraction from a polymer, (ii) decay of a G-pair consisting of **BH**$^{\cdot}$ and a polymer radical **R**$^{\cdot}$, (iii) recombination of F-pairs, see Scheme 1 below [8–11]:

Square brackets in the Scheme 1 designate the triplet radical pair (RP). We use here and below the known terminology of free radical kinetics and of MFE in free radical reactions [14,15]. A pair of radicals generated in proximity to each other is called G-pair or a pair in the cage. A pair of radicals which underwent an encounter in the solvent/polymer bulk is called free pairs or F-pairs. Scheme 1 clearly demonstrates what happens to G- and F-pairs. Recombination in the polymer bulk occurs with a formation of F-pairs. F-pars as well as G-pairs either recombine or dissociate (or separate, or escape the cage).

The observed $^3B^*$ spectrum in the non-polar solid polymer film is similar to the well-known absorption spectrum of $^3B^*$ in liquid hydrocarbon solvents and non-polar polymers: it has λ_{max} 525 nm and a shoulder at 600–700 nm [10–12,16–18], see Fig. 1:

The decay kinetics of $^3B^*$ was measured in the spectral area λ > 600 nm, where absorption by other transients is negligible [7–11]. The decay kinetics of $^3B^*$ fits well into exponent with $k_T = (3.0 \pm 0.3) \times 10^6$ s^{-1} in **E** at 293 K [11].

We studied effect of external magnetic field (MF) B = 0.2 T on kinetics of transients in different films. Effect of elongation and temperature of elastomer film on kinetics was studied as well. Elongation of the **E** film as well as application of magnetic field (MF) does not affect decay kinetics $^3B^*$ within determination error of the observation.
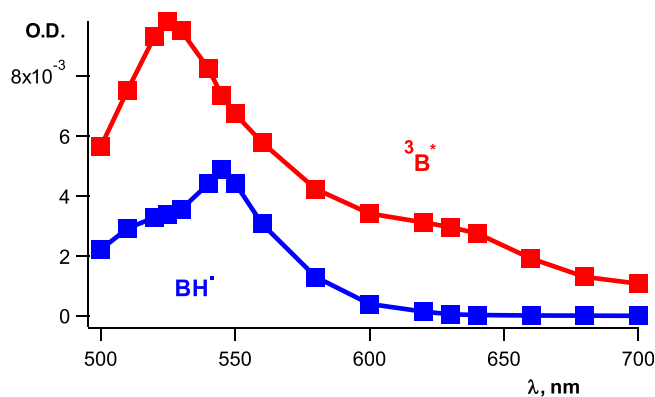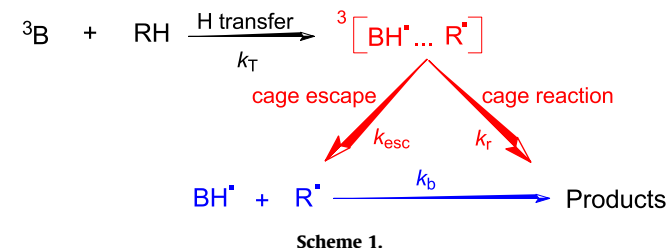

Fig. 1. Typical absorption of transients obtained under laser flash photolysis of **B** in film **E** at 293 K with a delay after laser flash of 1–20 ns (1) and 2–2.0 μs (2). Adopted from Ref. [7]. **O.D.** here and below stands for the optical density.

3. Kinetics of decay of BH in G-pairs and via F-pairs

Reactions of **BH**$^{\cdot}$ are presented in the Scheme 1. It should be assumed that **R**$^{\cdot}$, a radical centered on the polymer chain, is practically immobile compared with mobility of low MW species, and **BH**$^{\cdot}$ escapes the cage. According to a simple exponential model of RP [11,12,15], decay of G-pair consists of two competitive processes: recombination within the G-pair (k_r, s^{-1}) and escape from the G-pairs with k_{esc}, s^{-1}, see Scheme 1.

The radical **BH**$^{\cdot}$ with its characteristic absorption maximum λ_{max} 545 nm is observed after decay of $^3B^*$ at ~0.5 μs after the laser pulse [9–11], see Fig. 1. Therefore, $^3B^*$ and **BH**$^{\cdot}$ can be differentiated in **E** and other films not only by their absorption spectra (Fig. 1) but by the fact that the **BH**$^{\cdot}$ decays essentially slower than $^3B^*$, see below. C-centered aliphatic **R**$^{\cdot}$ of the polymer matrix absorbs in the UV-region and was not observed in our experiments.

Observed kinetic traces of $^3B^*$ and **BH**$^{\cdot}$ decay are presented in Figs. 2 and 3:

Quantitative estimations based on the initial O.D.s and extinction coefficients of $^3B^*$ and **BH**$^{\cdot}$ demonstrate that hydrogen abstraction is the main path of $^3B^*$ decay, and practically all $^3B^*$ is converted into **BH**$^{\cdot}$. That means the rise of **BH**$^{\cdot}$ should mimic the decay of $^3B^*$. Unfortunately, an overlay of $^3B^*$ and **BH**$^{\cdot}$ absorption spectra allows experimental observation of $^3B^*$ decay but not a rise of **BH**$^{\cdot}$ (Fig. 1).
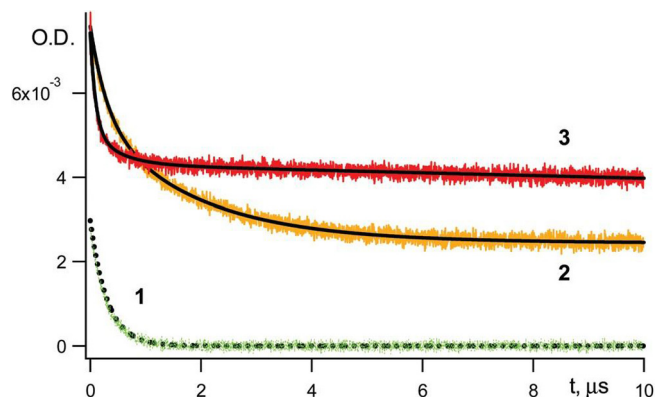

Fig. 2. Kinetics traces of transients at λ 630 nm ($^3B^*$) at 263 K obtained under laser flash photolysis of **B** in **E** film (1); decay kinetics of $^3B^*$ and **BH**$^{\cdot}$ measured at λ 545 nm at 263 (2) and at 313 K (3) in the same film. Solid black lines are the computer fit of experimental curves to kinetic formulas; see Scheme 1 and the text below. Adopted from Ref. [10].

^3B + RH $\xrightarrow[k_T]{\text{H transfer}}$ $^3[$ **BH**$^{\cdot}$ ... **R**$^{\cdot}]$

cage escape   cage reaction

k_{esc} k_r

BH$^{\cdot}$ + **R**$^{\cdot}$ $\xrightarrow{k_b}$ Products

Scheme 1.