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Photochemical Behavior of Poly(organophosphazenes). 5. Photochemistry of Poly[bis(4-benzoylphenoxy)phosphazene], $[NP(OC_6H_4COC_6H_5)_2]_n$, in Solution

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ABSTRACT: In air-equilibrated CH_2Cl_2 or in CH_2Cl_2/CCl_4 solutions, the irradiation of the poly[bis(4-benzoylphenoxy)phosphazene], $[NP(OC_6H_4COC_6H_5)_2]_n$, induces chain scission and degradation of the macromolecule. This process is believed to originate from the breaking of peroxy radicals formed by reaction of oxygen with phosphorus macroradicals derived from unreacted P–Cl groups in the phosphazene polymer. Evidence is given that the benzophenone ketyl radical, the primary photochemical species formed during the photolysis of BzPOP dissolved in hydrogen-donating solvents, is responsible for the formation of phosphorus macroradicals. In the absence of molecular oxygen, bimolecular processes, leading to extensive cross-linking and gel formation, prevail.

Introduction

The photochemical and photophysical behavior of poly(organophosphazenes) (POPs) has attracted considerable attention in recent years[1–4] owing to the substitutive synthetic approach used for the preparation of these polymers. The method, in fact, offers the unique opportunity of obtaining a large variety of different macromolecules just by changing the nucleophiles which substitute the highly reactive chlorine of a polymeric precursor, poly(dichlorophosphazene).[5,6] Due to the characteristics of the phosphorus–nitrogen "double bond" present in these polymers,[7] chromophores appended to the poly(phosphazene) backbone maintain almost unaltered their spectroscopic and photochemical properties, so that the photoreactivity of the resulting POPs appears to be dominated by the photochemical characteristics of the substituents.

In 1979 we started a series of investigations on the photoreactivity of aryloxy- and arylamino-substituted POP, both in solution and in film, with the aim of shedding some light in the photochemistry of these materials.[1,3,4] From these studies it came out that, in all the investigated POPs, the photoreactivity is originated from the first excited singlet state of the chromophore bonded at the phosphazene chain; moreover, it was clear that the presence of molecular oxygen in the irradiated polymer directs the overall photoreaction toward the degradation, while in the absence of oxygen cross-linking prevails. Finally, it was demonstrated that the formation of charge-transfer complexes between side substituent groups on the phosphazene backbone and high electron affinity halogenated solvents introduces in the photochemistry of these polymers alternative pathways for the degradation or cross-linking which enhance significantly the photoreactivity of these materials.

Further investigation on the photophysical behavior of both aryloxy- and arylamino-substituted cyclophosphazenes and poly(phosphazenes) revealed the existence of intramolecular interactions between excited- and ground-state chromophores on the phosphazene backbone, leading to the emission of excimeric species.[8,9]

Parallel studies on the photochemistry and photophysics of POPs performed by Allcock[2] and Webber,[10] respectively, substantially confirmed our results.

Recently,[11] we synthesized and characterized a new polymeric phosphazene material, the poly[bis(4-benzoylphenoxy)phosphazene], $[NP(OC_6H_4COC_6H_5)_2]_n$, BzPOP, in which two benzophenone moieties are attached to the phosphorus atoms of the phosphazene chain.

This polymer proved to be an excellent triplet-state energy donor in heterogeneous phase,[11] able to photosensitize some reactions, occurring in the triplet state, like the trans ⇄ cis isomerization of stilbene and of piperylene, the cycloaddition of indene, and the valence isomerization of norbornadiene to quadricyclene.

During these processes, however, it has been found that BzPOP undergoes a certain degree of insolubilization: the suspicion arose therefore that BzPOP could exhibit a completely different photoreactivity, compared to that of other aryloxy-substituted phosphazene polymers. Owing to the high efficiency by which the triplet state of BzPOP is populated,[11] a photoreactivity of this polymer completely different from that of other aryloxyphosphazenes is not unexpected. This is in agreement also with the fact that substantial differences in chemical reactivity are expected for S_1 and T_1 states of an electronically excited molecule, due to the rather different nuclear structure and electronic distribution of the two states.[12]

Therefore, we believed it was useful to investigate the direct photochemistry of the BzPOP in solution, and in this paper, we discuss research in this field.

Experimental Section

The synthesis, characterization, and spectroscopic properties of the BzPOP have already been reported elsewhere.[11] As previously stressed, the content of unsubstituted chlorine in the BzPOP ranged to 1.1%.

Tetrahydrofuran (THF), CH_2Cl_2, isopropyl alcohol, cumene, benzene, and CCl_4 were Carlo Erba solvents, analytical grade, and

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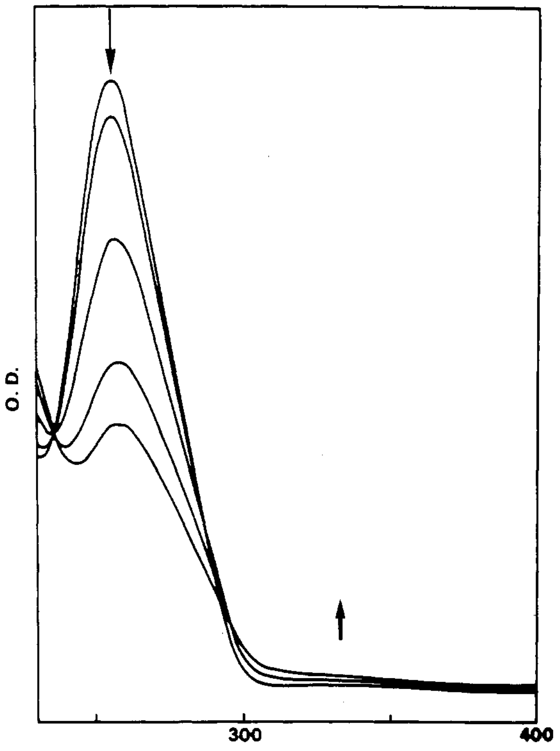


Figure 1. UV spectral variations following irradiation of poly[bis(4-benzoylphenoxy)phosphazene] in CH_2Cl_2 solutions. Irradiation times: 0, 1, 5, 10, 15 min.

were purified according to the literature.[13]

The UV and IR spectrophotometric measurements were performed with Perkin-Elmer spectrophotometers Models 320 and 399, respectively.

For the gas-chromatographic determinations of the photolysis products, a Perkin-Elmer Sigma 3B gas chromatograph was used.

The lifetime measurements of BzPOP excited triplets were performed by detecting the phosphorescence with a single photon counting apparatus (Applied Photophysics). The triplet and ketyl radical absorption spectra were obtained with a flash photolysis apparatus based on a N_2 laser (Lambda Physics) and a pulsed xenon lamp as analyzing beam.

The weight average molecular weight ($\bar{M}_w$) were measured by means of a Sofica spectrogoniodiffusometer and a Waters GPC apparatus.

Viscosity measurements were carried out in a Desreux-Bishoff suspended level viscosimeter at 25 ± 0.5 °C with quartz walls. The polymer solutions in the viscosimeter were irradiated with an XBO 900-W lamp, whose light was filtered with a cut-off filter at 300 nm.

Unless otherwise specified, all the photochemical reactions of the BzPOP have been run in air-equilibrated solutions.

Quantitative analysis of the hydroperoxidic groups in the irradiated BzPOP has been performed according to the procedure described by Carlsson and Wiles.[14]

Results and Discussion

Since the original discovery of Ciamician and Silber[15] that benzophenone in ethanol is reduced by the action of the sunlight to benzpinacol, the photophysical and photochemical behavior of this molecule and its derivatives has become one of the deepest investigated topics in the field of organic photochemistry.

It is now well established[12] that light excitation of the molecule results in the production of excited triplet, which is formed from the corresponding singlet with almost unitary intersystem-crossing efficiency. This state may transfer its excitation energy to other molecules to induce photosensitized reactions or may react in the presence of molecules able to supply hydrogen atoms bringing about the photooxidation of these species and the formation of benzophenone ketyl radicals.

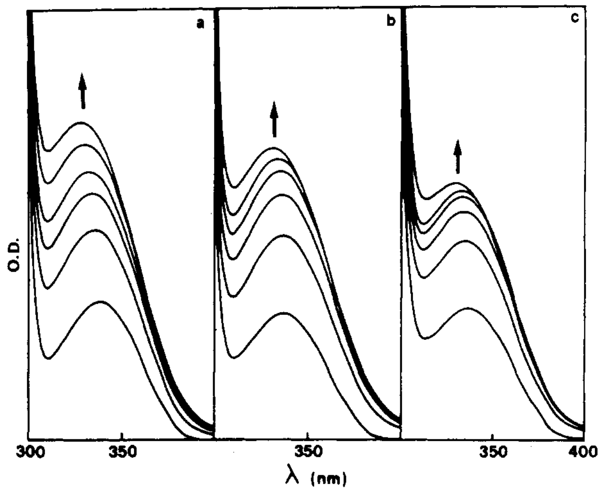
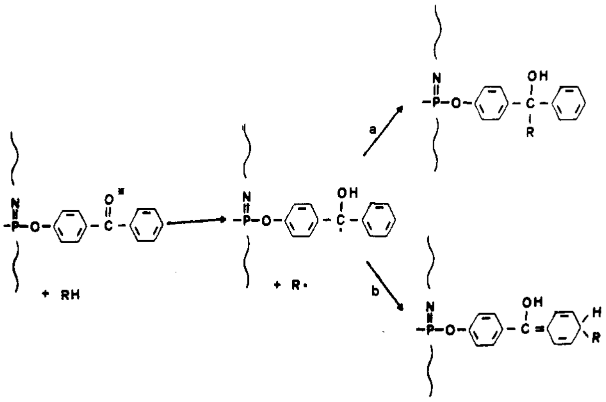


Figure 2. Spectral variations of the n,π* absorption band of (a) free benzophenone, (b) hexakis(4-benzoylphenoxy)cyclophosphazene, and (c) poly[bis(4-benzoylphenoxy)phosphazene], in CH_2Cl_2 solutions. In all cases the irradiation times were 0, 0.5, 1, 2, 3.5, and 7.5 min.

Scheme I



Our previous work on the characterization of the poly[4-benzoylphenoxy)phosphazene],[11] as a high molecular weight triplet sensitizer active in heterogeneous phase, has shown that the photophysical characteristics (absorption, emission spectra, and triplet energy) of the above compound are more similar to those of the free benzophenone rather than to those of the 4-hydroxybenzophenone.

This is supported by the behavior of benzophenone-substituted phosphazenes when irradiated in hydrogen-donating solvents. The irradiation of BzPOP, hexakis(4-benzoylphenoxy)cyclophosphazene (the cyclic trimeric derivative which can be considered the oligomeric analogue of the high molecular weight polyphosphazene[16]), and benzophenone in deaerated methylene chloride solutions leads to the spectral variations shown in Figures 1 and 2. A decrease of the solution optical density for wavelengths < 300 nm and an increase for wavelenghts > 300 nm were observed for the three compounds, the extent depending on the molecular structure. This confirms that the photoreactivity of phosphazene-supported benzophenone is like that of the free benzophenone. These spectral variations are attributed[17] to the formation of products resulting from different couplings of radicals formed by interaction of the triplet benzophenone and hydrogen-donating molecules, as shown in Scheme I.

For the phosphazene-appended benzophenones, this hypothesis was confirmed by the absence of any spectral variation when the hexakis(4-benzoylphenoxy)cyclo-

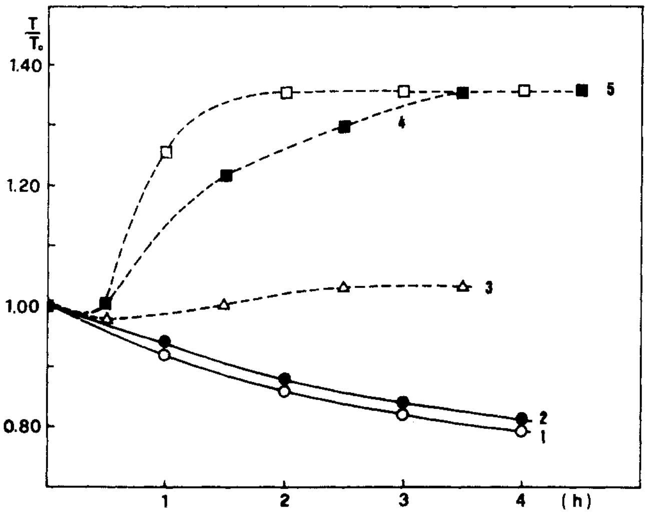


Figure 3. Viscosity variations of poly[bis(4-benzoylphenoxy)phosphazene] as a function of the irradiation time: (○) CH_2Cl_2 solutions; (●) CH_2Cl_2 + CCl_4, 6 M; (△) CH_2Cl_2 + THF, 0.82 M; (■) CH_2Cl_2 + THF, 2 M; (□) CH_2Cl_2 + THF, 4 M.

phosphazene was irradiated in carbon tetrachloride.

According to Scaiano,[17] path b in Scheme I is responsible for the increase of the absorption at wavelengths > 300 nm. The extent of the effect decreases with the increase of molecular weight of the irradiated species (see Figure 2): this is probably related to a reduced mobility of the species R, in the viscous environment of the polymer solution.

The irradiation of air-equilibrated solutions of BzPOP in CH_2Cl_2 induces a decrease of the initial viscosity of the solution, which is indicative of a light-induced degradation of the polymer, as shown in Figure 3, curve 1. After 20 h of irradiation, the weight average molecular weight ($\bar{M}_w$) is reduced from the original 1.9×10^6 to 6×10^5, while no viscosity variation has been found for polymer solutions kept in the dark for 50 h.

Irradiation of polymer solutions, degassed by the freeze–pump–thaw technique, induces precipitation of the polymer, which is, reasonably, due to cross-linking phenomena. After 20 h of irradiation, ~50% of the starting polymer was recovered from the solution as insoluble product. The insolubility which occurs has been also observed in the previously studied aryloxy- and arylamino-substituted poly(phosphazenes).[1,3,4] Evidence is presented below that the photochemical behavior which leads to the insolubility in BzPOP is different. In fact, gas-chromatographic and thin-layer-chromatographic analysis showed that, after 20-h irradiation of both BzPOP and benzophenone trimer solutions, no benzophenone or 4-hydroxybenzophenone is released in solution, while in the case of poly[bis(2-naphthoxy)phosphazene] and of poly[bis(4-methylanilinophosphazene][3,4] a considerable amount of free chromophores, 2-naphthol and 4-methylaniline, is produced under comparable conditions. Flash photolysis experiments indicated that the primary photochemical act of the photoreaction (in low electron affinity solvents) is the homolytic scission of the P–OPh or P–NHPh bonds, followed by the release of substituent groups at the phosphorus and formation of phosphorus localized macroradical species.[3,4]

Another difference which can be found in the photochemistry of the BzPOP in solution compared with that of the already investigated POP[1,3,4] may be found in the fact that the addition to the CH_2Cl_2 solution of BzPOP of ~6 M CCl_4 does not appreciably modify the photoreactivity of the polymer, as it can be seen from Figure 3, curve 2. By contrast, for poly[bis(2-naphthoxy)phosphazene][3] and poly[bis(4-methylanilino)phosphazene],[4] as well as for polystyrene,[18] the addition of $CHCl_3$ or CCl_4 to THF solutions of the polymer strongly modify their reactivity. In the presence of halomethanes, a larger quantity of radicals is formed by light excitation, which is the result of charge-transfer processes between the ground and the first excited singlet state of the polymer and the electron-acceptor molecules ($CHCl_3$ and CCl_4).

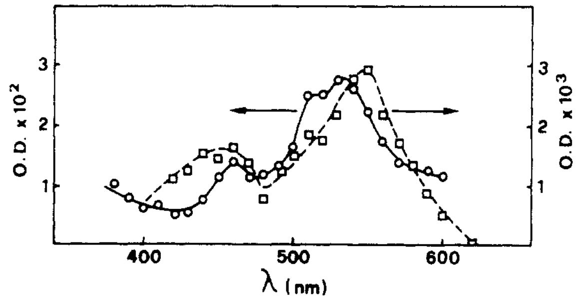


Figure 4. Transient absorption spectra following light excitation of a CH_2Cl_2 solution of poly[bis(4-benzoylphenoxy)phosphazene]: (○) immediately after the laser pulse and (□) 100 μs after the laser pulse.

Table I
Triplet-State Quenching Rate Constants (M^{-1} s^{-1}) of Benzophenone, Hexakis(4-benzoylphenoxy)cyclophosphazene, and Poly[bis(4-benzoylphenoxy)phosphazene] in CH_2Cl_2 Solutions by THF, Isopropyl Alcohol, and Cumene[a]

compound	THF	isopropyl alcohol	cumene
benzophenone (7.2 μs)	6.7×10^6	1.5×10^6	1.3×10^6
hexakis(4-benzoylphenoxy)cyclophosphazene (1.8 μs)	7.9×10^6	2.4×10^6	1.4×10^6
BzPOP (1.5 μs)	4.8×10^6	1.9×10^6	0.5×10^6

[a] The lifetime (τ_0) in pure CH_2Cl_2, is given in parentheses.

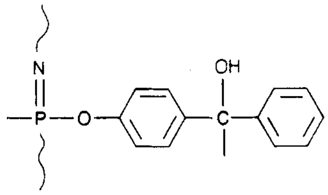
For BzPOP, ground-state interaction with the solvent, due to charge-transfer phenomena, can hardly be evidenced by variation in the absorption spectrum (differences < 5% are observed in the absorption spectrum of BzPOP on going from CH_2Cl_2 to solutions of 6 M CCl_4 in CH_2Cl_2).

Since triplet states have a low polar character compared with that of the corresponding singlets,[19,20] charge-transfer interactions between a molecule in the excited triplet state and an electron-donor or -acceptor molecule are unfavored.

Laser flash photolysis experiments on BzPOP degassed solutions in methylene chloride confirm that a benzophenone-type triplet state is formed, with nearly unitary yield, following light excitation. In Figure 4 are reported the transient absorption spectra of a CH_2Cl_2 solution of BzPOP immediately after the laser pulse (○) and 100 μs after the end of the laser pulse (□). The spectra are practically identical with those obtained, in the same experimental conditions, by flashing solutions of free benzophenone or of benzophenone trimer with the same optical density. With the reasonable hypothesis that the molar extinction coefficients for the T–T absorption are similar for the three molecules, the conclusion can be drawn that the triplet state of the benzophenone chromophore appended to the phosphazene backbone is populated with practically unitary yield.

The lifetimes, in CH_2Cl_2 solutions, of the triplet state of the cyclophosphazene- and poly(phosphazene)-bonded benzophenones are reported in Table I together with those of the free benzophenone, for comparison purposes. The lifetime of the phosphazene-appended benzophenone is shorter than that of the free chromophore, supporting the hypothesis[11] that in the polymer an interaction between an excited chromophore and a chromophore in the ground state is operative.

The spectrum □ in Figure 4, which is formed as evolution of the spectrum ○, is that of the ketyl radicals, whose structure is



formed by hydrogen abstraction from the solvent by the triplet $n\pi^*$ state of the ketone. The formation of this radical is favored by the addition of hydrogen-donating molecules whose quenching rate constants on the triplet state are also reported in Table I. The values obtained for the free benzophenone and the phosphazene-appended benzophenone are very similar, and the same trend, i.e., a decrease of k_4 on going from THF to isopropyl alcohol to cumene, is observed for the three compounds. This could be interpreted as an evidence that, in CH_2Cl_2, the BzPOP has an extended structure in which the benzophenone moieties are quite easily accessible to small molecules present in solution.

The presence of "good" hydrogen donors strongly modifies the photochemical behavior of CH_2Cl_2 solution of the polymer, as shown in Figure 3 (curves 3–5).

At relatively low THF concentrations (0.82 M), in fact, the viscosity of the solution exhibits a very weak decrease at short irradiation times, followed by a small increase for longer illuminations. However, by increasing the concentration of THF in solution up to 2 M, the photochemical behavior of the BzPOP changes markedly: after a short induction period at the beginning of the photolysis, characterized by an almost constant viscosity of the solution, the viscosity increases very steeply, reaching a constant value at roughly 3-h irradiation. After this point no further increase of the viscosity is observed even for the THF concentrations of 4 M. This effect is clearly related to the amount of THF present in solution and is indicative of the onset of a photocross-linking process and of an increase of the BzPOP molecular weight.

Photocross-linking has been found also when the BzPOP is irradiated in air-equilibrated CH_2Cl_2/isopropyl alcohol solutions or in deaerated CH_2Cl_2; in these cases, however, the effect is very striking since extensive gel formation has been observed after short periods of illumination.

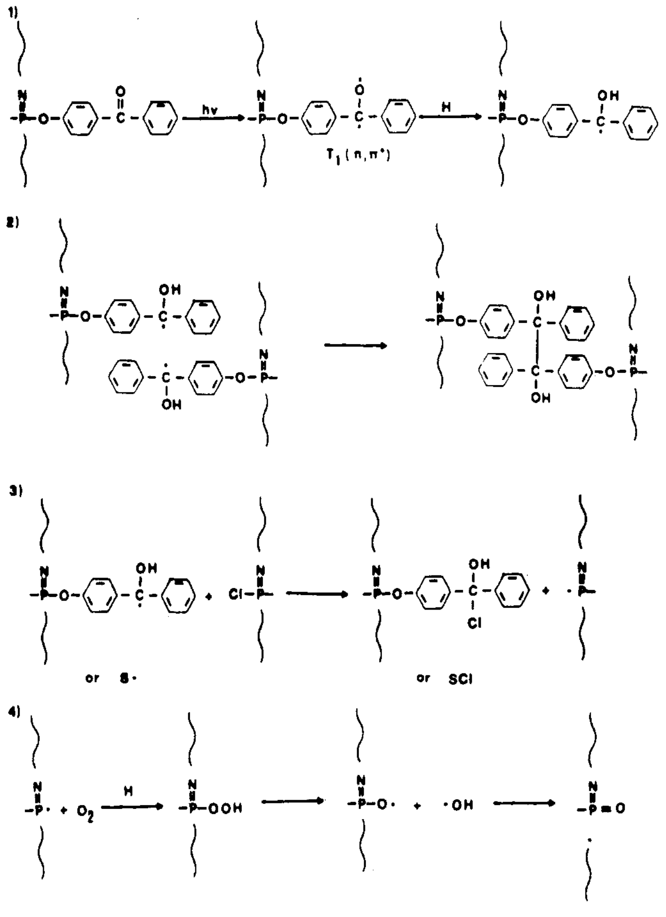
In light of previously reported results, i.e., the absence of free chromophore in the irradiated solutions and the increase of molecular weight in CH_2Cl_2-containing variable amounts of easily hydrogen-donating molecules, an overall photoreaction pattern, which could reasonably explain the photochemical behavior of BzPOP in solution, is reported in Scheme II.

The light absorption by the benzophenone moieties bonded to the polyphosphazene chain induces first the formation of excited benzophenone triplets on the polymer, from which ketyl radicals are generated by hydrogen abstraction from the solvent(s).

Since these radicals have a considerably long lifetime (see Figure 4), they may survive long enough to allow a coupling reaction to occur, bringing about the cross-linking of the polymer and eventually gel formation.

When the solvent used for the photolysis of the BzPOP has hydrogen atoms not easily abstractable, like in the case of CH_2Cl_2, only few radical species are formed, which have a reduced probability of encountering each other and of inducing cross-links. On the other hand, they may have sufficiently long lifetimes to react with residual P–Cl functions present in the polymer due to uncomplete substitution of the parent $(NPCl_2)_n$, originating phosphorus macroradicals (reaction 3 in Scheme II).[21]

Scheme II



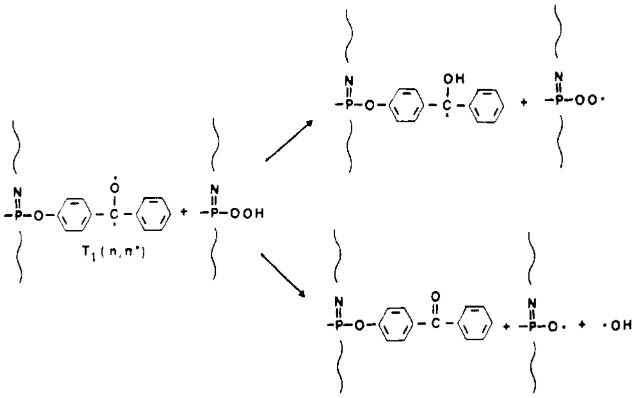
The same reaction is of course possible for the radicals "S" formed from the solvent molecules, generating "SCl" species.

In the presence of molecular oxygen, the phosphorus macroradicals produced in this way may form polymeric peroxides whose thermal or photochemical breaking may induce chain scission and degradation of the macromolecule. In this case, the general reaction sequence already reported for poly[bis(2-naphthoxy)phosphazene][3] and poly[bis(4-methylanilino)phosphazene][4] has been hypothesized also for the photochemistry of BzPOP in solution.

The presence of hydroperoxidic functions in the irradiated BzPOP has been shown by iodometric titration, according to the procedure proposed by Carlsson and Wiles:[14] $\sim 2.2 \times 10^{-7}$ mol of hydroperoxides are formed in 5 mg of BzPOP in CH_2Cl_2 after 10-h irradiation.

It should be stressed, however, that the photochemical decomposition of the hydroperoxidic groups on the BzPOP by direct photolysis of these species seems to be unlikely, since their absorption is very low and overlaps with benzophenone n,π^* transition. Since these groups are present in very large quantities in comparison to the formed hydroperoxides, they prevent these functions from absorbing light directly and undergoing photochemical scission. Another reaction mechanism which may be put forward for explaining the decomposition of the PO–OH groups involves the energy transfer from the excited benzophenone triplets to the polymeric hydroperoxides, inducing

Scheme III



their scission, according to Scheme III. Energy transfer from excited aromatic molecules to hydroperoxides has been reported in several systems.[22-25] In polymeric materials, such a mechanism was proposed by Geuskens[26] for the photooxidative degradation of the polystyrene and by Guillet[27] for the photooxidation of an ethylene–propylene copolymer.

The photosensitized decomposition of hydroperoxidic groups on the phosphorus atoms should give rise to P–O$^\bullet$ radicals, from which chain scission proceeds followed by degradation of the macromolecule.

Conclusions

In this paper the photolysis of the poly[bis(4-benzoylphenoxy)phosphazene], BzPOP, in CH_2Cl_2, or CH_2Cl_2 containing variable amounts of CCl_4, THF, or isopropyl alcohol solutions has been investigated. The irradiation of the BzPOP in CH_2Cl_2 or CH_2Cl_2/CCl_4 mixtures leads to degradation of the polymer, while in CH_2Cl_2-containing species which easily supply hydrogen atoms (THF, isopropyl alcohol) cross-linking and gel formation has been found. Flash-photolysis experiments indicate that, unlike poly(phosphazenes) previously investigated, the photoreaction occurs from the first excited triplet state of the benzophenone chromophore. The triplet state gives ketyl radicals by hydrogen abstraction from the solvents. This species and/or the radical of the solvent react with residual P–Cl groups (present in BzPOP owing to uncomplete substitution of the parent $(NPCl_2)_n$ with 4-hydroxybenzophenone) and produce phosphorus macroradicals, from which degradation or cross-linking occurs following (a) the presence or the absence of molecular oxygen in solution and (b) the quantity of ketyl radicals present (high ketyl radical concentration favors, of course, cross-linking and gel formation).

Acknowledgment. We are indebted to the "Progetto Finalizzato per la Chimica Fine e Secondaria" del Consiglio Nazionale delle Ricerche for financial support.

Registry No. O_2, 7782-44-7.

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(21) Following the suggestion of one of the reviewers, we have synthesized a new sample of BzPOP according to the experimental procedure proposed by Allcock (Austin, P. E.; Riding, G. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719). The characterization data for this polymer are similar to those already reported,[11] with the exception of the weight average molecular weight, $\bar{M}_w$, which was found to be 1.3×10^6, roughly 30% less than that of the polymer studied in this work. The elemental analysis of the freshly synthesized polymer showed a chlorine content of 0.7% (1 P–Cl group every 12 repetitive P═N units) as compared with the 1.1% (1 P–Cl group every 8 repetitive phosphazene units) present in the sample used in this work. We examined successively the photochemical behavior of both new and old BzPOP under comparable experimental conditions, and we determined, after 4-h irradiations of methylene chloride solutions of these polymers, a decrease of the viscosimetric flowing time ratios (t/t_0) of 0.88 and 0.78, respectively. This can be interpreted as a reduced probability of the occurrence of reaction 3 in Scheme II owing to the lower unreacted chlorine content in the freshly synthesized BzPOP.
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