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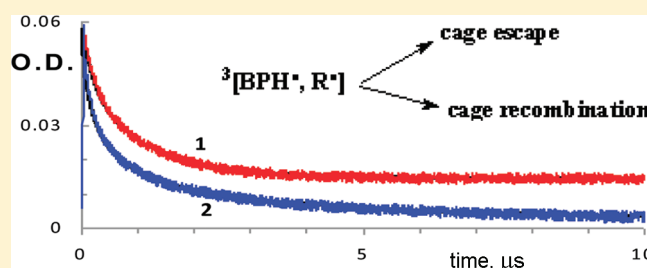
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Laser Flash Photolysis of Benzophenone in Polymer Films

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ABSTRACT: With a nanosecond laser we studied flash photolysis of benzophenone (BP) dissolved in four different polymer films. We measured kinetics of decay of a triplet state of benzophenone ^3BP as well as kinetics of decay of benzophenone ketyl free radicals BPH^\bullet . Polymer matrices have plenty of reactive C–H bonds, and the hydrogen abstraction by ^3BP leads to a formation of geminate pair which either recombines into molecular products or dissociates. Decay kinetics of ^3BP is well described by dispersive kinetics and in particular by the kinetic law suggested in Albery, W. J.; et al. *J. Am. Chem. Soc.* 1985, 107, 1854. We observed a broader distribution of rate constants in hard films. It was observed that the decay kinetics of transients radicals in the “hard” polymers is quite satisfactory described by the same law for dispersive kinetics. Kinetics of radicals decay in “soft” polymers is satisfactorily described as a diffusion-enhanced reaction. Effect of a hardness of polymer matrix on the measured kinetic parameters is discussed.



INTRODUCTION

Study of photochemistry of photoactive additives in polymer films is an area of active basic and applied research. Photocure of coatings usually ends up with a residual photoinitiator. Benzophenone (BP) is a widely used photoinitiator. Outdoor application of the cured coatings leads to a photoexcitation of BP during the daytime with subsequent photoinduced reactions accelerating degradation of the coatings.

The well-documented reaction of photoexcited BP is hydrogen abstraction from almost any C–H bond with the formation of a triplet radical pair (RP).¹ Study of reactivity of such pairs, their geminate recombination and exit in a polymer bulk, allows understanding of cage effect in polymers; cf. a review article² and our previous publications.^{3–5} One can compare the cage effect of the same RP and its dynamics in a (viscous) liquid⁶ and in a polymer host.

The present work is devoted to study of the primary photo-reactions of BP in four polymer films with a goal of elucidation of cage effect in polymers.

EXPERIMENTAL PART

1. Devices. The absorption spectra and the kinetics of formation and decay of intermediates were measured with a nanosecond laser photolysis apparatus [7]. A PRA LN 1000 N₂ 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 paper 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 with an optical path length $l = 0.2$ mm. A piece of polymer film with BP (vide infra) was immersed into the cell. All samples were vacuumed. In the experiments with magnetic field, the cell was placed between the poles of a permanent magnet (magnetic flux density $B = 0.2$ T). Electronic absorption spectra were taken with a Shimadzu UV–Vis–NIR UV-3101PC spectrophotometer.

2. Reagents and Reactive Mixtures. We used the following reagents: BP of Aldrich, reactive acrylate monomers isobornyl acrylate (SR506A of Sartomer or IBOA) and tripropylene glycol diacrylate (SR306 of Sartomer or TPGDA), oligomers of Bomar Specialties:⁸ difunctional aliphatic polyester urethane acrylates BR-371, BR-372; BR-374 and difunctional hydrogenated polybutadiene urethane acrylate BR-641. BR oligomers like most of the oligomers are very viscous liquids at room and even elevated temperatures;^{8,9} BRs were mixed with IBOA or TPGDA. We added 30 wt % IBOA to BR-371, BR-372, and BR-641. BR-374 is not miscible with IBOA, and we added 30 wt % of TPGDA to BR-374. A high concentration of BP was dissolved in each of four formulations, namely 9.0% or ca. 5 M. All reagents were used as received.

3. Photopolymerization of the Formulations. Formulations were successfully cured with a Fusion 300 W/in. processor with D-bulb in the air. Three passes under the lamp at a conveyor with a speed of 20 ft/min were performed in each of the four cure experiments. We will abbreviate these cured films further as 371, 372, 374, and 641 following the BR name of the used oligomer.

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Table 1. Mechanical Properties of the Cured Films^a

| film ^b | film ^c | durometer A hardness | tensile strength, MPa | elongation- to-break, % | tensile modulus, MPa |
|-------------------|-------------------|-------------------------|--------------------------|----------------------------|-------------------------|
| 641 | A | 23 | 0.25 | 126 | 0.37 |
| 374 | B | 30 | 0.44 | 33 | 1.6 |
| 372 | C | 37 | 1.3 | 68 | 2.2 |
| 371 | D | 65 | 5.3 | 49 | 67 |

^a Determination error of the measured and presented in the table values is 10%. ^b Designation of films, cf. Experimental Part, Section 3.

^c Abridged designation of films.

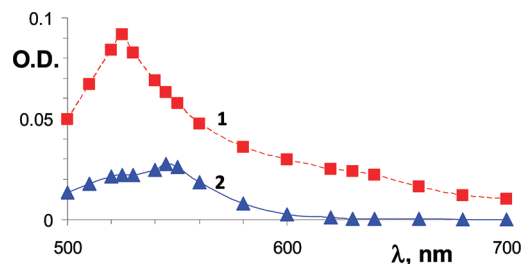


Figure 1. Absorption of transients obtained under laser flash photolysis of film A with a delay after laser flash of 1–20 ns and 2–2.0 μs. OD here and below stands for the optical density.

Evidently, BP serves as a photoinitiator of polymerization (cross-linking of difunctional oligomers).¹⁰ The thickness of the cured films was 0.2 mm, and the concentration of residual (after cure) BP in films estimated by BP absorption in UV region was ~0.5 M in all films.

RESULTS AND DISCUSSION

1. Mechanical Properties of the Cured Films. We measured mechanical properties of the four cured films by a rather standard procedures described in detail in ref 9. The data are presented in Table 1. Measurements were made at ambient temperature. The higher the Durometer hardness, the harder is the film. The harder is the film, the smaller is the elongation-to-break of the film, and the higher is tensile modulus and tensile strength.⁹ We abbreviated designations of films further as A–D; cf. Table 1. We conclude that hardness of films increases (softness decreases) from A to D. (We mention here the obvious regularities, and some deviations are not surprising. Film B (Table 1) has a smaller elongation-to-break than film C, but considering all of the measurements, we conclude that film B is softer than film C.)

2. Triplet State ³BP. Laser excitation of BP in the films described above leads to a formation of a triplet state of BP. ³BP has a characteristic absorption spectrum (Figure 1, curve 1).^{1,7} The observed spectrum in films is similar to the absorption spectrum of ³BP in other media: it has λ_{max} = 525 nm and a shoulder at 600–700 nm.^{1,7} The decay kinetics of ³BP was measured in the spectral area λ > 600 nm where absorption by other transients is negligible. In particular, we selected λ = 630 nm for kinetic measurements (Figure 2). We approximated decay kinetics of ³BP by the exponent (the first order, not presented). However, a nice fit was observed only up until conversions ξ̄ = 0.5–0.7. Corresponding first-order rate constants k^T, s^{−1} obtained under simulation of experimental data up until such ξ̄ are presented in Table 2.

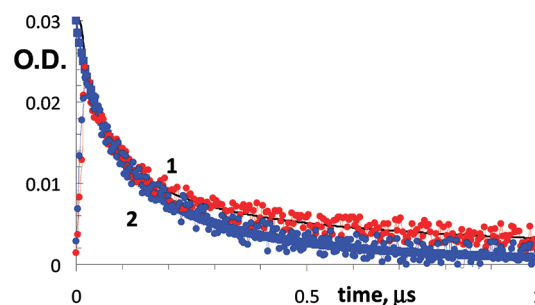


Figure 2. Decay kinetics of ³BP measured at λ = 630 nm obtained under laser flash photolysis of films D (1) and A (2). Solid lines are the simulation of kinetic data with eq 1.

Table 2. Kinetic Parameters of ³BP Decay^a

| film | 10 ^{−6} k _T , s ^{−1} | 10 ^{−6} k _{av} , s ^{−1} | γ _T |
|------|---|--|----------------|
| A | 5.2 | 8.2 | 1.3 |
| B | 9.2 | 37 | 2.3 |
| C | 8.0 | 14 | 1.4 |
| D | 3.2 | 26 | 2.9 |

^a Cf. the text for definition of parameters. Determination error of the values in the table is 10–15%.

It is known that the reactivity of molecules (radicals) in polymers and in the solid state is controlled by other principles rather than by kinetics in homogeneous liquids.^{11–14} Kinetics of many elementary reactions in the solid state and in polymers are described by dispersive kinetics, where the kinetic nonequivalence of chemically identical species (radicals) is accepted as a model for the analysis of the decay kinetics.^{11–14} A possible promising approach for quantitative description of kinetics in polymers was suggested by Albery et al.¹⁴ It is assumed that the first-order elementary reactions in polymers have a Gaussian distribution of a logarithm of the first-order rate constants.¹⁴

Such a suggestion leads to the following analytical expression for a kinetic curve:¹⁴

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

where C(t)/C(0) are current and initial concentrations of reagents, respectively, k_{av} is the average value of first order rate constant, and γ is the half-width of a distribution. We used eq 1 to simulate the kinetics of ³BP decay. The values of k_{av}^T and γ_T obtained as a result of the fit into eq 1 are presented in Table 2.

We use in this paper subscript and superscript “T” for values related to the decay of the triplet ³BP, and we will use subscript and superscript “R” in parameters related to the decay of the radical BPH[•]; vide infra.

We noticed that a decay of ³BP in the four studied films is essentially faster than such a decay in the common polymers PVC and PMMA.^{3,4}



Evidently, each of the four studied films has an abundance of C–H groups, even activated C–H groups by α-oxygen in polyethers, and ³BP reacts with a polymer matrix RH; cf. below.

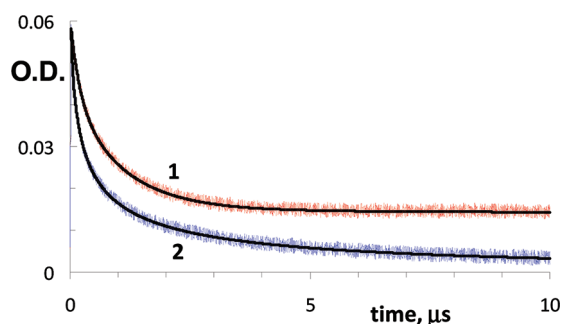


Figure 3. Decay kinetics of transients at $\lambda = 550$ nm obtained under laser flash photolysis of films A (1) and D (2). Solid curve 2 is a fit of experimental data into eq 1. Solid line 1 is a fit into two-exponential law.

Table 3. Kinetic Parameters of BPH[•] Decay^a

| film | $10^{-6}k_g$, s^{-1} | $10^{-9}k_b$, s^{-1} | φ_∞ | $10^{-6}k_{av}^R$, s^{-1} | γ_R | α | $10^{11}D$, cm^2 s^{-1} |
|------|----------------------------|----------------------------|------------------|---------------------------------|------------|----------|---------------------------------|
| A | 1.5 | 9.1 | 0.61 | 1.7 | 12 | 0.95 | 15 |
| B | 0.65 | 1.5 | 0.22 | 0.11 | 15 | 0.91 | 0.015 |
| C | 0.76 | 2.5 | 0.56 | 1.4 | 8.5 | 0.82 | 11 |
| D | 0.27 | 0.51 | 0.86 | 0.84 | 2.4 | 1.1 | 1.1 |

^a Cf. the text for definition of parameters. Determination error of the values in the table is 10–15%.

k_T correlates with k_{av} with an exception of the hardest film D because both constants describe ³BP decay; cf. Table 2. γ_T has a tendency to increase with the hardness increase with an exception of film C now. At the same time, this introductory work on four different films does not allow trustworthy correlations of parameters.

3. Radicals BPH[•]. New transients are observed at ~ 1 μs after the laser flash (cf. Figure 1); they follow the disappearance of ³BP. These new transients are the well-documented ketyl radicals^{1,7} of BP formed in the reaction:



Initially formed triplet radical pair (eq 3) either dissociates into free radicals or recombines within a polymer cage:^{2–7}



In this work under *geminate recombination* we will understand the decay of pairs (eq 4) by both processes.

BPH[•] has a characteristic absorption maximum at $\lambda_{max} = 545$ nm (cf. Figure 1, curve 2),^{1,7} and we studied the decay of BPH[•] at λ_{max} . C-centered aliphatic R[•] of a polymer matrix absorbs in the UV region and is not observed in our experiments. Thus, ³BP and BPH[•] can be differentiated in many cases by their absorption spectra and by the fact that the major part of the radicals decay much slower than the triplet state.⁷ It is possible to find a spectral area where only ³BP absorbs ($\lambda > 600$ nm, vide supra) but the spectrum of BPH[•] overlays with the ³BP spectrum (Figure 1). We excluded the initial spike on a kinetic curve due to ³BP decay in our kinetic study of BPH[•], and we considered the time of ³BP disappearance as $t = 0$; cf. Figures 3 and 4. Kinetic data

were fit into eq 1; the corresponding k_{av}^R and γ_R are presented in Table 3.

It is expected that γ is a relatively low value of, e.g., 1–10.^{14,15} We recall that γ is a width of a distribution of a *logarithm* of a rate constant. High γ (more than ~ 10) means a huge span of rate constants and does not have physical meaning that way. We obtained $\gamma_R = 2.4$ for the hardest film D (Table 3), which is close to $\gamma_T = 2.9$ (Table 2) for the same film. We conclude that eq 1 is applicable for kinetics in the hard polymers. Obtained high values of $\gamma_R = 12, 15$ (Table 3) indicate, in our opinion, that eq 1 does not describe kinetics of radical pair decay in soft polymers.

Kinetic curves of BPH[•] decay (Figure 3) can be easily simulated by two exponents. The fast part of decay can be tentatively ascribed to geminate recombination with rate constant k_g , s^{-1} , and a very slow part of decay is associated with recombination in the solvent bulk with k_b , s^{-1} . Obtained k_g and k_b values are presented in Table 3. There is a difference of several orders of magnitude between k_g and k_b (Table 3), and apparently such an approach makes sense: fast geminate recombination and a slow recombination in the bulk of polymer matrix. We assume an exponential model of the cage effect,⁶ and recombination in the solvent bulk is formally considered as a first-order reaction. Radicals in the solvent bulk should decay in the self- and cross-recombination reactions described by one or another distribution of second-order rate constants. The fraction of radicals that decayed in the cage (a fast stage; cf. Figure 3) is the cage effect value φ_∞ .⁶ A plateau observed at a time scale of geminate recombination is the absorption of BPH[•] escaped from the cage. Data obtained from the kinetic curves φ_∞ are presented in Table 3. φ_∞ has the highest value in the hardest film D. Diffusivity/reactivity of radicals is apparently expected to slow down in hard polymers. We obtained the lowest k_g value and the low k_{av}^R for film D (Table 3).

One can see relatively high φ_∞ for films A, C, and D; cf. Table 3. Such observation is important from the standpoint of the study of the degradation of polymers. It turns out that the most of the photogenerated radicals decay inside the cage and a small fraction of radicals exits into the polymer bulk and damages the polymer.

We speculated above that eq 1 is not applicable for analysis of BPH[•] kinetics in the soft polymers (A and B here). We can verify a suggestion that in soft polymers radicals undergo diffusion-enhanced recombination like in a very viscous liquid. We will address the kinetics of geminate recombination of freely diffusing reagents that have a sum of van der Waals radii σ ; and reagents were generated at $t = 0$ at a distance L from each other. The probability of their recombination during encounter is α ; D is a coefficient of mutual diffusion. Equation 5 described kinetics of such pairs decay or kinetics of geminate recombination:¹⁶

$$\frac{C(0) - C(t)}{C(0)} = \frac{\sigma\alpha}{L} \operatorname{erfc}\left(\frac{(1-\alpha)\sigma}{2\sqrt{\pi Dt}}\right) \quad (5)$$

We simulated kinetic curves like those presented in Figure 4, with eq 5 giving “the best” D and α . We assume that $\sigma \approx L$ and equals 0.7 nm. (The latter value is a reasonable assumption.) Obtained D and α are presented in Table 3. Figure 4 exemplifies a good fit into eq 5 in the wide range of time up to 10 ms. Comparison of sums of square errors (SSE) demonstrates that for the hard film D, eq 1 described experimental data better than eq 5. Moreover, simulation with eq 5 of the kinetics in film D leads to an erroneous $\alpha > 1$ (Table 3).

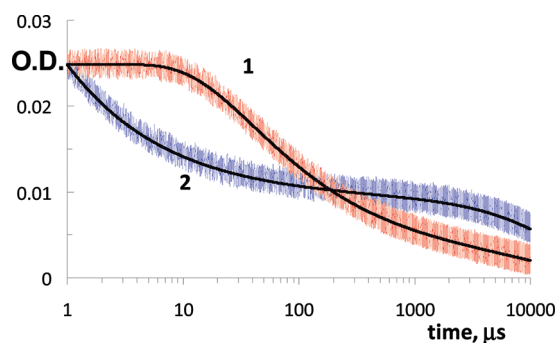


Figure 4. Decay kinetics of transients at $\lambda = 550$ nm obtained under laser flash photolysis of the films B (1) and A (2). Solid lines 1 and 2 are obtained as a result of a fit into eq 5.

It is easy to estimate time of encounters of radicals in the solvent bulk. The OD of BPH \cdot exiting the solvent bulk corresponds to a plateau on a dependence of OD vs time; cf. Figure 3. According to Lambert–Beer law,

$$\text{OD} = \varepsilon \times l \times c \quad (6)$$

where $\varepsilon = 3220 \text{ M}^{-1} \text{ cm}^{-1}$ for BPH \cdot at its absorption maximum¹ and $l = 0.02 \text{ cm}$ (cf. the Experimental Part, section 1). Thus, one can get c . We obtained $c \approx 3 \times 10^{-4}$ and $1 \times 10^{-4} \text{ M}$ for BPH \cdot in film A (curve 1) and in film D (curve 2), respectively; cf. Figure 3.

The average distance r between homogeneously distributed radicals is

$$r, \text{ cm} = [10^3 / (N_A \times c)]^{1/3} \quad (7)$$

where N_A is the Avogadro constant and c is the concentration of radicals; cf. above. The following relationship is generally valid:

$$t = \langle r^2 \rangle / (6D) \quad (8)$$

where $\langle r^2 \rangle$ is the mean square displacement of diffusing molecules, D is a mutual diffusion coefficient (Table 3), and r is the mean distance over which a couple of radicals can move during time t .

We approximate r^2 (eq 7) as $\langle r^2 \rangle$. D values were estimated previously (Table 3). Thus, one can obtain encounter time of radicals in the solvent bulk from eqs 7 and 8.

We obtained ~ 3 ms for encounters of radicals in film A and ~ 2 s for film D for the curves presented in Figure 3. These values are 3–6 orders of magnitude larger than the time of geminate recombination; cf. Figure 3. The same conclusion was made for two other case studies in this work: a decay of radicals in the solvent bulk occurs at much larger times than the geminate recombination. And the same conclusion can be drawn from most of the reported literature results on liquid-phase recombination.⁶

4. On the Magnetic Field Effect on Recombination of Radicals. We have not observed a magnetic field effect (MFE) on the kinetics of BPH \cdot decay within the accuracy of our measurements (determination error of kinetic parameters is 10%; cf. Table 2). A MFE on BPH \cdot geminate recombination was observed in micelles and in viscous liquids.^{1,7} The yield of BPH \cdot into the solvent bulk from a cage or escape from a micelle increases in the moderate magnetic field predominantly due to action of the hyperfine coupling mechanism (HFC).^{1,7} Detailed discussion of the HFC mechanism can be found in the literature.¹ In our previous work we also did not observe a MFE on geminate recombination in polymer media.³ Triplet RP undergoes intersystem

crossing (ISC) into singlet RP and recombines. That mechanism of ISC might be paramagnetic relaxation in long-lived pairs or MF-independent spin–orbit coupling.¹⁷

CONCLUSIONS

Benzophenone BP was dissolved in four different polymer films. Primary reactions of BP photoreduction in the films were studied by nanosecond laser flash photolysis. We managed to separate decay kinetics of ^3BP (fast) and of BPH \cdot (slow) and spectra of both transients. Decay kinetics of ^3BP and of BPH \cdot in the hardest film is well described by eq 1. Rate constants and other parameters obtained from experimental kinetic curves are discussed. Our data testify to a conclusion that elementary radical reactions in the “hard” polymers are described by dispersive kinetics and can be satisfactorily described by a liquid-phase approach in the “soft” polymers. Soft polymers can be treated, at least for a current case, as very viscous liquids. We have not observed magnetic field effect ($B = 0.2 \text{ T}$) on BPH \cdot decay.

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