



# PHOTOCHEMICAL BEHAVIOR OF POLY(ORGANOPHOSPHAZENES)—XIII. SENSITIZED PHOTOCHEMISTRY OF POLY[BIS(4-BENZYLPHENOXY)PHOSPHAZENE] IN SOLUTION AND IN FILM

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**Abstract**—In this paper we report the solution and solid-state photochemistry of poly[bis(4-benzylphenoxy)phosphazene] sensitized by benzophenone. u.v. and i.r. spectroscopic characterizations and weight average molecular weight data indicate that the main reaction under irradiation for this polymer dissolved in benzene is the increase in molecular weight due to an efficient crosslinking process. Moreover, gel is formed very rapidly after a few minutes of light exposure, when the polymer is photolyzed in film. These results are attributed to an intermolecular hydrogen atom abstraction reaction that takes place between the electronically excited triplets of the benzophenone photosensitizer and the methylene group present in the side 4-benzylphenoxy substituent of the phosphazene polymer that generates radicals able to couple forming inter-chain links. The different behavior of the poly[bis(4-benzylphenoxy)phosphazene] when the photolysis is carried out in air or in inert argon atmosphere is also described and the presence of a post-photochemical effect in the irradiated phosphazene films is discussed.

## INTRODUCTION

During the last decade the great deal of investigations [1-4] carried out on the photochemistry of poly(organophosphazenes), (POPs), showed the remarkable importance of monomolecular [2] and bimolecular [3] processes that take place during the irradiation of these macromolecules.

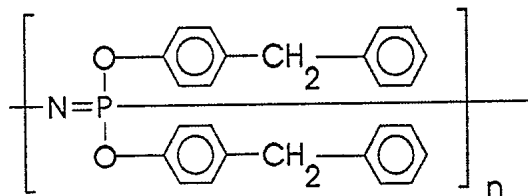
Monomolecular reactions, in fact, occur during the direct photolysis of polyphosphazenes substituted with alkoxy [5], aryloxy [6-8] and arylamino [6, 9] groups, when the photoreactivity of the POPs originates from the first excited singlet state [6] of the chromophore appended to the inorganic —P=N— backbone. During these processes the homolytic cleavage of the P—Y substituent or PY—substituent (Y = O or —NH—) bonds takes place with the formation of phosphazene macroradicals; as the evolution of these species leads to the degradation or the crosslinking of the polymeric substrates depending on the adopted experimental conditions [6, 9] (i.e. the presence or the absence of molecular oxygen, the solvent used for photolysis, etc.), these processes are responsible for the modifications observed in the molecular weights, mechanical properties and morphological aspects of the irradiated phosphazene substrates.

Bimolecular processes [3] that take place during the photochemistry of poly(organophosphazenes) are also important because they can be applied to enhance [7, 10] (photosensitization) or to depress [11, 12] (quenching) the photoreactivity of POPs by interactions of the phosphazene side substituents both with external (i.e. free in solution or physically blended in POP films) or internal (i.e. chemically attached to phosphazene polymers) additives. Phosphazene-supported chromophores, in turn, can be used themselves as photosensitizers to favor the formation of singlet oxygen [13] or to induce photoisomerization and photoaddition reactions [11].

As an example of this type of investigation we may mention the sensitized photochemistry of poly[bis(4-*iso*propylphenoxy)phosphazene] (PiPP) performed in the presence of benzophenone [7, 10, 14]. The main reaction observed during the irradiation of this polymer is crosslinking regardless of whether the benzophenone sensitizer is free in solution (or dispersed in the polymer film) [7, 10] or co-substituted together with the 4-*iso*propylphenoxy groups on the same polydichlorophosphazene macromolecule [14, 15]. In both cases, in fact, the electronically excited benzophenone triplets abstract hydrogen atoms from the 4-*iso*propylphenoxy groups originating phosphazene macroradicals whose coupling brings about the crosslinking of PiPP and the total insolubilization of the phosphazene material.

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Starting from these studies we recently considered another phosphazene polymer that bears labile hydrogens in the side phosphorus substituents, i.e. poly[bis(4-benzylphenoxy)phosphazene] (PBPP)



This polymer, in fact, shows an interesting reactivity that originates from the secondary hydrogen atoms present in the benzylphenoxy side substituents, as demonstrated by thermal and mechanical investigations [16], direct photochemistry [8], photooxidation [17] and grafting processes [18].

In these studies, moreover, we observed the concurrent formation of phosphazene-supported hydroperoxides and carbonylic groups [8, 17], that are photochemically very active and can be involved in

secondary reaction steps during the irradiation of PBPP, greatly improving the photoresponsiveness of this material.

On this basis, therefore, we decided to investigate the photochemistry of PBPP in solution and in film sensitized by the presence of benzophenone, under the selective excitation of this last species. The results reported in this paper concern the use of the benzophenone photosensitizer as an external additive, free in solution or physically blended into PBPP films. Further studies regarding the photochemical activity of phosphazene copolymers containing variable percentages of 4-hydroxy-benzophenone groups geminally substituted on the same phosphorus with 4-benzylphenoxy moieties, will be reported successively [19].

#### EXPERIMENTAL

Poly[bis(4-benzylphenoxy)phosphazene], PBPP, was synthesized and characterized according to literature [8, 20]. Benzophenone (BP) and the 4-hydroxy-diphenylmethane were Aldrich products and were purified by vacuum sublimation prior to use. All the solvents used for photolysis and

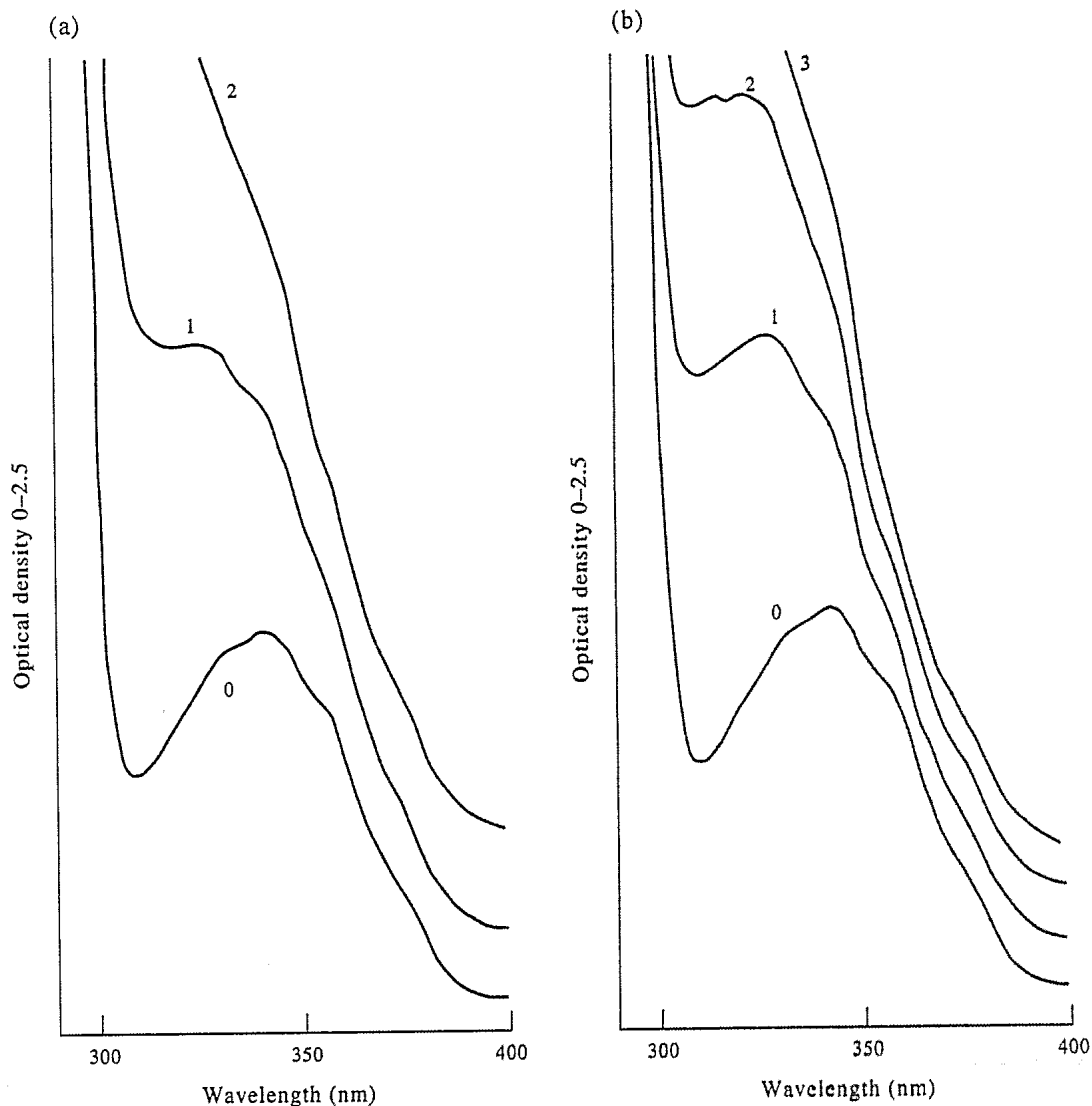


Fig. 1. Optical density variations of PBPP benzene solutions during the benzophenone sensitized photochemistry of PBPP. Excitation wavelength  $\lambda > 340$  nm. (A) Irradiation in air. Curve 0:  $t = 0$  min; curve 1:  $t = 30$  min; curve 2:  $t = 45$  min. (B) Irradiation in argon atmosphere. Curve 0:  $t = 0$  min; curve 1:  $t = 12$  min; curve 2:  $t = 24$  min; curve 3:  $t = 30$  min.

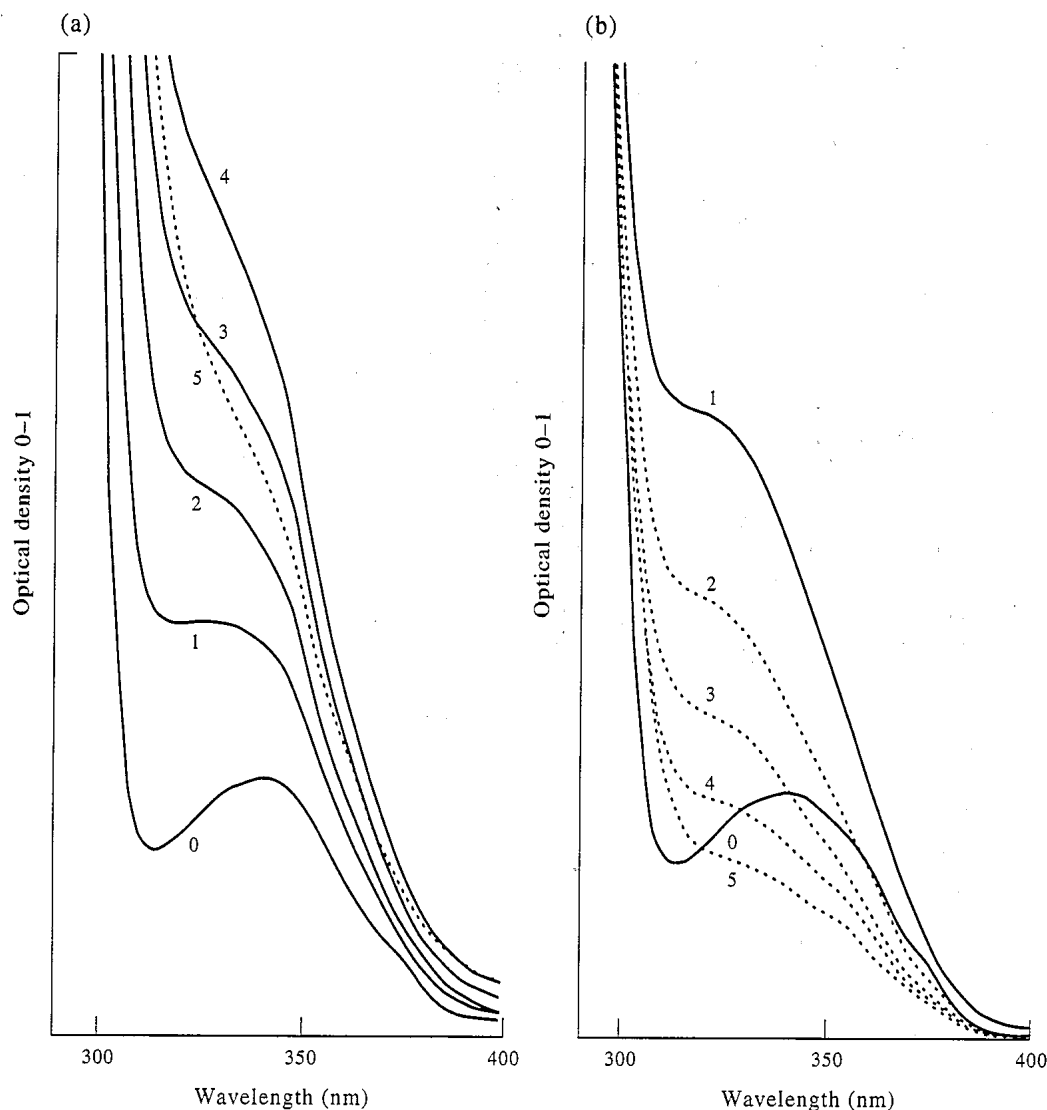


Fig. 2. Optical density variations during the benzophenone sensitized photochemistry of PBPP films. Excitation wavelength  $\lambda > 340$  nm. (A) Irradiation in air. Curve 0:  $t = 0$  min; curve 1:  $t = 3$  min; curve 2:  $t = 9$  min; curve 3:  $t = 18$  min; curve 4:  $t = 36$  min of irradiation; curve 5:  $t = 36$  min of irradiation and 48 hr of dark storage. (B) Irradiation in argon. Curve 0:  $t = 0$  min; curve 1:  $t = 36$  min of irradiation; curve 2:  $t = 36$  min of irradiation and 9 min of dark storage; curve 3:  $t = 36$  min of irradiation and 27 min of dark storage; curve 4:  $t = 36$  min of irradiation and 100 min of dark storage; curve 5:  $t = 36$  min of irradiation and 48 hr of dark storage.

for the preparation of samples were C.Erba analytical grade; when necessary, they were purified or dried according to literature [21].

u.v. spectra were carried out with a Perkin-Elmer spectrophotometer model 322.

i.r. characterizations were performed with a Perkin-Elmer spectrophotometer model 399.

Average molecular weight ( $M_w$ ) determinations were obtained by the light scattering technique using a Sophia spectrogoniodiffusimeter.

Viscosity measurements were run in a Desreux-Bischoff, suspended-level, viscosimeter, at room temperature using  $\text{CH}_2\text{Cl}_2$  as a solvent. An intrinsic viscosity value of 1.35 dl/g was measured for PBPP.

Irradiation was performed with a high pressure mercury lamp HBO 150 W and cut off filters at  $\lambda > 340$  nm.

During the benzophenone-sensitized photochemistry of PBPP in benzene solutions the concentrations used were as follows: PBPP:  $C = 5.3$  g/l ( $= 1.3 \times 10^{-2}$  M in monomeric units); BP:  $C = 1.48 \times 10^{-2}$  M. Films of PBPP containing BP were obtained by the solvent evaporation of PBPP solutions in  $\text{CH}_2\text{Cl}_2$  at the following

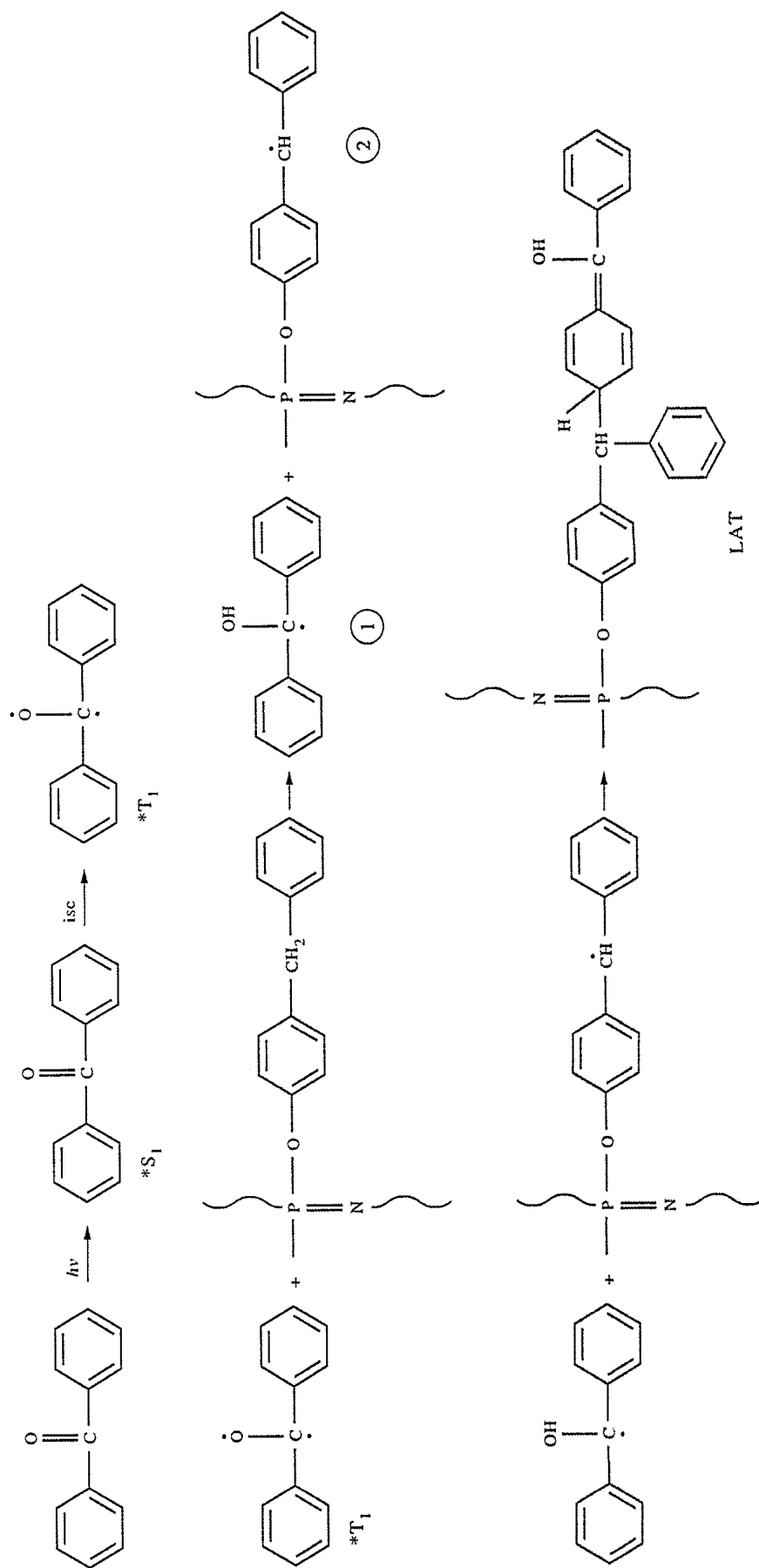
concentration: PBPP:  $C = 28$  g/l; BP:  $C = 5$  g/l. The final dimensions of the films obtained were 24 mm  $\times$  24 mm  $\times$  4  $\mu\text{m}$ .

The amount of gel obtained following the irradiation of PBPP films containing BP was calculated gravimetrically according to the reported procedure [8, 14].

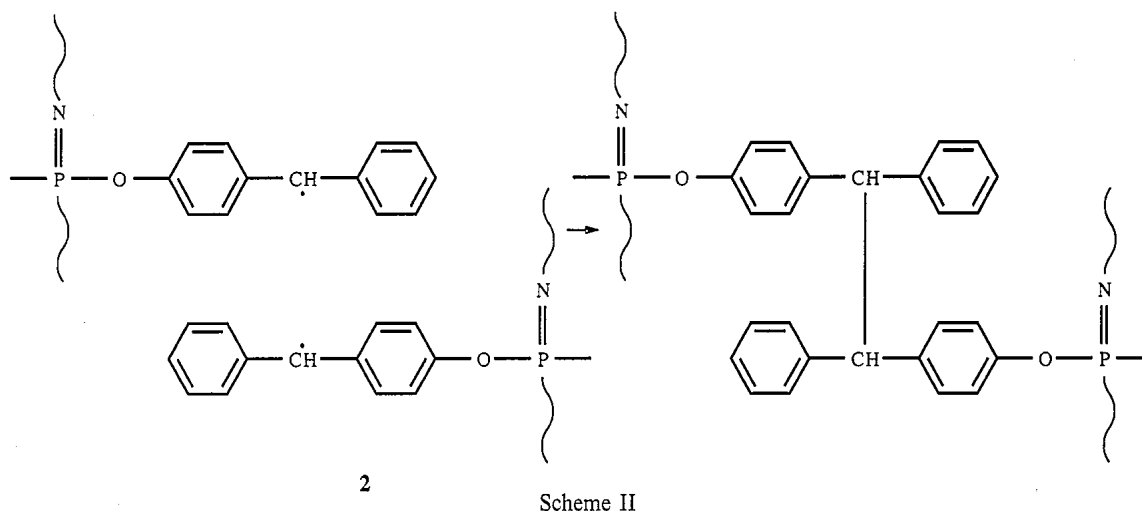
## RESULTS AND DISCUSSIONS

The selective irradiation of the benzophenone photosensitizer dissolved in aerated and argon-saturated benzene solutions of poly[bis(4-benzylphenoxy) phosphazene], PBPP, leads to the optical density variations reported in Fig. 1(A) and (B).

In both cases, these pictures show a sharp increase in the absorption spectrum of the reaction mixture in the range of 290–370 nm (assigned to the  $n-\pi^*$  transition of the carbonyl group [22]) that is more pronounced when photolysis is carried out in the absence of molecular oxygen. Similar results are obtained when the benzophenone sensitized



Scheme I



photochemistry of PBPP is carried out in film both in air and in argon atmosphere [see Fig. 2(A) and (B), respectively].

According to our previous findings on the direct photolysis of poly[bis(4-benzoylphenoxy)phosphazene] (BzPOP) [23] and on the benzophenone sensitized photochemistry of PiPP [7, 10], we attributed the increase of the optical density of PBPP benzene solutions and films irradiated in the presence of BP to the production of LATs (light absorbing transients) [24, 25], i.e. relatively long-living intermediates formed by the rearrangement of ketyl radicals (1) (primarily generated by the excited benzophenone triplets via hydrogen atom abstractions from PBPP), and successive coupling reactions. These facts are summarized in Scheme I.

As a result of the above described reactions, the PBPP macroradicals (2) are also formed during the photochemical processes; these species are very reactive intermediates able to participate in several different types of reactions.

We have already reported, in fact, that these radicals can initiate the grafting copolymerization of vinyl monomers onto polyphosphazene matrices giving rise to very interesting new classes of phosphazene materials [18, 26, 27].

They can also undergo coupling reactions, thus inducing the increase of the PBPP molecular weight and eventually the crosslinking and the insolubilization of the POP according to reaction Scheme II. This is demonstrated by the data in Table I where we have reported the variations in the weight average molecular weight  $M_w$  vs irradiation time for the benzophenone sensitized photochemistry of PBPP dissolved in aerated benzene solutions. As can be seen from the table, the selective irradiation of the BP photosensitizer induces an initial decrease of the molecular weight followed by a successive increase of the  $M_w$  values, to indicate the presence of an initial photodegradation of the polymer with very short illumination times, followed by remarkable photocrosslinking effects with a longer time exposure. The same is also true in the case of the benzophenone-sensitized photochemistry of PBPP in film, where 95% of the polymer crosslinks after 3–4 min of illumination (see Fig. 3).

The benzoylphenoxy radical (2) produced during the BP photosensitized photochemistry of PBPP can also

uptake molecular oxygen to form the polyphosphazene-based hydroperoxides (3) (see reaction Scheme III).

These species can undergo homolytic cleavage of the —O—OH hydroperoxidic groups by thermal and/or photochemical events producing the phosphazene macroradical (4). The same species, which may also be formed by energy transfer processes involving excited carbonyl triplets and the phosphazene hydroperoxide (3) as demonstrated by Geuskens [28] and Guillet [29], has a high reactivity that can follow at least four different reaction pathways. They can, for instance, participate in the overall reticulation process of PBPP by coupling reactions with other radical intermediates (pathway "a" in Scheme II); they can abstract hydrogen atoms from suitable donors forming the phosphazene macroalcohol (5) (pathway "b"), or they can undergo  $\beta$ -scission reactions leading, eventually, to the formation of free carbonyl groups on the polyphosphazene matrix (pathways "c" and "d" in the scheme).

All these facts are supported by i.r. spectroscopy [see Figs 4(A), (B) and 5]. In Fig. 4(A) in fact we reported the i.r. transmittance variations measured during the BP sensitized photochemistry of PBPP films in air. Three main modifications are observed located in the spectral range of 3650–3150, 3000–2800 and 1900–1600  $\text{cm}^{-1}$  respectively. The first band [30] refers to the formation of hydroxylic groups (3570  $\text{cm}^{-1}$ ) and hydroperoxidic moieties (3500–3100  $\text{cm}^{-1}$ ) under illumination. The —OH group-containing species may be formed, for instance, by coupling reactions of the ketyl radicals (1) to produce benzopinacol according to literature [31], or by a hydrogen atom abstraction reaction from the macroradical (4) to form the secondary alcohol (5) bonded to the phosphazene polymer. Hydroperoxides (3), in turn, may originate according to

Table I

Irradiation time (min)	Weight average molecular weight
0	$4 \times 10^6$
1 min 30 sec	$3.5 \times 10^6$
3 min 30 sec	$4.4 \times 10^6$
5 min	$4.9 \times 10^6$
8 min	$8.1 \times 10^6$
10 min	$1.2 \times 10^7$

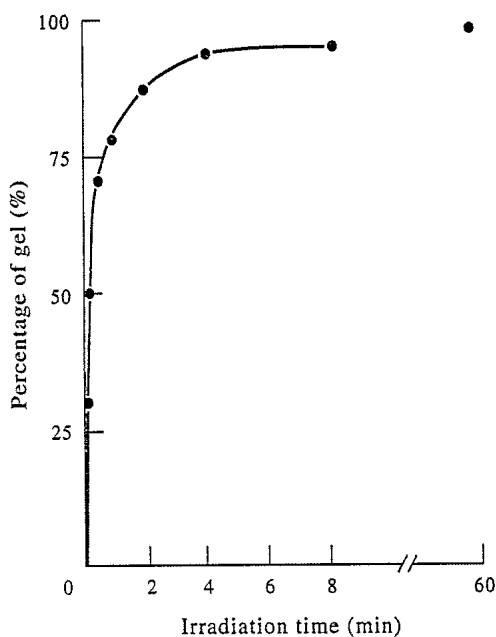


Fig. 3. Percentage of gel formed during the benzophenone sensitized photochemistry of PBPP in air vs irradiation time.

Scheme III, by oxygen uptake from the macroradical (2). The second variation is observed in the peaks located at 2910 and 2840  $\text{cm}^{-1}$  attributed respectively to the asymmetric and symmetric vibrations [32] of the  $-\text{CH}_2-$  groups of PBPP. The decrease of these bands is indicative of the occurrence of light-induced hydrogen atom abstraction reactions on the methylene site. Finally, in the range of 1900–1600  $\text{cm}^{-1}$  the band at 1660  $\text{cm}^{-1}$  is assigned to the stretching of the benzophenone carbonyl groups [30] that is consumed under irradiation, while the broad band located between 1800–1700  $\text{cm}^{-1}$  may envelop different carbonyl absorptions attributable to polymer supported benzaldehyde, peracids, esters, etc. that may be formed during light exposure as previously reported [8, 17].

Figure 5, where we show the absorbance variations at 1660, 3400 and 3570  $\text{cm}^{-1}$ , give a more precise representation of the above described phenomena. From this picture, in fact, it appears that the phosphazene hydroperoxide (3) (absorption at 3400  $\text{cm}^{-1}$ ) is the first species formed during illumination in a concentration that increases almost immediately in the early steps of the photolysis, reaches a plateau after 30 min of light exposure and undergoes no further changes for longer irradiation times. Moreover, the phosphazene macroalcohol (5) (absorption at 3570  $\text{cm}^{-1}$ ) starts to be formed only after the decomposition of the hydroperoxide species (3) in a concentration that increases continuously during the photochemistry of PBPP. Finally the benzophenone species (absorption at 1660  $\text{cm}^{-1}$ ) show during photolysis a sharp decrease of concentration due to hydrogen atom abstraction reactions. These species, however, do not disappear completely during the sensitized photochemistry of PBPP in air and a significantly high amount of benzophenone residues are always present in the PBPP system even at long irradiation times.

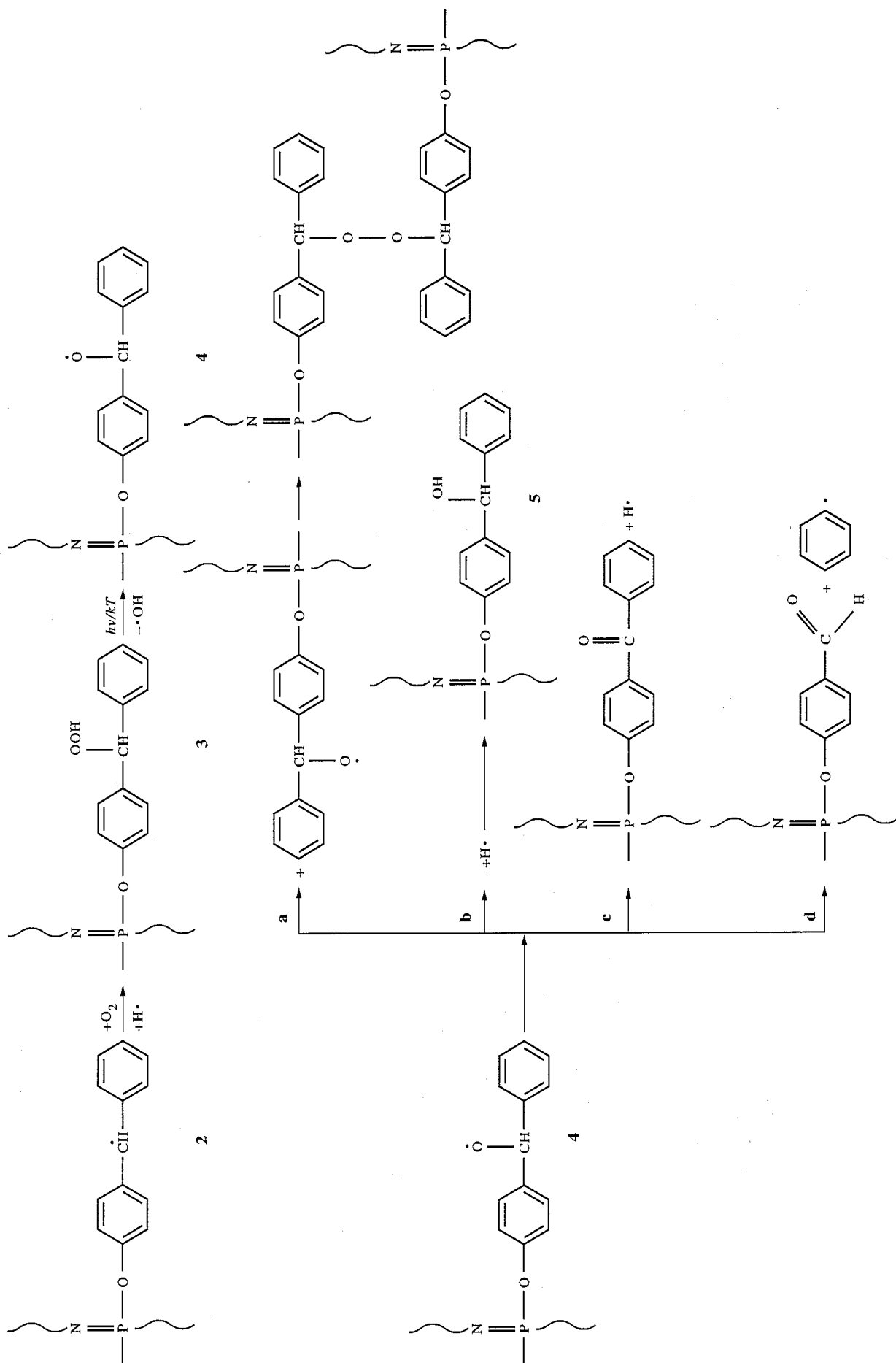
Parallel experiments concerning the benzophenone sensitized photochemistry of PBPP carried out

in argon atmosphere for comparable periods of times (6 hr of illumination) [see Fig. 4(B)] show only the formation of the peak at 3570  $\text{cm}^{-1}$  (stretching of the  $-\text{OH}$  groups of the benzopinacole), the sharp disappearance after irradiation of the peak at 1660  $\text{cm}^{-1}$  due to the benzophenone system, and the decrease of the peaks at 2910 and 2840  $\text{cm}^{-1}$  assigned to the methylene groups. No polymer-supported hydroperoxides (3), additional benzophenone moieties, or other carbonyl-containing species, appear to be formed during the PB photosensitized photochemistry of PBPP films in these conditions.

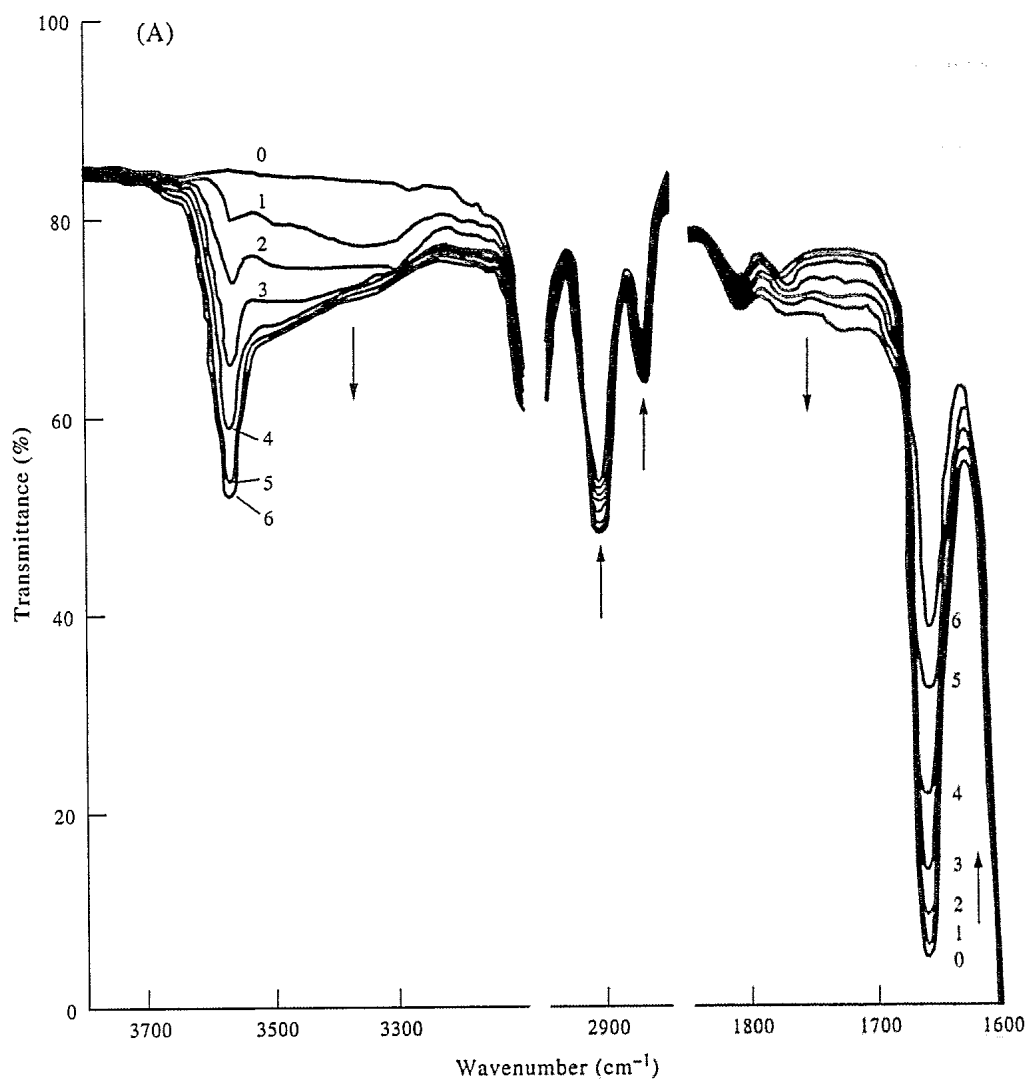
A reasonable explanation that can be put forward to account for these facts deals with the real fate of the benzophenone photosensitizer molecules during the photolysis of PBPP in different experimental conditions. As proved by u.v. [Figs 2(A) and (B)] and by i.r. [Figs 4(A), (B) and 5] spectroscopy, in fact, these species are consumed during the photolysis of PBPP, both in the presence and in the absence of air, by hydrogen atom abstraction reactions. However, when oxygen is excluded from the reaction system, the benzophenone disappears almost completely after 6 hr of irradiation, probably forming benzopinacole [31], without producing new, carbonyl-containing, moieties; by contrast, when the sensitized photochemistry of PBPP is run in air for comparable periods of time, the disappearance of the BP photosensitizer is much slower due to the continuous regeneration of this species through the modification of the phosphazene macroradical (2) (see Scheme III). This phenomenon is of remarkable importance as the regenerated carbonyl species can absorb light themselves during irradiation, and can participate in secondary photochemical events, thus greatly improving the photochemical responses of PBPP.

Moreover, it may be observed that new carbonyl-containing species attached to the phosphazene macromolecule (aldehydes, peresters, acids, etc. [8, 17]) are formed during irradiation, as demonstrated in Fig. 4(A), and these may also contribute to the overall photoresponsiveness of the PBPP.

The influence of molecular oxygen on the sensitized photochemistry of PBPP is also evident in another aspect of photoreaction. In fact, the irradiation of the BP chromophore physically dispersed into the polyphosphazene PBPP matrix for 36 min, in air or in argon atmosphere, produces a sudden increase in optical density attributed to the formation of LATs [24] [see Fig. 2(A) curves 0–4 and (B) curves 0–1]. However, a decrease in the optical density of the polyphosphazene films is observed after storing the irradiated films in the dark for 48 hr [Fig. 2(A) curve 5 and (B) curve 5]; this phenomenon is accounted for with the onset of a post-photochemical effect [8], whose entity is very different according to the presence or the absence of molecular oxygen in the system. In fact, the observed decrease in the optical absorption at 330 nm, indicative of the consumption of the BP photosensitizer during photochemistry, is remarkably rapid and high when the irradiation of PBPP is carried out in argon atmosphere [Fig. 2(B) curves 2–5]; this fact suggests that no alternative, carbonyl-containing, chromophores are generated during dark reaction. On the contrary, the decrease in the optical density is quite feeble and slow when the



Scheme III





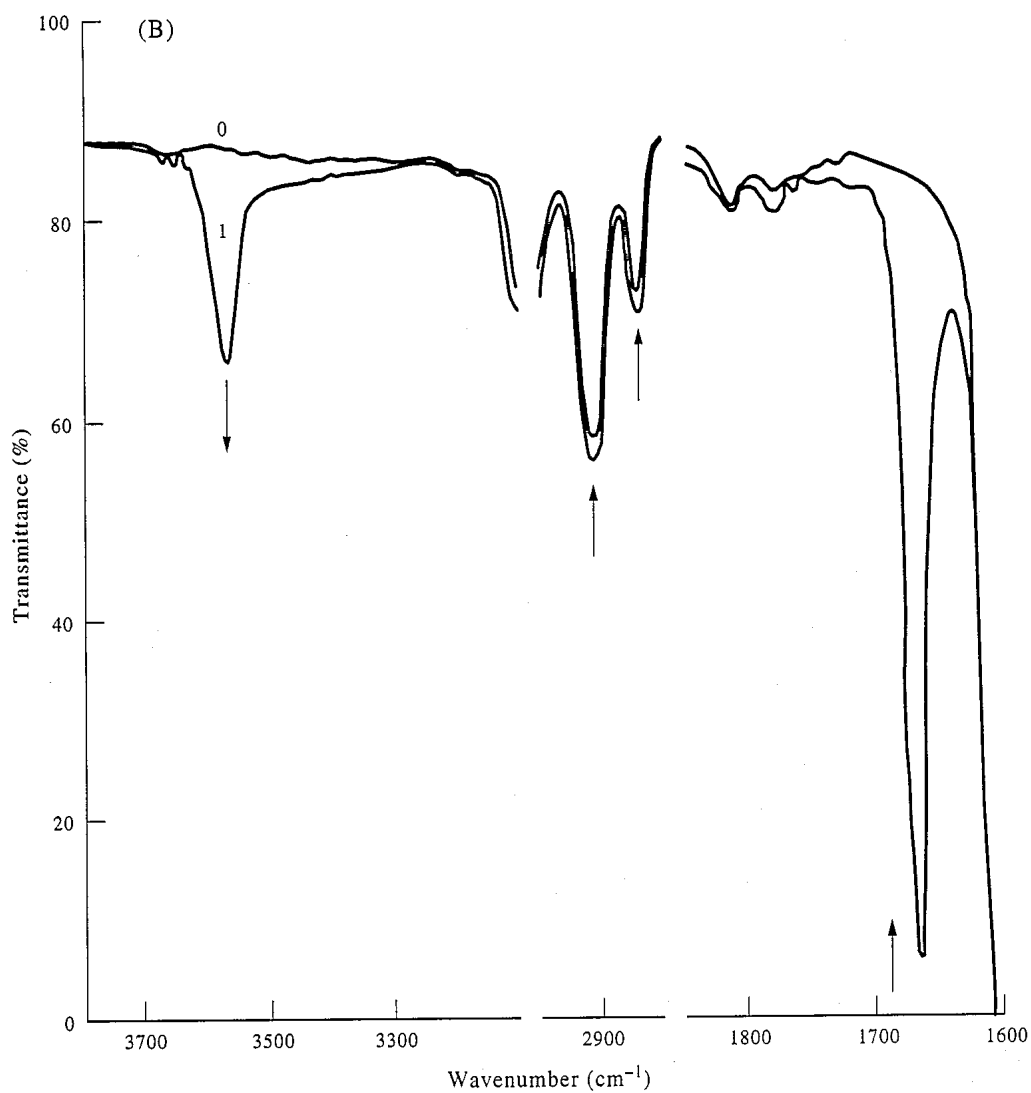


Fig. 4. i.r. transmittance variations during the benzophenone sensitized photochemistry of PBPP films. (A) Irradiation in air. Curve 0:  $t = 0$  min; curve 1:  $t = 5$  min; curve 2:  $t = 15$  min; curve 3:  $t = 45$  min; curve 4:  $t = 105$  min; curve 5:  $t = 225$  min; curve 6:  $t = 360$  min. (B) Irradiation in argon atmosphere: curve 0:  $t = 0$  min; curve 1:  $t = 360$  min.

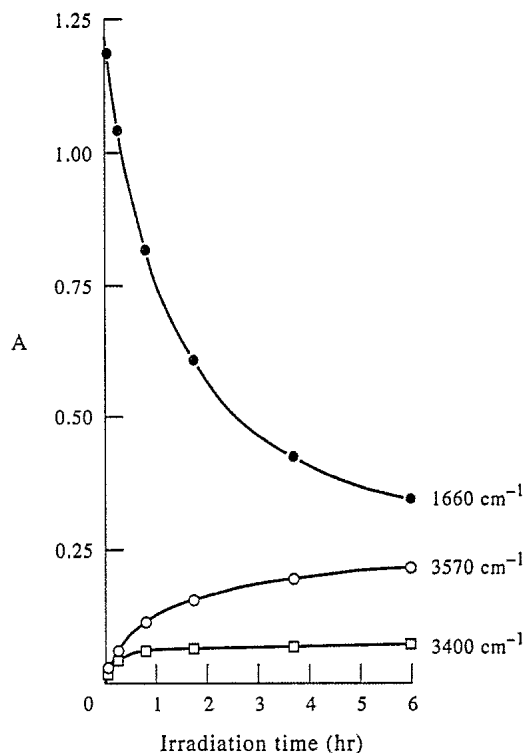


Fig. 5. i.r. variations of the peaks at 3570, 3400 and 1660  $\text{cm}^{-1}$  vs irradiation times during the BP sensitized photochemistry of PBPP films in air.

PBPP films are irradiated in air and successively stored in the dark for the same period of time [Fig. 2(A) curve 5], proving that carbonyl-containing chromophores, probably attached to the polyphosphazene skeleton, are irreversibly formed during photolysis from the primary radical (2) and the successive evolution of these species, according to Scheme III.

#### CONCLUSION

The benzophenone sensitized photochemistry of poly[bis(4-benzylphenoxy)phosphazene] in benzene solutions or in films shows, as the most important result, the crosslinking of the phosphazene polymer, accompanied by an increase in molecular weight and gel formation. This process is the consequence of the intermolecular reaction of hydrogen atom abstraction by the benzophenone excited triplets from the PBPP to produce the macroradicals (2) that can couple and induce the total reticulation of the system. In the presence of air, moreover, these radicals can uptake oxygen forming the polymeric hydroperoxides (3) from which several reactions may follow, such as the crosslinking of the polymer,  $\beta$ -scissions and the formation of carbonyl-containing phosphazene units, or hydrogen atom abstraction to produce the macroalcohol (5).

It is interesting to stress the remarkably different behavior of the benzophenone groups when the sensitized photolysis of PBPP is carried out in air or in an inert (argon) atmosphere. In the first case, in fact, the benzophenone moieties, consumed during the hydrogen atom abstraction reaction on the PBPP, are regenerated by the chemical modification of the phosphazene macroradical (2), according to reaction

Scheme III, thus decreasing the rate of disappearance of this species which has additional chances of participating in secondary photochemical events; on the contrary, in the absence of oxygen, benzophenone molecules disappear producing benzopinacol and no additional carbonyl-containing residues are generated.

These facts are also in agreement with the post-photochemical effect observed after the photolysis of PBPP films, since, after 36 min irradiation and 48 hr of dark storage, the u.v. spectra of the irradiated samples shown an almost complete absence of carbonyl absorptions in the spectral range between 310–370 nm for irradiations performed in argon atmosphere, and a remarkably high absorption in the same range when photochemistry is run in air.

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