

Photooxidation of Benzil Groups in the Presence of Hindered Amine Stabilizers in the Polystyrene Film

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ABSTRACT: The photoperoxidation at $\lambda > 400$ nm of benzil (BZ) groups with the air oxygen to benzoyl peroxide (BP) groups in the polystyrene matrices was investigated in the presence of hindered amine stabilizer (HAS). HAS was used as a free molecule or was bound in combined molecule with BZ. HAS was in the form of parent amine as 2,2,6,6-tetramethyl-4-hydroxypiperidine (TMP) and in the form of stable nitroxyl radical 1-oxo-2,2,6,6-tetramethyl-4-hydroxypiperidine (NO). Both HAS forms effected the photooxidation of BZ structures. The main product of the photooxidation in the presence of parent amine TMP as well as in its absence is benzoyl peroxide (BP). The rate of BZ consumption increases in the presence of TMP. Irradiation of BZ in the presence of sufficient concentration of freely added NO results only in the formation of benzoic acid esters and benzoic acid, which are the main decomposition products of BP. The benzoic

acid esters/benzoic acid ratio increases with the increasing concentration of NO. Bounding of BZ and TMP into one molecule (BZNH) results in slower dicarbonyl depletion, as compared with the case when mixture of BZ and TMP was used. Very slow depletion of BZ carbonyl absorption was observed in the case of bounded BZ and NO in one molecule (BZNO), in comparison with the mixture of free NO and BZ. In the case of BZNO, an effective intramolecular quenching of BZ excited triplet states with NO structures proceeds. Steady state and dynamic emission (phosphorescence) measurements also show an effective quenching of BZ excited states by unbounded or bounded NO. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 4420–4428, 2006

Key words: photoperoxidation; benzil; hindered amine stabilizers; polystyrene matrix

INTRODUCTION

Benzil (BZ) is an industrially important member of the class of molecules with 1,2-dicarbonyl functionality. It has been utilized in the preparation of light sensitive systems as photographic materials, polymer resists, and as photoinitiators in radical polymerization.¹ Solution-phase photochemistry of 1,2-diketones, including BZ, has been reviewed^{2–5} in the presence and absence of molecular oxygen. When molecular oxygen is available, photo-oxidation of BZ in benzene leads to phenyl benzoate, benzoic acid, biphenyl, and a small amount of benzoyl peroxide (BP).⁶ BZ can be converted almost quantitatively to BP in aerated amorphous glassy polymer films, below glass transition temperature by irradiation at $\lambda > 400$ nm (i.e., the long wavelength edge of the $n \rightarrow \pi^*$ absorption band wherein BP does not absorb) (Scheme 1).^{7,8}

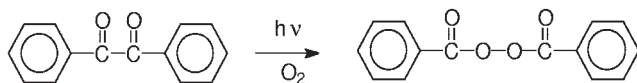
Covalently attached BP pendant groups have also been formed from BZ pendant groups by irradiation

of copolymer films in air.^{9–12} Decomposition of covalently attached BP pendant groups leads to crosslinking of the polymer. In this way it is possible also to crosslink polymers, which undergo main chain scissions, when the low-molecular-weight peroxides are decomposed in their matrix, e.g., polystyrene.¹³ Despite some suggestions,^{7,8} the precise mechanism of photoperoxidation of BZ has not been unequivocally established.

The hindered amine stabilizers (HAS) are very efficient protective additives for polymers. Their action is explained by the inhibition of photo- or thermooxidation of polymers. N-oxyl radicals formed during HAS action were proved to be an active species,^{14,15} but the details of the mechanism of their action are still not yet clear.^{16–18} To contribute to the understanding of the mechanism of action of HAS and at the same time to elucidate the mechanism of phototransformation of BZ groups in solid polymer matrix, the effect of unbounded or bounded HAS (Scheme 2) is examined on photoperoxidation of BZ groups in polystyrene (PS) matrices. In aerated PS film the BZ is converted to BP almost quantitatively by irradiation at $\lambda > 400$ nm.^{7,8} The advantage of PS films, is their easy preparation and suitability to follow chemical changes by means of IR spectroscopy.

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Scheme 1 Photoperoxidation of BZ in polymer matrices.

EXPERIMENTAL

Chemicals used

Benzil (BZ) (Lachema Brno, Czech Republic), 1-oxo-2,2,6,6-tetramethyl-4-hydroxy piperidin (NO) and 4-hydroxy-2,2,6,6-tetramethyl piperidin (TMP) (both Chemko Strážske, Slovak Republic), diphenylmethane-4,4'-diisocyanate (Aldrich), polystyrene (PS) (Vestyron N, Chemische Werke HÜLS, Germany), poly(methyl methacrylate) (PMMA) (Chemical Works, Žilina, Slovak Republic), chloroform and dichloromethane (Slavus, Slovak Republic), diazabicyclooctane (DABCO) (Merck, Germany), ethylacetate (Lachema, Brno, Czech Republic). 1-(4-(2-acetyloxyethoxy)phenyl)-2-phenyl-1,2-ethanedione (BZAC), and 1-(4-(2-hydroxyethoxy)phenyl)-2-phenyl-1,2-ethanedione were prepared previously¹⁹

4-(4-Benzilyl-2-ethoxy carbonylamino)phenyl-4'-(1-oxo-2,2,6,6-tetramethyl-4-piperidinyl-carbonyl amino)phenyl methane (BZNO)

To the stirred solution of 5 mmol (1.35 g) of 1-(4-(2-hydroxyethoxy)phenyl)-2-phenyl-1,2-ethanedione and 5 mmol (1.25 g) of diphenylmethane-4,4'-diisocyanate in 50 mL of dry toluene, 50 mg of DABCO was added. Reaction was maintained at 50°C for 2 h until isocyanate peak at 2260 cm⁻¹ reduced to half in the FTIR spectrum. Then NO (5 mmol, 0.86 g) was added and the mixture was additionally stirred for 15 h at 60°C, and during this time the isocyanate peak disappeared completely. Pink crystals appeared after evaporation of the solvent from reaction mixture. Product was purified by column chromatography using mixtures of dichloromethane with ethyl acetate (change from pure dichloromethane to pure ethyl acetate) as an eluent. The 0.4 g (15% yield) of product was obtained as pink crystals m.t. 81–84°C. ¹H-NMR spectra δ

= 1.26 (m, 12H, 4 × CH₃); 1.53 (d, 4H 2 × CH₂ piper.); 3.9 (s, 2H, Ar—CH₂—Ar); 4.28 (t, 2H CH₂—O—C=O); 4.54 (t, 2H, Ar—O—CH₂); 5.15 (m, 1H, CH); 6.99 (d, 2H, 2 × CH of Ar); 7.12 (d, 2H, 2 × CH of Ar); 7.19 (d, 2H, 2 × CH of Ar); 7.3 (bs, 4H 4 × CH of Ar), 7.51 (t, 2H, 2 × CH of Ar); 7.65 (t, 1H, CH of Ar); 7.96 (d, 2H, 2 × CH of Ar); 7.98 (d, 2H, 2 × CH of Ar); δ_{NH} cannot be seen on the spectra.

4-(4-Benzilyl-2-ethoxy carbonylamino)phenyl-4'-(2,2,6,6-tetramethyl-4-piperidinyl-carbonyl amino)phenyl methane (BZNH)

To the stirred solution of 2.5 mmol (0.393 g) of TMP and 2.5 mmol (0.625 g) of diphenylmethane-4,4'-diisocyanate in 20 mL of dry toluene, 50 mg of DABCO was added. Stirring is continued at 50°C for 3.5 h until isocyanate peak at 2260 cm⁻¹ is reduced to half in the FTIR spectrum. Then 1-(4-(2-hydroxyethoxy)phenyl)-2-phenyl-1,2-ethanedione (2.5 mmol, 0.675 g) was added and the mixture was stirred for 1.5 h more at 50°C. The reaction was stopped when the isocyanate peak disappeared completely. Light yellow-green crystals appeared after evaporation of the solvent m.t.: 109–112°C. Yield: 0.34 g (20%). ¹H-NMR spectra δ = 1.26 (s, 6H, 2 × CH₃); 1.31 (s, 6H, 2 × CH₃); 1.83 (s, 1H, NH of piper.); 2.02 (d, 4H 2 × CH₂ piper.); 3.89 (s, 2H, Ar—CH₂—Ar); 4.30 (t, 2H CH₂—O—C=O); 4.54 (t, 2H, Ar—O—CH₂); 5.17 (m, 1H, CH); 6.58 (s, 1H, NH); 6.68 (s, 1H, NH); 7.0 (d, 2H, 2 × CH of Ar); 7.10 (d, 4H, 4 × CH of Ar); 7.28 (d, 4H, 4 × CH of Ar); 7.51 (t, 2H, 2 × CH of Ar); 7.65 (t, 1H, CH of Ar); 7.95 (d, 2H, 2 × CH of AR); 7.97 (d, 2H, 2 × CH of Ar).

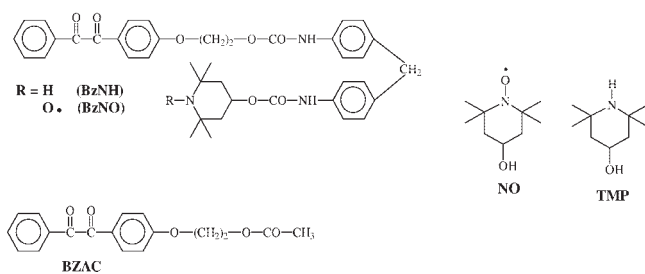
Sample preparation

Polymer films (PS or PMMA) of 0.02 mm thickness were prepared by casting from chloroform solutions (1 mL) containing 20 mg of polymer and the additive (Table I) on a 2.5 × 4 cm glass plate. The plate was covered by Petri dish to slow down solvent evaporation. This procedure resulted in good optical quality of

TABLE I
Influence of HAS on the Observed Rate Constant of BZ (0.476 mol kg⁻¹) Depletion Upon Irradiation at $\lambda > 400$ nm in PS

HAS	Concentration of HAS (mol kg ⁻¹)	k_{obs} (min ⁻¹)	Ester/acid ^a
Any	0	0.025	
NO	0.238	0.008	0.44
NO	0.476	0.010	0.81
NO	0.951	0.014	1.41
TMP	0.476	0.034	

^a Empty cells represent that the main product is BP and ester and acid are formed in negligible amount.



Scheme 2 Structures of the studied compounds.

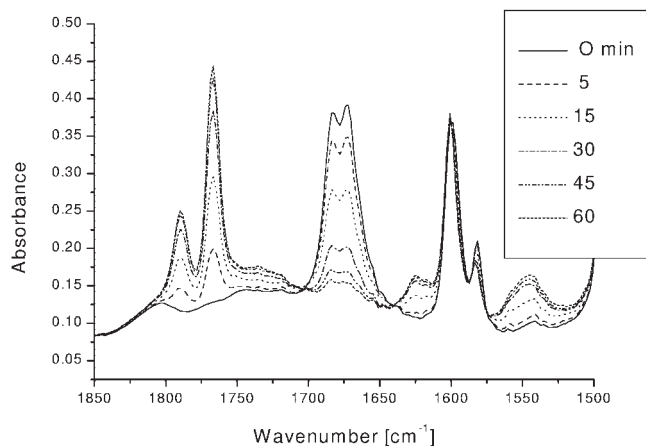


Figure 1 FTIR spectra of BZ (0.476 mol/kg) and TMP (0.476 mol/kg) irradiated for different periods in air in a PS matrix in Spectramat®.

the films. The self-supporting films were separated from the glass by dipping shortly into the distilled water and by drying in vacuum.

Irradiation and measurements

The samples covered with a UV CL SR HPR plastic film filter (Lumar, USA) were irradiated at ambient temperature at 400 nm in a Spectramat® (Ivoclar A.G., Schaan, Liechtenstein) apparatus. A homemade “merry-go-round” apparatus was employed in some experiments.¹¹ The radiation >400 nm was filtered with glass filter 73087112 (Carl Zeiss, Jena, Germany).

Fluorescence emission spectra were recorded on Perkin–Elmer MPF 4 spectrofluorimeter (Perkin–Elmer, Norfolk, USA), which was connected through A/D converter card to ISI slot of PC. The emission data were processed by Origin 6. Emission of polymer films was measured in front-face arrangement of the solid sample holder.

The emission (phosphorescence) lifetime measurements were performed on a homemade setup consisting of pulse excitation source, monochromator, and detection electronics. The pulsed nitrogen laser ($\lambda = 337$ nm) IGL 300/2 (Lasertechnik Ltd., Berlin, Germany) was used as excitation source. The emission of polymer films, taken in front-face arrangement, was selected by high radiance monochromator (Applied Photophysics, London, UK). The emission was detected by a head-on photomultiplier (6256B, EMI, London, UK) fed by high voltage source (Tesla, Liberec, Czech Republic). The signal was fed on 100 MHz digital oscilloscope card (ETC Ltd. Zilina, Slovak Republic) terminated by 10 k Ω load. The data were sent to MS Excel and then processed in Origin 5.

Static and time resolved emission measurements in solutions were performed in inert atmosphere (argon

bubbling, 5 min). All measurements on polymer films were performed in the presence of air.

UV spectra were measured by Shimadzu 1650 UV–VIS spectrophotometer (Shimadzu, Japan) and FTIR spectra by NICOLET 400 (NICOLET, Germany).

The transient absorption in the time scale 20 ns to 500 μ s was performed on nanosecond laser flash photolysis set up LKS 60 (Applied Photophysics).

ESR measurements were taken on E-4 (Varian AG, Palo Alto, CA, USA).

RESULTS AND DISCUSSIONS

Photooxidation of BZ in PS film with HAS additives

Influence of HAS additives in the photoperoxidation of BZ moieties in PS films was monitored by infrared spectroscopy. For this study, free HAS in the form of parent amine (TMP) and its stable nitroso radical (NO) and NO or TMP and BZ structures bounded to one molecule (BZNO or BZNH, respectively) were used.

The changes in IR spectra of BZ and its derivatives without additive during irradiation ($\lambda > 400$ nm) correspond to photoperoxidation of 1,2-dicarbonyl moiety.^{7–12} Transformation is clearly demonstrated by the decrease in absorbance of 1,2-dicarbonyl band at 1650–1700 cm^{-1} and by the formation of new absorption band corresponding to BP structures in the region 1750–1800 cm^{-1} .

The effect of parent TMP and its *N*-oxy radical NO on the BZ photooxidation products was compared (Figs. 1 and 2). The main product of irradiation of BZ in aerated PS matrix in the presence of TMP is BP, the same as without the addition of TMP (Fig. 1). But in the presence of equimolar concentration of NO additive, the absorption band corresponding to BP structures is fully suppressed (Fig. 2). The BP formation

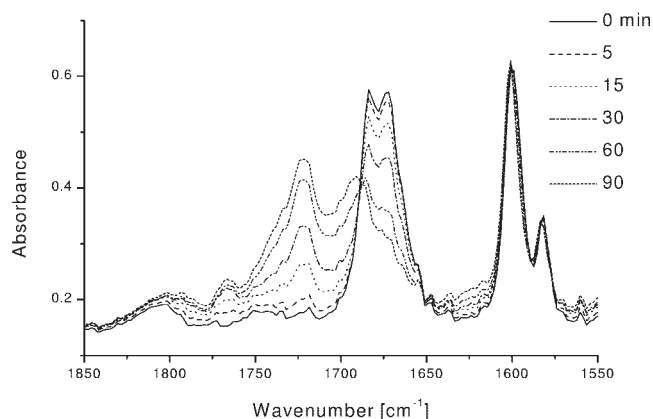


Figure 2 FTIR spectra of BZ (0.476 mol/kg) and NO (0.476 mol/kg) irradiated for different periods in air in a PS matrix in Spectramat®.

strongly depends on the nitroxyl radical concentration. Figure 3 represents IR spectra of products formed after complete BZ conversion in the presence of different concentrations of NO. At lowest NO concentrations the BP absorption formed was significant, while at the highest concentrations no BP absorption was observed (Fig. 3). The main products in these cases are the benzoic acid with its maximum centered to 1690 cm^{-1} and its esters with maximum at 1720 cm^{-1} . The benzoic acid esters/benzoic acid ratio increases with increase in N-oxy radical concentration (Table I). In the presence of NO, the products can be formed either by the known NO-induced decomposition of primarily formed BP,^{20–22} or theoretically by the reaction of NO with excited triplet state of BZ (Scheme 3), or by the interaction of NO with the 1,2-diketone triplet state adduct with oxygen (1,4-biradical). But GC-MASS and liquid chromatography analysis of low molecular products obtained after precipitation of the irradiated polymer films containing BZ and NO does not give evidence for the reactions according to Scheme 3. The common existence of the 1,2-diketone triplet state adduct with oxygen (1,4-biradical) was discussed²³ and was proved for 2,2'-thenil in solution by laser flash photolysis. But similar direct evidence as for 2,2'-thenil is missing for the BZ excited triplet state adduct with oxygen. Because no photoreactions of NO with intermediates of BZ photoperoxidation were observed, most probably, the induced decomposition of the primarily formed benzoyl peroxide only occurs.

It is well-known that the HAS in their nitroxyl radical form decomposes BP.^{20–22} Although mixture of BP and nitroxyl radicals in liquid monomers, e.g., styrene, react slowly, the mixing of net nitroxyl radicals and BP causes violent induced decomposition of BP.²² Thus,

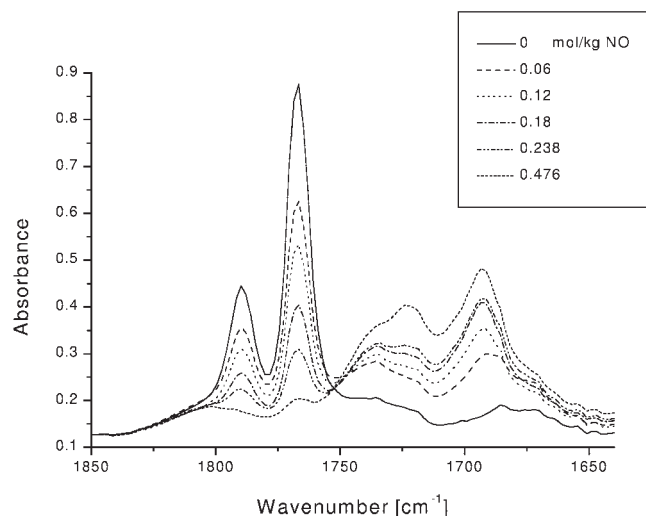
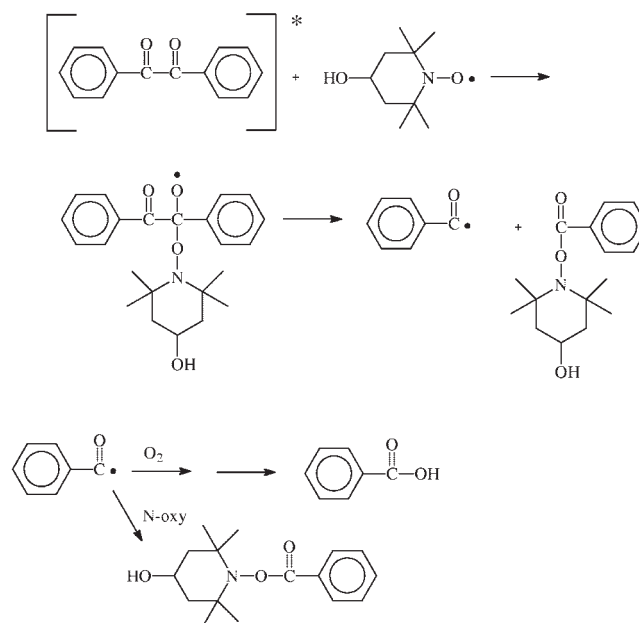


Figure 3 FTIR spectra of BZ (0.476 mol/kg) irradiated for 26 h in air in the presence of different concentrations of NO in a PS matrix in a merry-go-round apparatus.



Scheme 3 Possible deactivation route for BZ excited triplet in the presence of NO.

also PS film containing BP and NO from the chloroform solution is impossible to prepare. BP is decomposed during film formation after evaporation of the solvent. Reason for the decomposition is increased mutual concentration of BP and NO during evaporation of solvent, and the induced decomposition can proceed in concentrated form. Therefore, the only main products of inductive decomposition of BP (benzoic acid and its esters formed from benzoyloxy radicals) were observed in the IR spectra of prepared films. The same reaction is assumed to take place also with the BP formed during irradiation in PS film from BZ in presence of the sufficient concentration of NO.

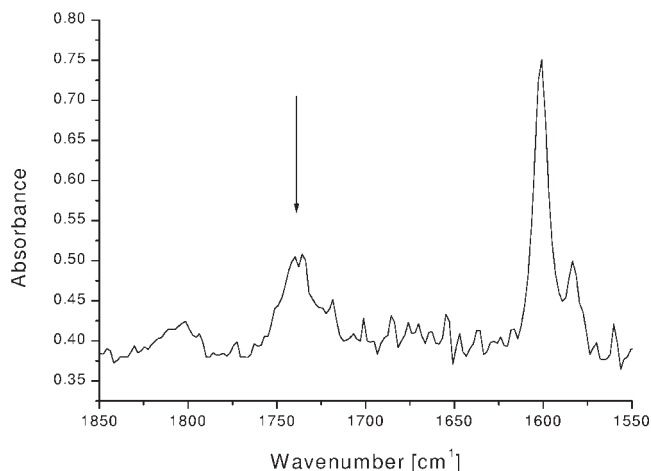
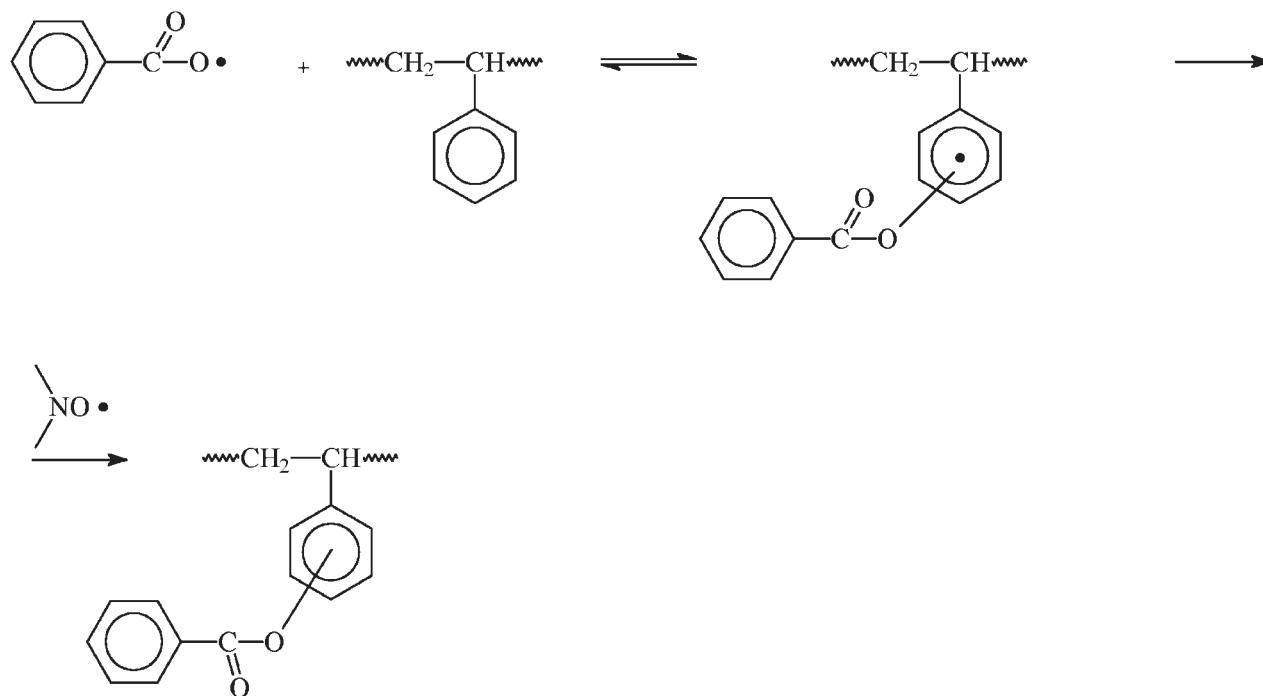


Figure 4 FTIR spectra of polymer reprecipitated upon irradiation of BZ (0.476 mol/kg) in the presence of equimolar concentration of NO.



Scheme 4 Addition of benzoyloxy radical to aromatic ring under ester formation.

BP undergoes induced decomposition by 2,2,6,6-tetramethylpiperidiny1-1-oxy to form benzoyloxy radical and benzoic acid in equimolar amounts.^{20,21} Formation of the benzoic acid does not involve free benzoyloxy radical.^{20,21} Large quantities of benzoic acid were also formed during decomposition of BP in PS¹³ and during decomposition of pendant BP groups in styrene copolymer in the absence of nitroxyl radicals.^{9–12} Therefore, in the polymer matrix in the absence of nitroxyl radicals, benzoic acid is also formed by H-abstraction of benzoyloxy radical from polymer matrix.

As indicated in the IR spectra of PS film containing BZ and NO after irradiation and upon reprecipitation (Fig. 4), the ester groups are bound to polymer chains similarly as was observed for the thermal decomposition of BP in PS.¹³ Benzoic acid esters can be formed in the recombination of benzoyloxy radicals with C-radicals.²⁰ In the presence of aromatic structures, the addition of benzoyloxy radicals to the aromatic rings proceeds during the formation of cyclohexadienyl radical intermediate.^{20–22} It is known that the reverse reaction of the addition of benzoyloxy radicals to a variety of aromatic rings (Scheme 4), including styrene monomer, is extremely fast.^{20–22} Despite the fast back reaction, the decomposition of BP molecules in PS films leads to the addition of benzoyloxy radical^{9–13} to aromatic rings under ester formation (Scheme 4). The reason for the additions to the aromatic rings is related to the presence of molecular oxygen in the films, presumed to be higher than those as in benzene or tolu-

ene solutions, in which similar phenomena occur.^{24,25} Molecular oxygen can remove a hydrogen atom at the ipso carbon of addition at a rate that is at least comparable to the rate of benzoyloxy radical formation from the intermediate. Trapping of various radicals formed in the reaction of benzoyloxy radicals in styrene monomer with 1-oxo-2,2,6,6-tetramethylpiperidin was described.²⁰ Besides the formation of radicals on styrene monomer, the benzoyloxy radicals are also added to the aromatic rings during formation of intermediate. In the presence of nitroxide, cyclohexadienyl radicals intermediates formed are readily oxidized. When 1-oxo-2,2,6,6-tetramethyl piperidin was employed, the yield of aromatic substitution of benzoyl radical increased and above 0.02 M nitroxide concentration, the yield of benzoates remained essentially constant.²⁰ This proceeds also in our case and therefore the benzoic acid esters/benzoic acid ratio increases with increase in concentration of NO (Table I).

The effects of parent TMP and its N-oxy radical (NO) concentration on the rate of BZ depletion was studied as well. The corresponding dependence of $\ln A/A_0$ (the concentrations of BZ moieties were expressed by 1,2-dicarbonyl absorbance) on time are shown in Figure 5. The calculated rates of BZ depletion from Figure 5 are presented in Table I. Despite that repeated set of experiments gave change of the rate constant values up to 15%, the trends described below were maintained for every round set of experiments.

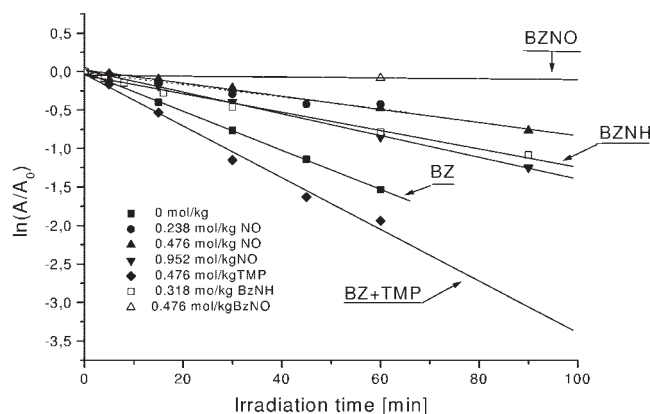


Figure 5 Semilog plots of absorbances at 1684 cm^{-1} for photooxidation of BZ (0.476 mol/kg) in the presence of NO and TMP in PS matrices.

The rate of BZ consumption in aerated PS matrix in the presence of TMP is slightly higher as in its absence. Chemical scavenging of alkylperoxy radicals and benzophenone triplet by HAS in their parent amine form is known.¹⁸ Analogously the triplet of BZ can react with TMP and increase the depletion of BZ in its presence. Beside the photochemical reaction, physical influence of TMP on oxygen solubility and polarity of the matrix on the rate of BZ photoperoxidation cannot be excluded, too.

The rate of BZ consumption in the presence of NO (Table I and Fig. 5) has two features. The rate is lower than that in the case of BZ alone and, in studied range, it surprisingly decreases as NO concentration decreases. The quenching of the triplet state of ketones and aromatic hydrocarbons by nitroxides is known.^{18,26} Full triplet quenching in solution is reached²⁶ at 1-oxo-2,2,6,6-tetramethylpiperidin concentration of 2–4 mM. Therefore, the lowest rate of BZ depletion in the presence of the lowest NO concentrations used (0.24 and 0.48 mol/kg) probably corresponds to the highest quenching of BZ excited triplet state. The further increase of NO concentration can influence the rate of dicarbonyls depletion similarly as TMP.

Irradiation of BZNO for 90 min, the time necessary for complete conversion of BZ in the presence low molecular weight NO (in equimolar concentration), gives only negligible depletion of 1,2-dicarbonyls in the BZ structural units of BZNO. Only prolonged irradiation for 24 h gives complete conversion of BZ structures of BZNO (Fig. 6). The photoreaction of BZ structures in BZNO is suppressed due to the presence of linked N-oxy radicals. In BZNO, very effective intramolecular quenching of BZ excited triplet state by NO structures, similarly as was observed for the thioxanthone derivative,²⁶ can proceed. The intramolecular (BZNO) and intermolecular quenching of BZ emission by N-oxyls was demonstrated in solution as well as in PMMA matrix (see later).

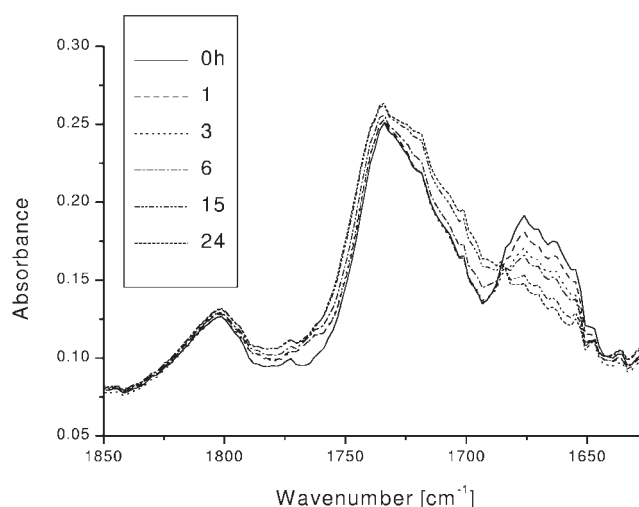


Figure 6 FTIR spectra of BZNO (0.476 mol/kg) irradiated for different periods in air in a PS matrix in Spectramat®.

Surprisingly, the rate of photoconversion of BZ structures in BZNH, in which BZ group is linked with TMP, is lower in comparison with the case of BZ irradiation in the presence of nonlinked TMP (Figs. 5 and 7). In both cases, BZNO and BZNH, no benzoyl peroxide is formed; only small increase of absorption in the region $1700\text{--}1750\text{ cm}^{-1}$ is observed, which can be caused by benzoic acid and esters of benzoic acid. Probably the phototransformation of 1,2-dicarbonyls in both BZNO and BZNH occurs by different mechanism as BZ without additives or in the presence of TMP.

Photophysical measurements

While the BZ photoperoxidation and formation of BP decomposition product can be easily monitored using IR spectroscopy, these measurements does not yield

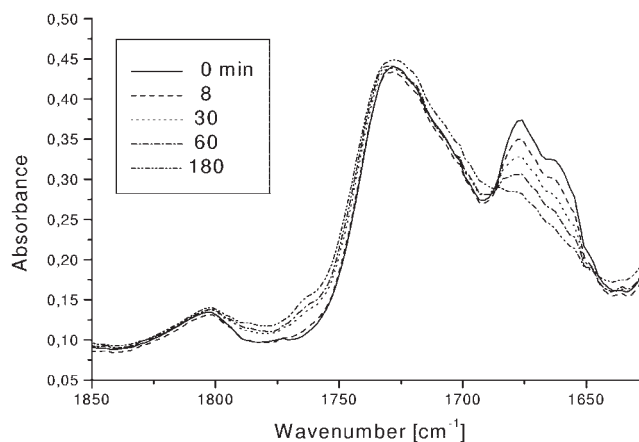


Figure 7 FTIR spectra of BZNH (0.476 mol/kg) irradiated for different periods in air in a PS matrix in Spectramat®.

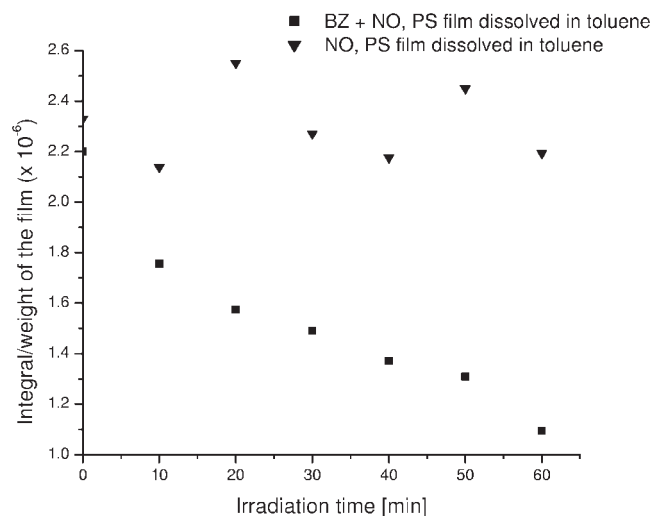


Figure 8 The rate of NO consumption upon irradiation of PS film doped with BZ (0.476 mol/kg) and equimolar concentration of NO (■) and NO in PS matrix (▼) in Spectramat®.

any information about NO. The transformation of the free radicals can be monitored by ESR spectroscopy. Changes in characteristic ESR triplet signal of NO were monitored during the irradiation of PS films containing equimolar concentration of BZ and NO and it was compared with PS films containing only NO. The rate of NO radical consumption was calculated from the integrated intensities (Figs. 8 and 9). As is shown in the Figure 8, no NO radical consumption was detected upon irradiation of PS films doped only with NO radical in Spectramat® apparatus at $\lambda > 400$ nm, while the depletion of NO concentration was observed for the PS films doped with equimolar concentration of BZ and NO.

PS film is relatively stable against the irradiation at $\lambda > 400$ nm in the time scale of our experiment and no

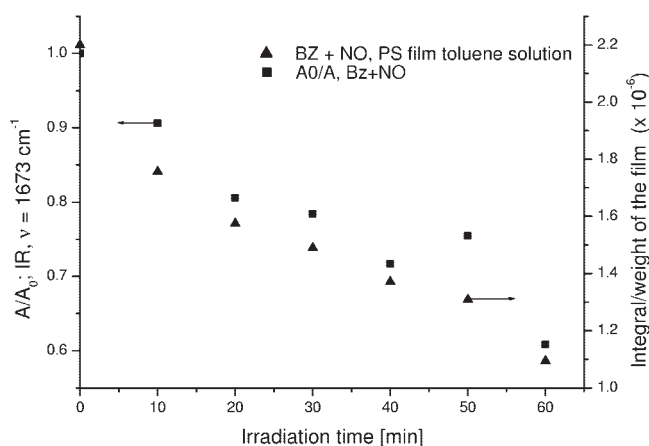


Figure 9 The rate of BZ (■) and NO (▲) consumption upon irradiation of BZ (0.476 mol/kg) in the presence of NO in PS matrix in Spectramat® at $\lambda > 400$ nm.

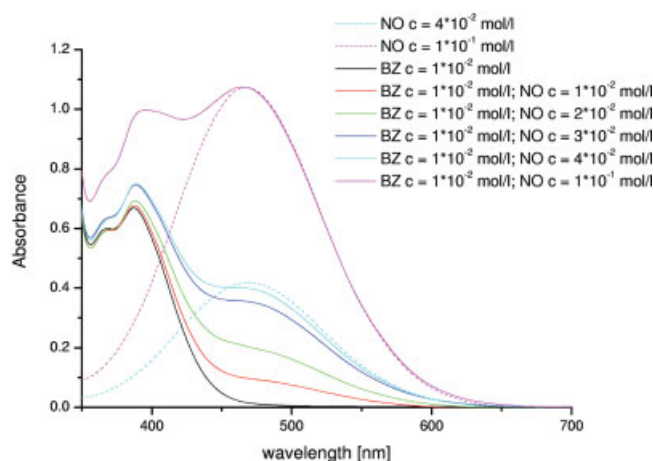


Figure 10 UV spectrum of BZ in absence and in presence of various concentrations of NO as well as the UV spectrum of NO observed in toluene solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

free radical or other reaction center for the possible reaction with NO are formed. Therefore, no depletion of NO upon irradiation of PS film doped only with NO radical should be observed. On the other hand, in the case of benzil photoperoxidation at $\lambda > 400$ nm, the NO radical reacts easily with primarily formed BP.

Benzil and its derivatives shows an intensive absorption band in the π - π^* region of absorption spectra and the less intensive shoulder in the n - π^* region at long wavelength edge. Figure 10 shows the n - π^* region of UV spectra of BZ in toluene solution ($c = 10^{-2}$ mol/L) without and in the presence of various concentrations of NO as well as the UV spectrum of NO at the same region. The observed UV spectra does not give any evidence for the formation of complex between BZ and NO as was observed for the benzil and polar solvents.²⁷

The emission spectra of BZAC and BZNO in PMMA matrices were measured upon excitation at 385 nm under equal conditions. The emission spectrum typical for BZ type dicarbonyl groups is the broad band in the region between 480 and 620 nm (Fig. 11) without any vibration structure. In benzene solution, BZ shows both fluorescence and phosphorescence²⁸ and both are effectively quenched by triethylamine with the rate constants near to the diffusion controlled. The PMMA matrix stabilizes more effectively the longerlived excited triplet state as singlet excited state. The maximum of emission in Figure 11 is closer to phosphorescence maximum. Although the concentration of BZ groups was equal, large difference in emission intensity was observed for BZAC and BZNO (Fig. 11). As it is clearly seen, the emission intensity for BZNO is substantially lower as observed for BZAC. This lower emission intensity is due to effective intramolecular

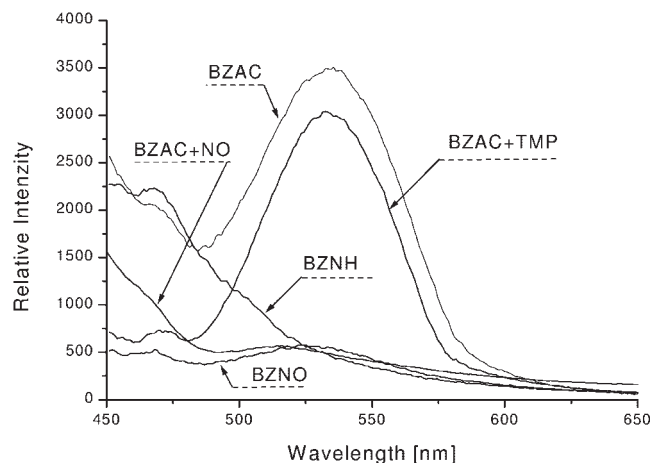


Figure 11 Emission spectra of BZAC, BZAC + NO, BZAC + TMP, BZNH, and BZNO in equal concentration (0.318 mol/kg) in PMMA matrix upon excitation at 385 nm.

quenching probably the excited triplet state of BZ structures by bound N-oxyl radical as was indicated also by lowering the rate of photo-conversion of BZ structures (see earlier).

Support for intramolecular quenching was obtained by the dynamic measurements as well. The decay curve for emission (phosphorescence) using excitation at 337 nm monitored at 530–550 nm were fitted to biexponential function. Typically, the decay of emission (phosphorescence) of chromophores doped in polymer matrices can be fitted to monoexponential only at low temperature.²⁹ At laboratory temperature, the decay can be fitted to stretched exponential or biexponential. The typical data for two rate constants of emission decay of 1,2-diketo chromophore are given in Table II. Clearly, both BZNO and equimolar mixture BZAC and NO exhibited faster decay than those exhibited by BZAC and equimolar mixture of BZAC and TMP. It is interesting to note that the rate constants of BZNO alone and equimolar mixture BZAC and NO in the frame of experimental error are equal. Despite that, the decay of BZAC emission is only little influenced by TMP, surprisingly the BZNH decay equally as BZNO. Probably a weak intramolecular

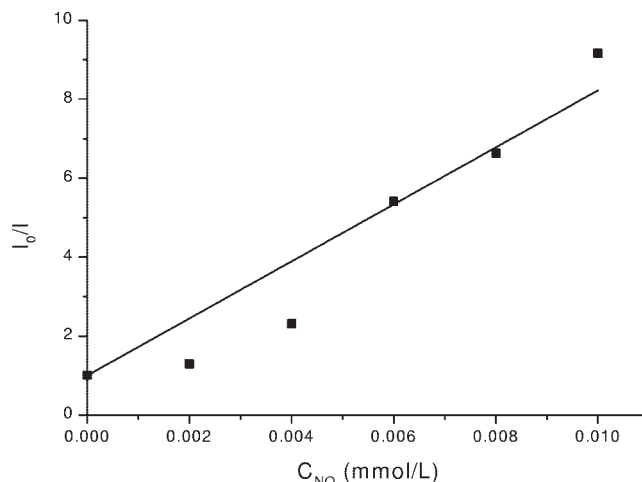


Figure 12 Concentration dependence of BZAC (10^{-3} mol dm^{-3}) phosphorescence intensity in 1,1,2-trichloro trifluoro ethane solution in the presence (I) and absence (I_0) of NO ($\lambda_{\text{exc}} = 385$ nm and $\lambda_{\text{em}} = 560$ nm).

charge-transfer complex between BZ and amino groups is formed, which facilitates the electron transfer.

To obtain information about the quenching of excited triplet of BZ moieties by NO radicals, the emission spectra of BZAC in the presence of various concentration of NO radical were measured in argon atmosphere in 1,1,2-trichloro trifluoro ethane solution. Quenching obeys the Stern–Volmer dependence (Fig. 12).

Formation and decay of transient absorption of triplet states of BZ chromophore alone and linked with sterically hindered amine (BZNH and BZNO) was studied by laser flash photolysis after 355 nm excitation in submicrosecond region. The transient absorption of all studied compounds exhibits maximum around 480 nm in polar methanol and in nonpolar cyclohexane or toluene in nitrogen atmosphere. The time-resolved transient spectra for BZ and BZNO in methanol are shown on Figures 13 and 14. The rate constant of decay in methanol increases in the following order: BZ, BZNH, and BZNO (6.00×10^5 , 1.2×10^6 , and 3.7×10^6 s^{-1}). The higher rate constants of decay for BZNH and BZNO can explain the absence of phosphorescence of these compounds (see earlier).

TABLE II
Phosphorescence Decay Constants of BZ Moieties Upon Excitation by Nitrogen Laser at $\lambda = 337$ nm in PMMA Matrix

Sample (N)	Sample description	Concentration of additives (mol kg^{-1})	λ_{em} (nm)	Phosphorescence decay (10^{-3} s^{-1})	
				k_1	k_2
1	BZAC	0.318	535	17.3	2.9
2	BZNO	0.318	535	52.2	9.3
3	BZAC/NO	0.318/0.318	535	51.0	9.5
4	BZNH	0.318	530	53.2	8.4
5	BZAC/TMP	0.318/0.318	535	19.7	3.3

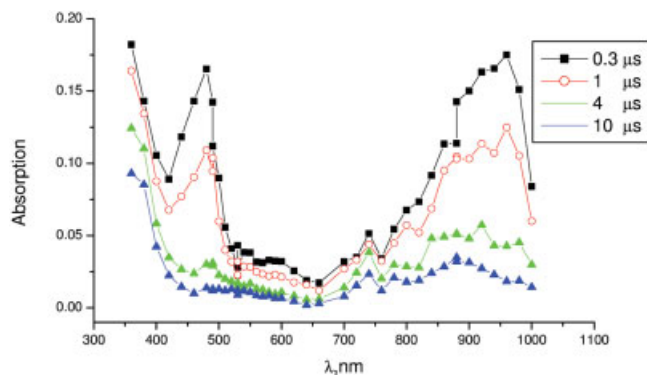


Figure 13 Transient absorption spectra of benzil (BZ) in methanol at 355 nm of excitation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The transient absorption of all studied compounds was quenched by added 1-oxo-2,2,6,6-tetramethyl piperidine (TEMPO) almost equally in all studied solvents, with the rate constants of quenching $k_q = 2.3\text{--}3.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Study of the influence of HAS in their amine or nitroxyl radical form on the photophysical and photochemical processes of BZ in PS matrix in the presence of oxygen support the origin of the photoperoxidation from the excited triplet state of BZ structure. Beside the indication of the chemical reaction of nitroxyl radicals with BZ photoperoxidation intermediates, no

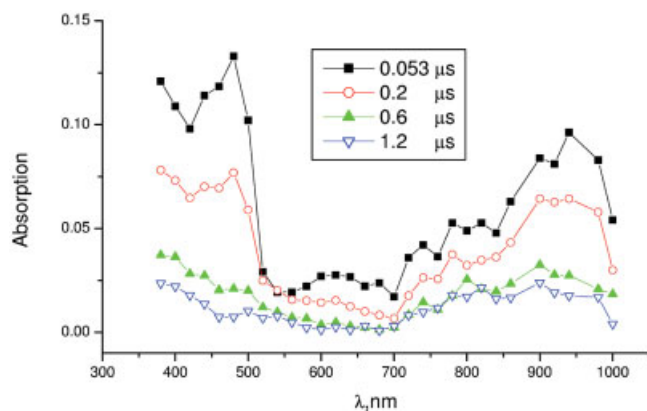


Figure 14 Transient absorption spectra of 4-(benzyl-2-ethoxycarbonylamino)phenyl 4'-(1-oxo-2,2,6,6-tetramethyl-4-piperidinylcarbonylamino)phenylmethane (BZNO) in methanol at 355 nm excitation. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

products were estimated. HAS in their parent amine form do not influence negatively the formation of BP from BZ in intermolecular reaction. In the case of BZ and TMP structures bounded in one molecule (BZNH), the photoperoxidation of BZ structures do not precede. Clearly HAS in their nitroxyl radical form decomposes the formed BP.

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