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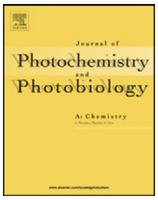

Chemical reactions of benzophenone photoirradiated in 1,2-polybutadiene

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ABSTRACT

The photolysis of benzophenone (BP) in 1,2-polybutadiene (1,2PB) was studied at low radiation intensity in order to clarify some aspects of BP photochemistry and of 1,2PB photocrosslinking. The expected primary photoreactions of hydrogen abstraction and carbonyl-vinyl cycloaddition were observed. In addition, it was established that the appearance of light absorbing transients (LATs) is not as significant as in polar media, and that the kinetics of BP consumption are more complicated than for a pseudo monomolecular process. Theories are available for reactions between excited species and BP molecules in ground state. An approximate kinetic model was developed by defining a global BP consumption as the sum of the photoreduction and a BP concentration-dependent term. It was also found that the polymerization of vinyl groups in 1,2PB is probably the most significant crosslinking process and that almost all BP-originating products are bonded into the network of crosslinked chains. Observations of the photolysis of BP in 3-methyl-1-butene were used to estimate what happens in the polymer.

1. Introduction

Benzophenone (BP) is one of the most extensively investigated photoactive reactants because the lifetime of its excited triplet state (^{3}BP*), when the molecule behaves as a biradical, is long enough to ensure significant yields in many reactions. It is known that the primary photoreactions are the generation of radicals by hydrogen abstraction from hydrogen donor moieties and the addition of the carbonyl bond to carbon–carbon double bonds [1], but the secondary processes complicate a detailed understanding of the BP photochemistry. The goals of the present study are (i) to better understand BP photochemistry by clarifying a generally unexpected observation, namely that the rate of BP photo-consumption may be non-linearly concentration-dependent, and (ii) to report information useful for optimum design of photosensitive materials.

The photochemistry of benzophenone has a very long history. So, the photoreduction of BP in 2-propanol reported by Ciamician and Silber in 1900 is one of the earliest photochemical studies [2] that demonstrated the intermolecular hydrogen atom abstraction. Nevertheless, systematic studies have been performed in the second half of the last century and the first results about the photochemistry of ketones were reviewed by Schönberg and Mustafa [3].

Many applications of BP photochemistry are presented in patents for photoresists [4–7]. The combination of BP with 1,2-polybutadiene (1,2PB) studied in this paper is an actual photoresist where BP is the crosslinking promoter for irradiation in the 300–400 nm region. The studies of photocrosslinking induced by BP in polymers began in the mid 1950s with the work of Oster et al. on the crosslinking and grafting reactions induced by aromatic ketones irradiated with far UV light (200–300 nm) [8]. Numerous investigations on BP and its derivatives in combination with polyolefins irradiated with near UV light (300–400 nm) have been carried out by Rånby’s group [9–15].

The basic BP photochemistry has been investigated in both liquid solutions and solids. The mechanism of photoreduction of BP by hydrogen abstraction has been elucidated first in alcohols [2,16]. Subsequent studies of BP photolysis in hydrogen donor media have evidenced the formation of unstable photoproducts, which absorb just in the n–π* region of the aromatic ketones [17–28]. Observed initially by Pitts and co-workers for the photolysis of benzophenone in oxygen-free isopropyl alcohol [16], these intermediates are known as light absorption transients (LATs) and found to be a regular presence in hydrogen donor media. It was reported that they act as quenchers of the benzophenone triplet state and are very sensitive to oxygen, in the absence of which their lifetime is quite long (several days) [18,19]. By their disappearance from the system, the triplet absorption partially gets recovered [18]. Many studies have been carried out in an attempt to clarify the chemical structure of these intermediates, mainly in alcohols [16,18,20–23], but also in benzene [18,24], n-hexane and cyclohexane [18], benzhydrol and tetrahydrofuran [23]. The LAT structure has been attributed to hemiketals [16] or isobenzopinacols [21], assumed to appear by dimerization of two diphenylketyl radicals [18,21], or by cross-coupling reaction between the diphenylketyl radical and a solvent radical created by hydrogen abstraction [19].

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The LAT products appear also in solid samples (i.e., polymeric films) when these are exposed to radiation in the range of 350–365 nm [25–27] or the extended range 250–365 nm [28]. It has been confirmed that the photoreduction yield is highly dependent on the rigidity of the photolysis medium because the hydrogen abstraction is a diffusion-controlled process that is very slow in polymers with high glass transition temperature [26]. The reactions considered in the present study were performed in a high elastic polymer matrix because 1,2PB (T_g = −20 °C) is a flexible rubber at room temperature.

One unwanted consequence of LAT's presence would be that quantitative kinetic studies and precise quantum yield determinations of photoreduction of BP could not be performed. Therefore, the determination of BP photoreduction yield [26,27] was done with a lower degree of accuracy.

The present study refers to 1,2-polybutadiene (1,2PB) which is itself a photocrosslinking elastomer at $\lambda < 300$ nm [29]. But its photosensitive properties can be significantly improved by use of photoinitiators, like benzophenone, that extends the photosensitivity in the region of near UV light. There have been several recent attempts to create aromatic ketone–1,2PB photocrosslinkable systems by radiation processes to be used as foamed materials [30] or as photosensitive printing plates [31]. On the other hand, 1,2PB is rather different from the polymers in which the photolysis of benzophenone has been studied up to now because: (i) its glass transition temperature, T_g, is lower than the room temperature where the irradiation studies are usually carried out and, consequently, the molecular mobility of the reactive species is rather high, (ii) the allylic hydrogen atom is easily abstracted by the species ^{3}BP*, (iii) the pendant vinyl groups are potentially polymerizable by radicals generated during BP photolysis, and (iv) the carbon–carbon double bonds provide an additional path for the consumption of excited BP molecules by cycloaddition (Paterni–Büchi) reaction [31–35]. As shown further on, the formation of LAT products, although much diminished in 1,2PB than in the polymers considered in other studies [24–28], still complicates the kinetic analysis of BP photoconversion. Apart from modifications of physical properties originally considered, other observations lead us to gain a deeper insight into the mechanism of photocrosslinking induced by BP. For those mechanistic studies, 3-methyl-1-butene, which contains similar reactive sites as 1,2PB, was used as a model compound.

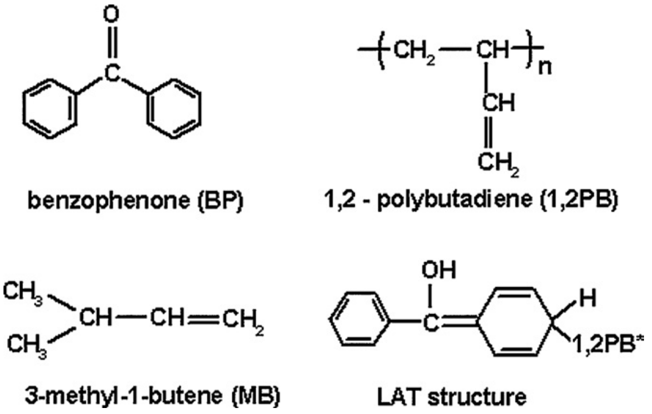
2. Experimental

2.1. Materials

1,2-Polybutadiene (1,2PB) with 92% 1,2-unit content, predominant syndiotactic microstructure, M_w of 92 000 g/mol and M_w/M_n = 1.75, glass transition at −20 °C, melting point of 80 °C (DSC data), and crystallinity of 25%, was kindly supplied by Japan Synthetic Rubber Company under the name JRS-RB 820. 3-Methyl-1-butene (MB) with purity higher than 95% and b.p. 20 °C from Aldrich and benzophenone with purity higher than 99% from Fluka were used as received. Scheme 1 shows the chemical formula of the reactants used.

2.2. Samples

Most samples investigated were support-free films prepared as follows. To a solution with 2.5 wt% 1,2PB in chloroform, BP was added to obtain four different concentrations (1, 2.5, 5 and 10 wt%) in the solid films, corresponding to molar concentrations of about 0.05, 0.125, 0.250 and 0.5 mol L^{-1}, respectively. The films used for spectral measurements were obtained by casting the solution on a glass plate into areas delimited with metal rings 30 mm in diameter. The solvent was allowed to evaporate freely, in the dark, at room temperature. The volume of solution was adjusted so that the thickness of dried films corresponds to base-10 absorbance of about 0.1 for each sample. The films were transparent and colorless. Sample codification and initial characteristics are presented in Table 1. It was very difficult to deoxygenate the solutions without affecting their concentration; hence oxygen could be present in the BP–1,2PB films in adsorbed form. We did not find quantitative data about the adsorption of oxygen in solid polymers but taking into account that the molar fraction of dissolved oxygen in liquid hydrocarbons is $1–3 \times 10^{-3}$, it is to be expected that the molar concentration of the adsorbed oxygen in the studied samples is much lower than 5×10^{-2}, the molar concentration of BP in the most diluted BP–1,2PB film. Moreover, in Section 3.1.2 we show that the photokinetics of this sample deviates least from that of a pseudo unidirectional first order reaction.



Scheme 1. Structure of the reactants and a LAT structure proposed in the literature [19].

Samples of at least 50 mg in weight were used for two measurements of gel fraction. In this case, the area exposed to radiation was about 20 cm^2 for the film of 2.5% BP concentration and about 60 cm^2 for the film of 10% BP concentration. When BP was photolysed in MB, its concentration was about 3% by weight.

2.3. Irradiation and measurements during irradiation

The film samples were exposed for various times to the 365 nm filtered radiation of a 350 W medium pressure mercury lamp mounted in a LOS-2 (Russian Federation) irradiation unit. The radiation intensity was I_0 = 7 W/m^2, which corresponds to an irradiance of 2.1×10^{-9} Einstein cm^{-2} s^{-1}. Such a radiation intensity is lower than that used by Viltres Costa et al. who reported that the LAT formation is little significant in non-polar media and decreases with the radiation intensity [23]. To avoid photo-oxidation, the samples

Table 1
Characteristics of BP–1,2PB film samples studied.

Sample	c_0 (%/mol L^{-1})	Thickness, d (μm)	A_0/ln 10 (365 nm)	B_0/ln 10 (1665 cm^{-1})
C010	1.0/0.049	160 ± 6	0.097	0.44
C025	2.5/0.124	68 ± 4	0.103	0.47
C050	5.0/0.249	30 ± 3	0.090	0.41
C100	10.0/0.50	17 ± 2	0.101	0.46

Mentions: c_0, A_0 and B_0 are the BP concentration, base-e absorbance at 365 nm and base-e absorbance at 1665 cm^{-1} (C=O stretching) of the non-irradiated samples, respectively. Equivalence: 1%BP → 0.0495 mol L^{-1}. Useful material characteristics: $\varepsilon_{1665\,\mathrm{cm}^{-1}} = 318$ mol^{-1} L cm^{-1}, $\varepsilon_{345\,\mathrm{nm}} = 110$ mol^{-1} L cm^{-1}, $\varepsilon_{365\,\mathrm{nm}} = 70$ mol^{-1} L cm^{-1} and $\varepsilon_{1665\,\mathrm{cm}^{-1}}/\varepsilon_{365\,\mathrm{nm}} = 4.54$. The values of $\varepsilon_{1665\,\mathrm{cm}^{-1}}$ and $\varepsilon_{365\,\mathrm{nm}}$ were determined in our laboratory and $\varepsilon_{345\,\mathrm{nm}}$ was taken from the literature [36].

were irradiated under argon atmosphere in home made cells with fused silica windows of about 3 cm diameter.

The modifications of chemical structure induced by BP photolysis were estimated from FTIR absorption spectra recorded after a series of irradiation times. The intensity of the stretching C=O vibration at 1665 cm^{-1} was used as a measure of the concentration of unmodified benzophenone, while the decrease in the 910 cm^{-1} (wagging $=CH_2$) band intensity gave information about the consumption of vinyl groups of 1,2PB. A curve fit analysis in the 1680–1620 cm^{-1} region was performed in view of extracting the accurate carbonyl integrated intensity. The integrated intensities of the peaks of interest were normalized by means of the band at 1218 cm^{-1} ($-CH_2-$ twisting) which was found that is not affected by the reactions induced by BP photolysis to the 1,2PB chains.

The two samples used for gel fraction measurements had surfaces too large to be exposed in irradiation cells. To be protected against photo-oxidation, these samples were tightly laminated on the both sides with a 25 μm polyethylene film. After irradiation, the soluble fractions were extracted using chloroform at room temperature for 24 h.

A solution of 3% benzophenone in 3-methyl-1-butene (10 ml) was irradiated in a home made cell of about 15 ml capacity and 5 mm thickness. Dry nitrogen was bubbled through the solution before irradiation. To diminish MB evaporation during irradiation, the cell was continuously cooled with an ice + water mantle (temperature was approximately 4 °C). The radiation of a 500 W mercury lamp filtered by a 4 mm Pyrex glass plate ($\lambda > 300$ nm) was used in this case. The irradiation time was prolonged to ensure the complete transformation of BP, finding that a 3 h exposure time was long enough for the disappearance of the IR carbonyl absorption. The reaction mixture showed a precipitated product (insoluble in MB) that, after separation and drying, was identified by FTIR spectroscopy as benzopinacol. Another product, a MB soluble product (SP), was obtained after the evaporation of unreacted MB. This product is a complex mixture but its NMR spectra allowed identification of some end groups and molecular fragments. In addition, its main components were separated by HPLC and their molecular structures were determined from mass spectra.

2.4. Spectral analysis

The initial samples and the photolysis products resulting from BP irradiation in 1,2-PB films and MB were analyzed using FTIR, ^{1}H NMR and mass spectra (MS) using Bruker FTIR VERTEX 70, Bruker NMR Advance DRX 400 and Agilent MS 6520 spectrometers, respectively. The FTIR spectra of the photolysis products were obtained in transmission mode. The mass spectrometer was an ESI-QTOF (Electrospray Ionization Quadrupole-Time of Flight) device operating in positive-ion mode. It was preceded by an HPLC accessory provided with an UV–VIS Diode Array detector. A tetrahydrofuran–isopropyl alcohol (80:20, v:v) solvent mixture was used.

3. Results and discussion

3.1. The photoproducts and kinetics related to the irradiation of benzophenone in 1,2-polybutadiene

3.1.1. Spectral observations on photoproducts

It is reported in literature that reactions of benzophenone with olefins start under irradiation at 365 nm from its triplet state through two competing processes: (i) hydrogen abstraction from the olefin reactant (most probable from allyl groups) when pairs of diphenyl ketyl or semibenzopinacol (sBzPi) and olefin radicals are generated, and (ii) addition of the excited carbonyl bond to olefin carbon–carbon double bonds with formation of oxetanes (Paterno–Büchi reaction) [32,33,37]. It is expected for the BP–1,2PB system that the recombination of the two radicals to lead to the following three possible products: benzopinacol (BzPi), sBzPi–1,2PB branchings and 1,2PB–1,2PB branchings and/or crosslinks, the last two being combined in a polymer network. These photoproducts should be normally transparent above 300 nm because they should not contain aryl-conjugated carbonyl or carbon–carbon double bonds. However, as it was mentioned before, the diphenylketyl radical may undergo disproportionation followed by coupling to a 1,2PB chain radical to give quinoid or LAT products [26–28]. The structure of such a product is given in Scheme 1.

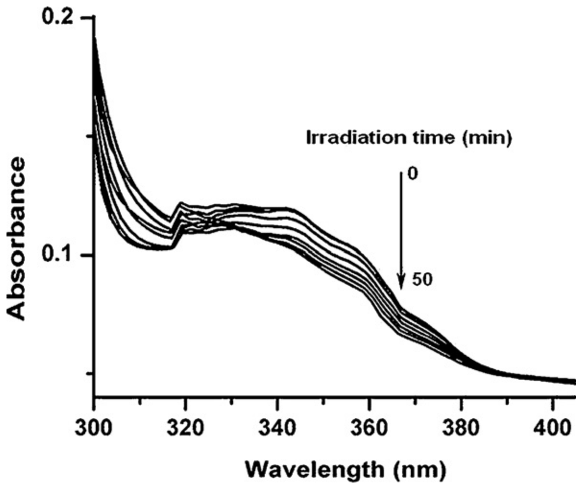


Fig. 1. The electronic absorption spectra in the 300–400 nm region of a 1,2PB film containing 5%BP (C050 sample) after a set of times of irradiation with 365 nm. Mentions: (i) the film thickness was 20 μm, and (ii) the small steps at about 320 nm are caused by an operating change in the optical system of the spectrometer.

On the other hand, unlike for the combinations of BP with polar hydrogen donor polymers [27,28], the LAT absorption at $\lambda > 300$ nm is less significant for the system studied by us, fact that might facilitate a kinetic analysis. As illustrated in Fig. 1, there is a weak new absorption at around 320 nm, too weak to produce strong effects near 365 nm, where the radiation frequency was centered. A similar picture we obtained when benzophenone was irradiated in cyclohexane at high dilution, in good agreement with the results of Viltres Costa et al. [23], who concluded that the quantum yield ratio of LAT formation and BP photoreduction is very low in non-polar media and that it decreases when the radiation intensity decreases.

The analysis of FTIR spectra of the BP–1,2PB films before and after UV-exposure reveals the decay of the BP carbonyl band (1665 cm^{-1}), as expected, and the rise of new absorptions at 3420, around 1720 and 1492 cm^{-1}. In addition, it was observed that the decrease in the C=O stretching intensity is not accompanied by similar changes in the phenyl bands of benzophenone. The spectra in Fig. 2 show that the relative intensity of vinyl bands (3009 cm^{-1} of =CH stretching, 1642 cm^{-1} of C=C stretching, 1335 cm^{-1} of =CH bending, and 908 cm^{-1} of $=CH_2$ wagging) is smaller for an irradiated and extracted sample than for the starting one. The band centered on 3420 cm^{-1} is associated with the hydroxyl group of semibenzopinacol type. The intensity of this absorption band increases with the initial BP concentration. The loss of conjugation and formation of alcoholic structure, characteristic to the semibenzopinacol moiety, are responsible for the appearance of new aromatic vibrations at 1492 and 702 cm^{-1}.

The intensity of the bands around 3400, 1722, 1260 cm^{-1} as well as the strong absorption between 1150 and 990 cm^{-1} also increase with the initial benzophenone concentration. The weak absorption around 1094 cm^{-1} may be assigned to eventual linear ether bridges between polybutadiene chains.

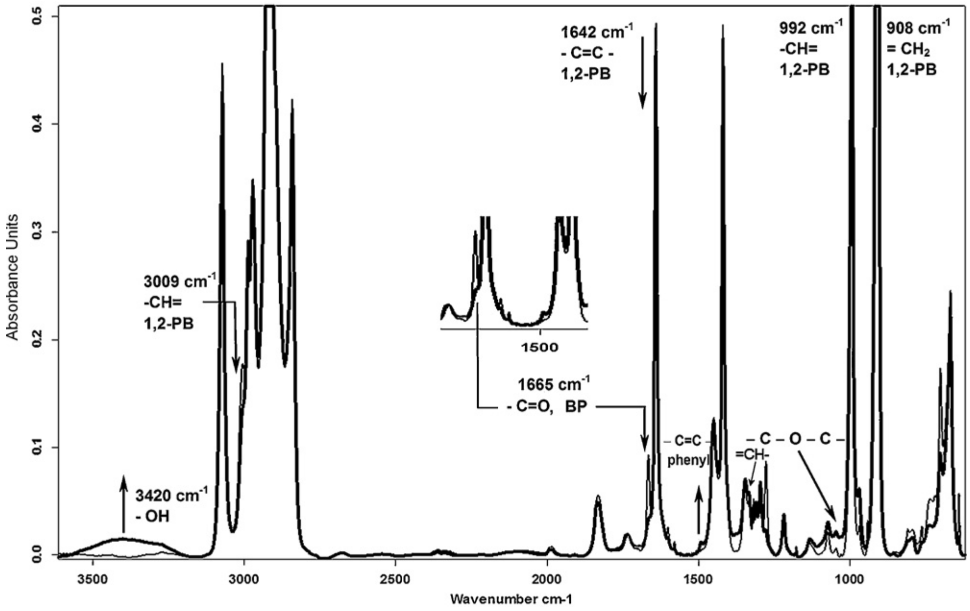


Fig. 2. FTIR spectra of a 1,2-polybutadiene containing 10% benzophenone in two situations: non-irradiated (thin trace) and 50 min irradiated and extracted with chloroform (thick trace).

The ratio between the numbers of transformed vinyl (from 1,2PB) and carbonyl (from BP) groups (Fig. 3) was found much larger than 1, suggesting a benzophenone photo-initiated polymerization of 1,2PB vinyl groups. Such a crosslinking path was already reported by Decker [38–40]. Another observation is that the ratio mentioned above shows a maximum for an initial BP concentration between 1 and 5%. To verify this fact, two films with very different BP concentrations were irradiated with Hg radiation filtered for $\lambda > 300$ nm until total conversion of BP. The crosslinking density – the fraction of crosslinked mers relative to the primary number of mers – was calculated from the insoluble fraction by using a relationship developed by us [41] as a solution for the mathematically intractable Flory–Charlesby equation [42,43]. This parameter was found to be higher for the sample C025 than for the sample C100 (Table 2), in support of the fact that the benzophenone concentration dependence of photocrosslinking yield shows a maximum. Such maximum is not easily explainable but leads to the assumption of reactions between diphenylketyl radicals and BP molecules in ground state.

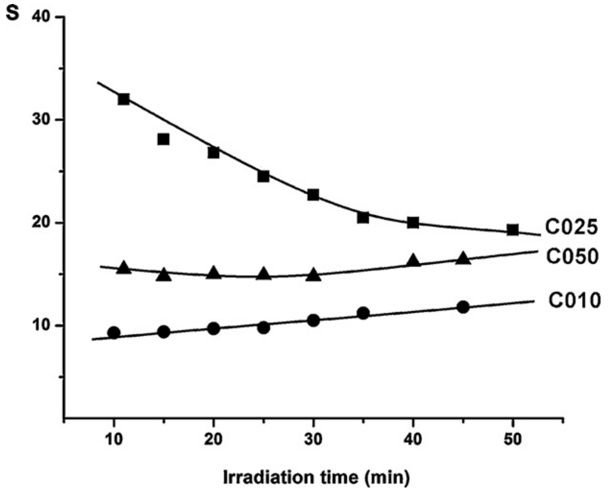


Fig. 3. Plots of the ratio *S* between the numbers of transformed 1,2PB vinyl groups and BP molecules versus irradiation time for 1% (a C010 sample), 2.5% (a C025 sample), and 5% (a C050 sample) BP concentration. The measurements were made on the samples in Table 1, and the values *S* were obtained from the relative intensity decreases of the IR absorptions at 910 cm^{-1} (H_2C=) and 1665 cm^{-1} (C=O).

Another interesting observation was made for the soluble fraction resulting by extraction with chloroform from BP–1,2PB films after their exposure under Hg radiation with $\lambda > 300$ nm. Thus, the ^{1}HNMR spectra of such extracts show only 1,2PB signals, regardless of the initial amount of BP. This means that all BP originating products are chemically bonded in the network of crosslinked chains. Therefore, one can conclude that if molecules of benzopinacol (BzPi) are formed, as expected, they react with species comprised in the polymer network. As it will be shown in Section 3.2, such reactions did not occur when BP was irradiated in MB, probably because the BzPi separates from the reaction medium due to its insolubility.

3.1.2. Kinetics of BP photoconversion in 1,2-PB

The kinetics of film samples of BP–1,2PB with approximately equal initial absorbances at 365 nm, but with different BP concentrations, were studied. Such a variation was chosen to verify if the BP concentration influences the kinetics of BP disappearance. In general, the samples of the same absorbance absorb equal doses of radiation, so that such samples should show identical BP decays regardless of the reactant concentration, if the photolysis of BP is a pure or pseudo monomolecular reaction.

Further on, the base-e initial and momentary absorbances, A_0 and $A(t)$, will be used. To ensure an acceptable measuring accuracy we preferred to use samples with the base-10 initial absorbance

Table 2
Photocrosslinking parameters[a] of 1,2PB for two BP concentrations.

Type of sample[b]	BP (%)	Exposed area (cm^2)	Gel fraction[c]	Crosslink density	γ[d]
C025	2.5	20	0.96	0.0045	7.5
C100	10	60	0.75	0.0015	2.5

[a] For samples irradiated for total transformation of the carbonyl groups of BP.
[b] Similar to those in Table 1.
[c] For overnight extraction with chloroform at room temperature.
[d] The average number of crosslinks for an average polymer chain of about 1700 mers.

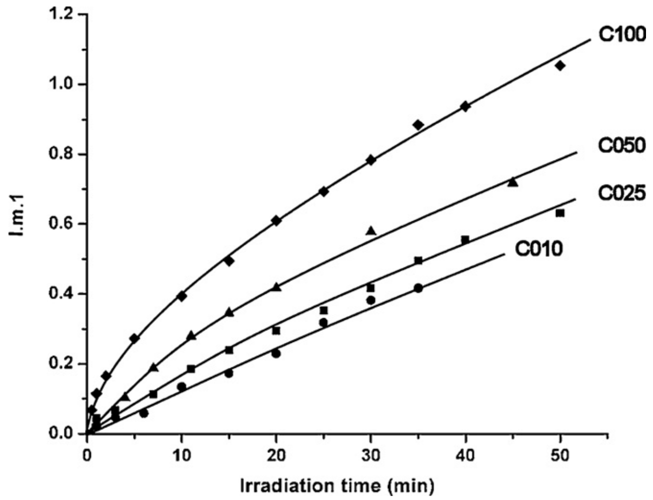


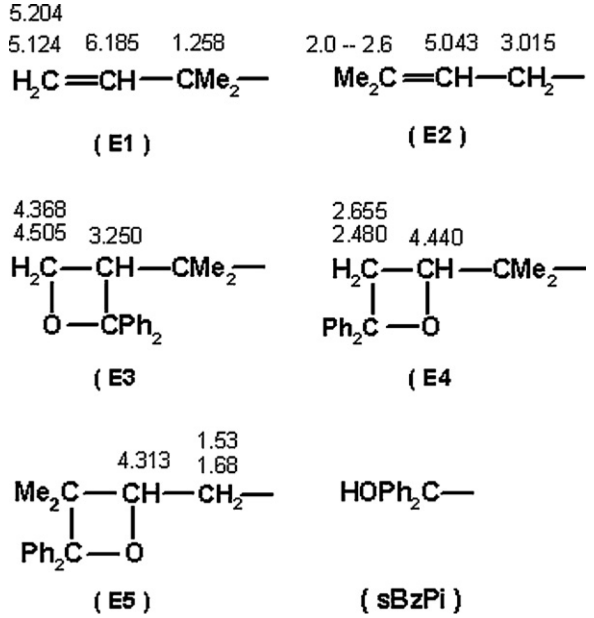
Fig. 4. Irradiation time dependences of the left member of Eq. (1) (l.m.1) for the BP–1,2PB film samples in Table 1 exposed to 365 nm radiation. The 365 nm absorbance values were indirectly obtained, from the carbonyl stretching absorbance (1665 cm^{-1}) by division with 4.54 (the ratio $\varepsilon_{1665}/\varepsilon_{365}$). The solid line curves are graphical Bezier trendlines.

at 365 nm, $A_0/\ln 10$, of about 0.1. Because the absorbance of samples was not much lower than 1, we considered that, under the assumption of unidirectional first order (UFO) photoreactions with transparent photoproducts, Eq. (1) is a better match than the well-known equation $\ln(A_0/A(t)) = \alpha \cdot \varphi \cdot I_0 \cdot t$. The notations α, φ, I_0 and t are for the base-e molar absorptivity of BP at the radiation wavelength of 365 nm ($\alpha = \varepsilon_{365} \cdot \ln 10$), the quantum yield of BP transformation, the intensity of the incident radiation, and the irradiation time, respectively. The relationship in Eq. (1) was recently derived for stirred liquid samples of any absorbance [44], but it is demonstrated in Appendix A.1 that, starting from specific expressions in the literature [45], the UFO photoreactions in rigid (non-stirring) media are characterized by a similar equation if the photoreactant is the only absorber.

$$\ln\frac{e^{A_0}-1}{e^{A(t)}-1} = \alpha \cdot \varphi \cdot I_0 \cdot t \qquad (1)$$

As seen, the plots in Fig. 4 show that the irradiation time dependence of the left part of Eq. (1) is not linear and the deviation from linearity increases with the initial BP concentration, c_0. Two explanations could be advanced for this fact: (i) the presence of LATs affects the radiation intensity and the measurements of BP absorbance, and/or (ii) the deviation from the condition of monomolecular reaction (i.e., by reactions of the diphenylketyl radical with BP molecules in ground state). As Fig. 1 shows, the presence of LAT products is proven and their absorption maximum is placed at 320 nm. But, their absorption at 365 nm is rather weak by comparison with the absorption of BP molecules, the maximum of which is closer, at 345 nm. In addition, the effect of LATs on the values of BP absorbance at 365 nm was avoided because the values of $A(t)$ used to generate the data points in Fig. 4 were determined from the carbonyl absorption in IR spectra. Referring to the second explanation, we also looked for products of the diphenylketyl radicals with non-excited BP molecules among the photolysis products of BP in 3-metyl-1-butene (MB).

It is worth mentioning that a situation similar to that in Fig. 4 was also found for the irradiation of BP in cyclohexane, where it is known that the quantum yield of LAT formation is much lower than that of BP photolysis [19,23]. Two cyclohexane solutions of $A_0/\ln 10 \approx 0.1$ were irradiated, one with 0.016% BP in a 10 mm cell and the other one with 0.16% BP in a 1 mm cell, the outset slope was 0.0062 and 0.0345 min^{-1}, respectively, hence the slope increases when the concentration of BP increases. Therefore, we conclude that in this case and also for polybutadiene, which is also a nonpolar medium, the deviation from UFO kinetics is not caused by the LAT absorption.



Scheme 2. End structures identified from ^{1}H NMR spectra (Fig. 5) and confirmed by the FTIR spectra for the product SP (MB soluble). Corresponding proton chemical shifts are given. Notation: Me for CH_3 and Ph for C_6H_5.

3.2. Photolysis of benzophenone in 3-methyl-1-butene

In order to verify some of the assumptions about the photoreactions of benzophenone when it is irradiated in 1,2-polybutadiene, we performed the photolysis of benzophenone in 3-methyl-1-butene. The irradiation time was sufficiently long for the disappearance of the carbonyl absorption at 1665 cm^{-1}. As affirmed in the experimental section, the ^{1}H NMR and FTIR spectra indicated that the product precipitated in the reaction medium is benzopinacol (BzPi), as expected, and the product dissolved in MB (SP noted) is a complex mixture. Scheme 2 presents the end groups or fragments identified from ^{1}H NMR signals between 2 and 6.5 ppm (Fig. 5) by analyzing positions, spin–spin splitting and COSY effects. These structures are vinyl (E1), olefinic (E2), oxetane (E3, E4 and E5) and semibenzopinacol (sBzPi) groups. In addition, the ^{1}H NMR spectrum does not exclude internal fragments containing vinyl polymerized MB units if the numerous and complex

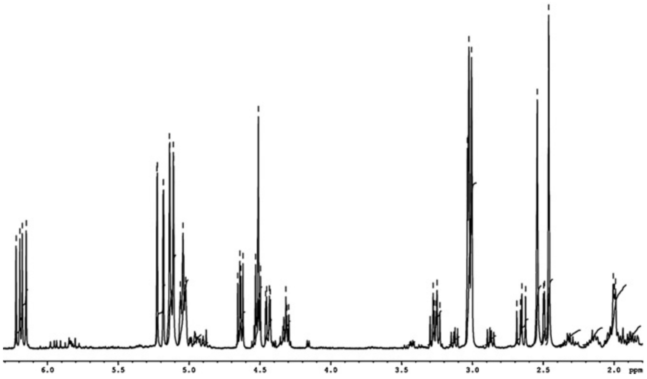


Fig. 5. ^{1}H NMR signals between 1.8 and 6.3 ppm of the spectrum in $CDCl_3$ from the reaction medium soluble products (SP) resulted from BP photolysis in MB.

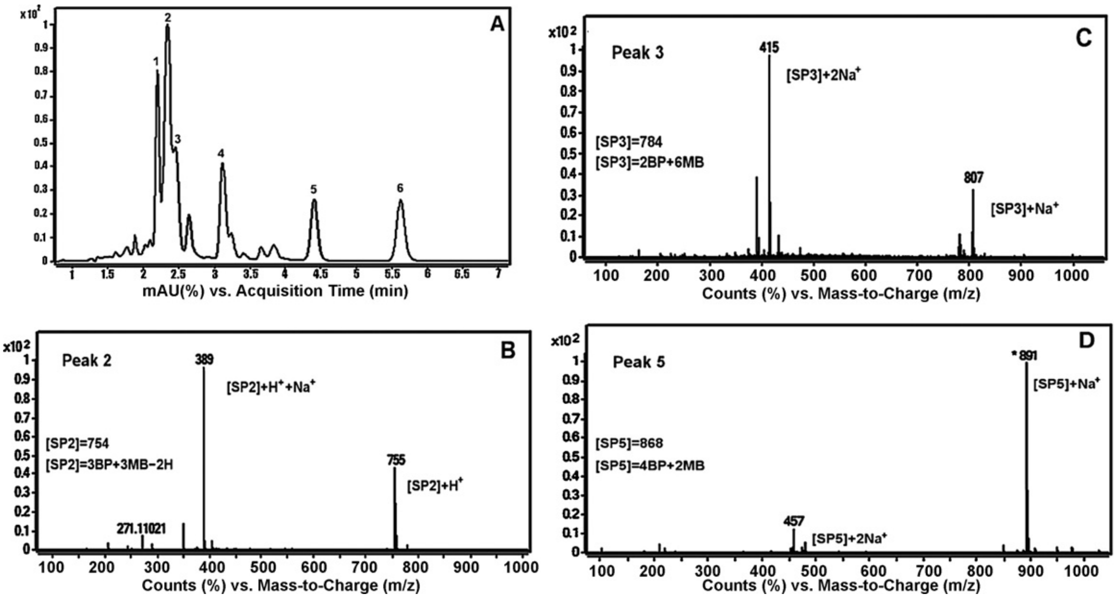


Fig. 6. HPLC peaks (A) and positive ion ESI mass spectra (MS) associated to the peaks 2 (B), 3 (C) and 5 (D).

signals between 0.8 and 1.8 ppm are considered. Also, few linear ether groups, like $–O–CH_2–$ and –O–CHR–, may be associated with the weak signals between 3.2 and 3.8 ppm.

From a mechanistic point of view, the end group E1 appears due to the extraction of the allylic hydrogen atom from a MB molecule by a BP*(T) excited molecule. The E2 end group may result by the isomerization of an E1 radical. The formation of E3, E4 and E5 oxetane rings can be explained by the cycloaddition of carbonyl groups of BP* molecules to carbon–carbon double bonds (a Paterni–Büchi reaction [32–35]) belonging to E1 and E2 end groups. The overlapping of singlet signals at about 3 ppm arises from hydroxyl protons and indicates at least three types of sBzPi groups. Regarding the molecular mass, the end structures E1 and E2 correspond to MB – H (69 Da), while the E3, E4 and E5 to BP + MB – H (251 Da), and sBzPi to BP + H (181 Da), respectively, where the notation H is for one hydrogen atom.

The signals of aromatic protons (7–7.5 ppm) of the product SP are also too complex and overlapped between them to allow a clear identification of chemical structures. However, a careful signal analysis showed that the main aromatic signals arise from structures other than BP and benzopinacol (BzPi). By comparing with the spectrum of MB, the following features in the FTIR spectrum of the product SP confirm the molecular structures derived from ^{1}H NMR spectra: (i) the intensity decreasing of the bands at 1640 (C=C stretching), 992 (=C–H out-of-plane bending) and 910 cm^{-1} ($=CH_2$ out-of-plane bending) for the significant loss of MB vinyl groups, (ii) absorptions for O–H (3496 cm^{-1}), C=C (1599, 1492 and 1447 cm^{-1}) and C–C–O (1217–1130 cm^{-1}, broad signal, and 1026 cm^{-1}, strong signal) groups for semibenzopinacol (sBzPi) groups in structures others than benzopinacol (BzPi) because the signal frequencies are different from those of BzPi, (iii) the broadening of the band at 1392 cm^{-1}, which indicates two or more different types of isopropyl groups and the new absorption as a shoulder at 1173 cm^{-1}, which may be attributed to a dimethyl quaternary carbon group ($>CMe_2$), and (iv) the complex pattern between 1120 and 950 cm^{-1} (C–O–C stretching) and the shoulder at 985 cm^{-1} for the presence of aliphatic ether and oxetane groups, respectively.

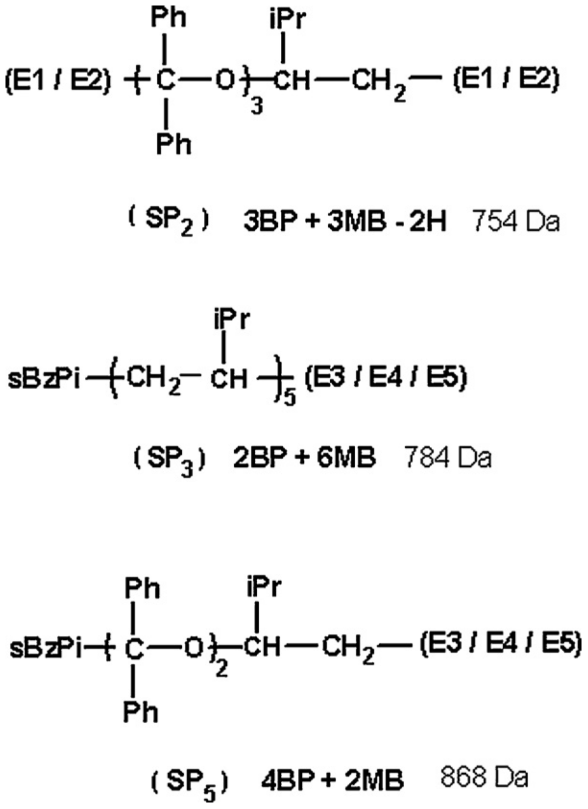
The great number of MB soluble products is also confirmed by the HPLC chromatogram in Fig. 6A. One observes six main peaks but only the mass spectra of the peaks 2, 3 and 5 were interpretable (Fig. 6B, C and D). The mass spectra from the other HPLC peaks show extremely numerous peaks which could be explained by various possible molecular structures and/or associations.

The analysis of the positive ion ESI mass spectra associated with the chromatographic peaks 2, 3 and 5 led to molecular mass values of 754, 784 and 868 Da, respectively. Taking into consideration the end groups in Scheme 2, the following compositions can only be attributed to these molecular masses: 3BP + 3MB – 2H for 754 Da, 2BP + 6MB for 784 Da and 4BP + 2MB for 868 Da. These compositions are noted as SP2, SP3 and SP5 in Fig. 6, and some possible molecules corresponding to them are presented in Scheme 3.

Some important observations can be made about the chemical compositions in Scheme 3: (i) the compositions SP2 and SP5 contain several (co and/or homo) polymerized BP units, hence means that there are cases when one absorbed photon can transform up to three BP molecules, (ii) the composition SP3 is a good support for the polymerization of vinyl groups, as was observed for the system BP–1,2PB (Fig. 3), and (iii) the presence of ether linkages, others than those in oxetane rings, as evidenced by the weak signals between 3.2 and 3.7 ppm and the new absorptions between 950 and 1120 cm^{-1} suggested for BP–1,2PB samples (Section 3.1.1). It is worth mentioning the presence of ether groups in products resulting from the photolysis of BP in vinyl acetate and that benzopinacol plays a prominent part in this case [46–47]. In our case, the linear ether groups are very rare because BzPi is practically insoluble in MB.

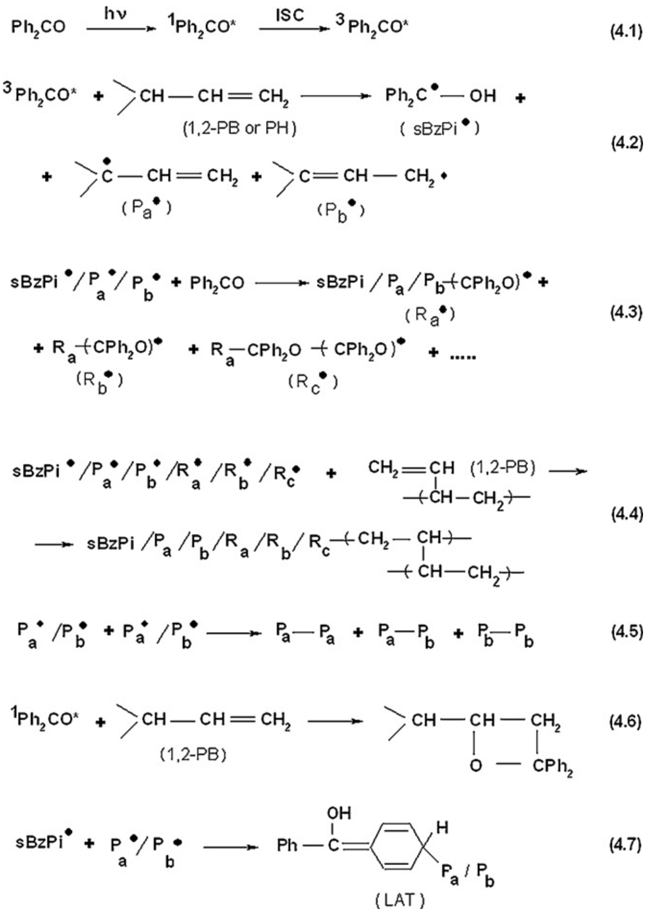
3.3. Reactions produced by photo-excited BP in 1,2-PB

The reactions in Scheme 4 are based on processes reported in the literature and on observations mentioned above, in the present article. The photo-excitation and energy transitions of BP lead to the triplet state BP*(T), (reactions 4.1), that is known to have a biradical behavior [1]. The hydrogen atom abstraction by BP*(T) from 1,2-PB, most likely from the allylic carbon, leads to diphenylketyl radicals, sBzPi$^\bullet$, and chain radicals, $P_a^\bullet$ and $P_b^\bullet$, (reaction (4.2)). The reactions of these radicals with BP molecules may produce $R_a^\bullet$, $R_b^\bullet$ and $R_c^\bullet$ oligo- and macroradicals (reactions (4.3)). The assumptions about these radicals as well as about their role in the polymerization of 1,2PB vinyl groups (reactions (4.4)) are based on the SP2 and



Scheme 3. Chemical structures corresponding to the HPLC peaks 2, 3 and 5 in Fig. 6A. Notation: –iPr is for a $-CHMe_2$ group.

SP5 products in Scheme 3 that were identified among the photolysis products of BP in MB. The formation of R_b and R_c sequences of successive BP units in the polymer network (reactions (4.3)) may be a cause for the deviation of BP photolysis from a monomolecular process with UFO kinetics. The crosslinking of 1,2PB can be explained by the polymerization of vinyl groups (reactions (4.4)). Such a process is initiated by radicals generated in reactions (4.2) and (4.3) and is supported by the results in Fig. 3 and Table 2. A maximum conversion of the vinyl group was observed when the concentration of BP was varied. Although not clearly evidenced by the photolysis products of BP and MB, the recombination of $P_a^{\bullet}$ and $P_b^{\bullet}$ macroradicals (reactions (4.5)) could lead to branching and crosslinking. The appearance of oxetane side groups by cycloaddition of carbonyl groups to the polymer double bonds (reaction (4.6)) is supported by the ^{1}H NMR and IR signals. The formation of LAT products (reaction (4.7)) is well argued in the literature and by the weak absorption at about 320 nm (Fig. 1). The radiation absorption of LATs must also be considered a cause for the deviation of the benzophenone absorption decay from a single exponential.



Scheme 4. Reactions occurring during the irradiation of BP at 365 nm in 1,2PB. The abbreviation PH is used instead of 1,2PB to evidence the hydrogen donor property of 1,2-polybutadiene.

3.4. About kinetics and reaction mechanism of the photolysis of BP in 1,2PB

An observation to be clarified is if the formation of LATs is the main cause for the BP concentration increasing non-linearity of the plots in Fig. 4. We presented in Appendix A.2 that, using expressions from the literature [45], the UFO kinetics at low conversion ($c(t)/c_0 \approx 1$) for the case with radiation-absorbing products follows the equation:

$$\ln\frac{e^{A_0}-1}{e^{z(A(t))}-1}=(\alpha-\beta)\cdot\varphi\cdot I_0\cdot t \qquad (2)$$

with

$$z(A(t))=\frac{(\alpha-\beta)A(t)+\beta\cdot A_0}{\alpha} \qquad (3)$$

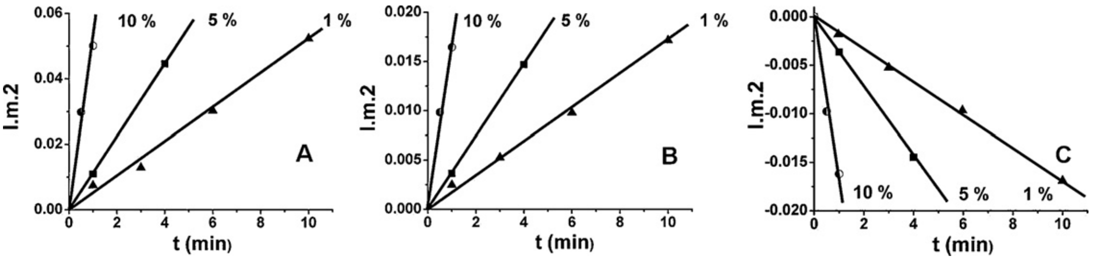
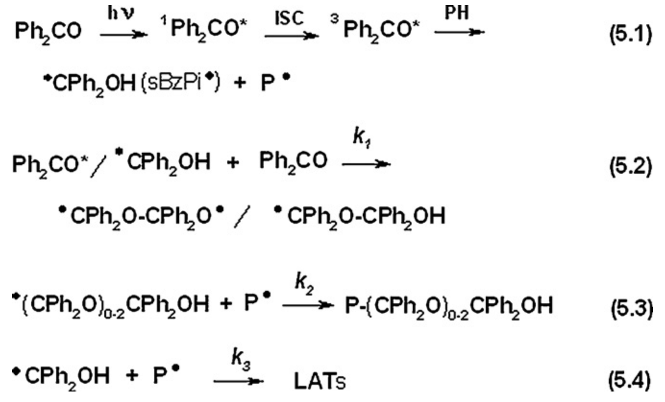


Fig. 7. Plots of the left member of Eq. (2) (l.m.2) by using the experimental data of low (up to 10%) BP conversion in Fig. 4 for several values of the α/β molar absorptivity ratio and of the initial BP concentration (given on each plot), as follows: (A) for α/β = 70/40, (B) for α/β = 70/60, and (C) for α/β = 70/80.



Scheme 5. Reactions that explain BP consumption. As in Scheme 4 4the abbreviation PH is used instead of 1,2PB.

where β is the base-e LAT molar absorptivity, and the other variables and parameters are defined in Section 3.1.2.

Nevertheless, the plots in Fig. 7 are not independent on the initial BP concentration, their slope increasing with c_0 and being negative for $\beta/\alpha > 1$. One could conclude that the radiation absorption of LATs may affect the radiation intensity and the measurements of BP absorbance, but this is not the main cause for the deviation from an UFO kinetic for the photolysis of benzophenone. Consequently, another explanation must be looked for.

Inferred from literature and based on reactions in Scheme 4, the reactions involving BP consumption are summarized in Scheme 5, as follows:

(i) the photo-physical process leading to the triplet state, BP*(T), that extracts hydrogen atoms mainly from allylic CH groups to form semibenzopinacol (sBzPi) radicals (reaction (5.1)),
(ii) the reactions (5.2) which mainly reproduce the reactions (4.3) proposed in Scheme 4 to explain the formation of $–(CPh_2O)_{2–3}–$ and $–(CPh_2O)_{1–2}–CPh_2OH$ fragments,
(iii) the reaction (5.3) that attaches the BP products on the network of crosslinked 1,2PB chains,
(iv) the formation of LATs (reaction (5.4)).

The recombination of sBzPi radicals leading to benzopinacol is neglected because this product was not found as a significant component of the soluble product of BP photolysis in 1,2PB.

It is not possible to obtain the expression of the momentary BP concentration because the differential equations describing the reactions in Scheme 5 are coupled between themselves and cannot be algebraically solved. In addition, there is also the complication caused by the presence of LATs that makes that the radiation intensity available for the excitation of BP molecules to be a variable parameter. However, an approximate solution could be obtained by considering the following system of two parallel reactions:

$$\mathrm{BP} + \mathrm{h}\cdot\nu \xrightarrow{\mathrm{H}^\bullet} \mathrm{sBzPi}^\bullet \tag{4a}$$

$$\mathrm{BP} + \mathrm{sBzPi}^\bullet \rightarrow \text{various products} \tag{4b}$$

the first being a pseudo monomolecular photoreaction and the second being a bimolecular thermal reaction. An explicit solution of their differential kinetic equations cannot be obtained although such a problem can be solved for some particular cases [48].

To obtain an approximate kinetic relationship, we used the following rate equation

$$\frac{dc(t)}{dt} = -\alpha\cdot\phi\cdot I\cdot c(t) \tag{5}$$

where $c(t)$ is the momentary BP concentration, I is the radiation intensity corrected by the absorption of LATs, and Φ is the overall yield of the disappearance of BP covering both the photoreaction (4a) and the reaction (4b). The last reaction explains the formation of $–(CPh_2O)_{2–3}–$ and $–(CPh_2O)_{1–2}–CPh_2OH$ fragments evidenced in the photoproducts of BP irradiated in MB.

It is showed in Appendix B that the solution of Eq. (5) has the expression (6) if the following acceptable assumptions are applied:

(i) the momentary concentration of LATs is a constant fraction, f, of the momentary concentration of transformed benzophenone, so that $[\mathrm{LAT}] = f(c_0 - c(t))$,
(ii) the radiation absorption of LATs is low enough so that the radiation intensity effectively felt by benzophenone can be approximated by the equation $I = I_0[1 - p(c_0 - c(t))]$, where $p = \beta\cdot l\cdot f$, with l as the sample thickness, and
(iii) the overall yield of effective transformation of benzophenone is a linear function of the momentary benzophenone concentration $c(t)$, with the expression $\phi = \phi_0 + r\cdot c(t)$ where ϕ_0 is the quantum yield of the photoreduction of BP, and r in $\mathrm{l\,mol^{-1}}$ is a non-temporal parameter which would arise from bimolecular secondary reactions

$$(1+p\cdot c_0)\ln\frac{A_0}{A(t)} + \left(1+\frac{p}{r}+p\cdot c_0\right)\ln\frac{(1/c_0)+r(A(t)/A_0)}{(1/c_0)+r} = \alpha\cdot\phi_0\cdot I_0\cdot t \tag{6}$$

Concentration-dependent values of the quantum yield of BP disappearance have been also reported [49], but using measurements carried out in 2-propanol, which is a medium that strongly promotes the LAT formation; hence those values are much affected by the LAT absorption.

As defined in Section 3.1.2, A_0 is the initial sample absorbance at the radiation frequency (365 nm) and $A(t)$ is the momentary sample absorbance due to non-reacted benzophenone. The parameters p and r should be determined by fitting the experimental values plotted in Fig. 4 to obtain a linear "left member versus t" plot, the same regardless of the c_0 concentration. Such a problem would need a very laborious solving method. However, with $f = 0.1$ and $\beta \le 60\,\mathrm{L\,mol^{-1}\,cm^{-1}}$, one obtains $p \le 0.1\,\mathrm{L\,mol^{-1}}$ for all studied samples, and such p values do not significantly affect the plots of Eq. (6). Therefore, we adopted $p = 0.1$ and then looked for the value r that leads to a linear plot containing the points corresponding to the all samples. It was found that this criteria is satisfactorily realized when $r = \sqrt{c_0/c_{0r}}$, where $c_{0r} = 0.54\,\mathrm{mol\,L^{-1}}$ would be a reference initial concentration and the ratio c_0/c_{0r} would be the normalized initial concentration, the both parameters being referred to the model before proposed.

Indeed, the experimental values for c_0, A_0, $A(t)$ and t used for the plots in Fig. 4 gave an approximate straight line irrespective of c_0 when plotted in accordance with Eq. (6) for $f = 0.1$ and $r = \sqrt{c_0/0.54}$ (Fig. 8).

The slope of the plot in Fig. 8 is $2.07\times10^{-4}\,\mathrm{s^{-1}}$ that, for $\alpha = 2.3\,\varepsilon_{365} = 161\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ and $I_0 = 2.1\times10^{-9}\,\mathrm{Einstein\,cm^{-2}\,s^{-1}}$, leads to $\phi_0 \approx 0.6$. It is to be mentioned that the values reported in the literature for ϕ_0 spread from near zero to about 2 [36].

4. Conclusions

We confirmed literature reports [23] that the yield of LAT formation during the irradiation of BP generally decreases when the radiation intensity decreases and may become almost negligible in non-polar media. This fact allowed us to establish that the photolysis of BP in 1,2PB is not a pseudo-monomolecular reaction. Based on the identification of $\mathrm{sBzPi–(BP)_{1–2}}$- and $\mathrm{–(BP)_{2–3}}$-sequences in the photoproduct resulted from the photolysis of BP in MB, the reac-

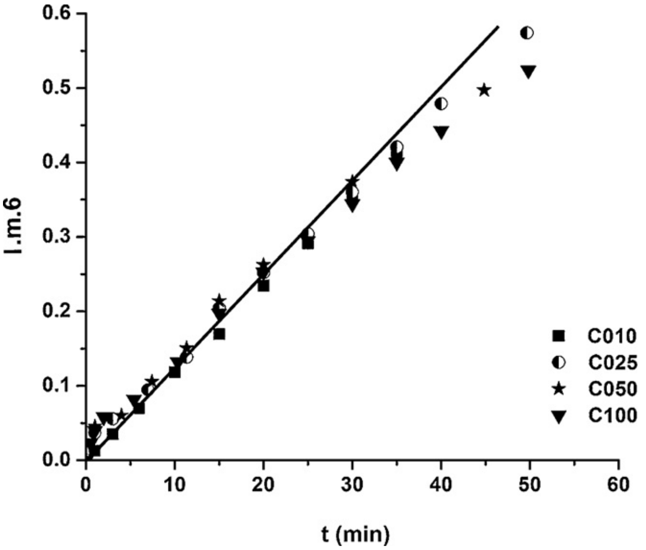


Fig. 8. Plot of the left member of Eq. (6) (l.m.6)) with $f = 0.1$ and $r = 5.6 \cdot c_0^{0.5}$ versus irradiation time by using the experimental values for c_0, A_0, A and t in Fig. 4. The points corresponding to the four BP concentrations are drawn using the similar symbols like in Fig. 4.

tion mechanism and a corresponding approximate kinetic model were developed for the photolysis of BP in 1,2PB. A decreasing of the radiation intensity due to LATs absorption was also considered in the proposed kinetic model. It was found that the yield of BP disappearance in 1,2PB is well described by the relationship $\phi = \phi_0 + \sqrt{c_0/c_{0r}} \cdot c(t)$, so that it increases with the initial and instantaneous BP concentrations.

A special finding reported in this study is the reaction (5.2), where the excited BP molecules and/or semibenzopinacol radicals react with BP molecules in ground state. Such a reaction, based also on the photolysis of BP in MB, explains the deviation of BP photolysis from quasi UFO kinetics and might lead to the formation of macromolecular structures containing sequences of BP molecules "polymerized" via the carbonyl group.

For the reaction induced by BP in 1,2PB, we conclude that (i) the polymerization of vinyl groups initiated by radicals generated during BP photolysis is a significant crosslinking path, and (ii) the BP containing photoproducts are linked into the network of crosslinked chains.

The reactions considered in the present study were conducted in a rather flexible medium as 1,2PB ($T_g = -20\,^\circ$C) is at the room temperature. Nevertheless, the conclusion (ii) suggests that secondary and primary photoreactions occur at the same site, probably due to a rather slow diffusion of reacting species.

The results reported in this manuscript are useful for designing photocrosslinking materials based on the finding that the BP concentration dependence of crosslinking density presents a maximum.

Appendix A. Equations for the UFO photokinetics in non-stirring samples of any absorbance

A.1. Case where the photoreactant is the only absorber

When the incident radiation intensity, I_0, is constant, the two coupled differential equations, the Lambert–Beer law for radiation absorption, and the UFO reaction rate, can be integrated, and the local momentary concentration of photoreactant has the expression [45]:

$$\frac{c(x,t)}{c_0} = \frac{e^{\alpha \cdot c_0 x}}{e^{\alpha \cdot c_0 x} + e^{\alpha \cdot \phi_0 \cdot I_0 \cdot t} - 1} \tag{A1}$$

where x is the depth where the concentration is considered.

The base-e momentary absorbance of a film sample of d thickness results by spatially integrating equation (A1) over the range $x \in [0, d]$. The expression obtained

$$A(t) = \ln(e^{\alpha \cdot \phi_0 \cdot I_0 \cdot t} + e^{A_0} - 1) - \alpha \cdot \phi_0 \cdot I_0 \cdot t \tag{A2}$$

where $A_0 = \alpha \cdot c_0 \cdot d$ is the base-e initial sample absorbance, can be easily rearranged under the expression (1) in Section 3.1.2:

$$\ln \frac{e^{A_0} - 1}{e^{A} - 1} = \alpha \cdot \phi_0 \cdot I_0 \cdot t \tag{A3}$$

A.2. Case when photoproducts absorb radiation

For low conversion, namely when $\ln(c/c_0) \approx c/c_0 - 1$, the Simmons expression for the local momentary concentration of photoreactant [45]:

$$\frac{c(x,t)}{c_0} = 1 - \frac{\alpha \cdot (e^{(\alpha-\beta)\cdot \phi_0 \cdot I_0 \cdot t} - 1)}{(e^{(\alpha-\beta)\cdot \phi_0 \cdot I_0 \cdot t} + e^{\alpha \cdot c_0 x} - 1)(\alpha - \beta)} \tag{A4}$$

leads, by spatial integration over the sample thickness, $[0, d]$, to the momentary sample absorbance due to the photoreactant,

$$A(t) = \alpha \frac{(\ln(e^{(\alpha-\beta)\cdot \phi_0 \cdot I_0 \cdot t} + e^{\alpha \cdot c_0 \cdot x} - 1) - (\alpha - \beta) \cdot \phi_0 \cdot I_0 \cdot t - \beta A_0/\alpha)}{\alpha - \beta} \tag{A5}$$

which can be rearranged under the expression (2) in Section 3.4, so that

$$\ln \frac{e^{A_0} - 1}{e^{z(A)} - 1} = \left(\alpha - \beta\right) \cdot \phi_0 \cdot I_0 \cdot t \tag{A6}$$

where

$$z(A) = \frac{(\alpha - \beta)A(t) + \beta \cdot A_0}{\alpha} \tag{A7}$$

with α and β as the base-e molar extinction coefficients or absorptivities of the photoreactant and the photoproduct, respectively, and $A = A(t)$.

Appendix B. Equation for a quasi UFO photoreaction where $\boldsymbol{\Phi}$ and $\boldsymbol{I}$ are dependent on $\boldsymbol{c(t)}$.

B.1. Case of optically thin sample

Under the assumptions in Section 3.4, namely that $\phi = \phi_0 + r \cdot c(t)$ and $I = I_0[1 - p(c_0 - c)] \approx I_0/(1 + p(c_0 - c))$, the rate equation $\partial c/\partial t = -\alpha \cdot \phi \cdot I \cdot c$ or

$$\frac{\partial c(t)}{\partial t} = -\frac{\alpha(\phi_0 + r \cdot c(t)) \cdot I_0 \cdot c(t)}{1 + p(c_0 - c(t))} \tag{A8}$$

can be integrated, resulting the Eq. (6) used in Section 3.4, so that

$$(1 + p \cdot c_0) \ln \frac{A_0}{A(t)} + \left(1 + \frac{p \cdot \phi_0}{r} + p \cdot c_0\right) \ln \frac{(\phi_0/c_0) + r(A(t)/A_0)}{(\phi/c_0) + r} = \alpha \cdot \phi_0 \cdot I_0 \cdot t \tag{A9}$$

Appendix C. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2011.05.018.

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