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PHOTOCHEMICAL BEHAVIOUR OF POLY(ORGANOPHOSPHAZENES)—PART VIII. FURTHER INVESTIGATIONS ON THE SENSITIZED PHOTOCHEMISTRY OF POLY[BIS(4-ISOPROPYLPHENOXY)PHOSPHAZENE]

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Abstract—The photochemistry of poly[bis(4-isopropylphenoxy)phosphazene] (PIPP) sensitized by hexakis(4-benzoylphenoxy)cyclophosphazene and by poly[bis(4-benzoylphenoxy)phosphazene] was investigated both in solution and in film. Air-equilibrated CH_2Cl_2 solutions of this polymer, also containing the above-mentioned benzophenone-containing phosphazene substrates, were irradiated with light absorbed exclusively by the carbonyl substituent. The irradiation causes a sharp decrease of the viscosity, attributed to chain scission of the PIPP backbone. In this process the solvent plays a key role. On the other hand, no photochemical change was observed for the same pair of molecules in the solid state. X-ray diffraction studies and DSC investigations on PIPP films, doped with benzophenone-substituted cyclo- or poly-phosphazenes, reveal that the lack of photoreactivity is due to phase segregation in these systems.

INTRODUCTION

Research on poly[bis(4-isopropylphenoxy)-phosphazene] (PIPP) has attracted considerable attention in the last ten years due to the outstanding characteristics of this polymer as compared to other poly(organophosphazenes) (POP) of similar structure. Since the earlier studies by Quinn *et al.* on the flame resistance and smoke-evolution properties of this polymer [1], many other investigations have been carried out on its thermal stability [2], thermodynamic [3] and structural [4] properties, chemical [5] and photochemical [6] reactivity, etc.

Very recently, in our Institute we focussed attention on the possibility of peroxidizing photochemically the surface of PIPP films, with the aim of using the resulting hydroperoxides as highly reactive sites for further functionalization studies, e.g. to start grafting of vinyl-like polymers onto the polyphosphazene substrate. Both direct and carbonyl-sensitized photochemistry of PIPP have been exploited [6, 7].

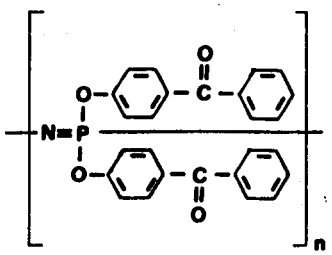
Of particular interest are the results obtained in the benzophenone (Bz) sensitized photochemistry of PIPP films because a remarkable amount of hydroperoxidic groups is introduced in the polyphosphazene film [7]. By irradiating the Bz/PIPP system with u.v. light absorbed only by Bz, a photosensitized hydrogen-abstraction takes place with formation mainly of cumene-like radicals on the polyphosphazene. Reaction of these radicals with molecular oxygen leads to the formation of hydroperoxides on PIPP. These hydroperoxides can be decomposed both thermally and photochemically to produce reactive radicals able to initiate the polymerization of vinyl-like monomers [5].

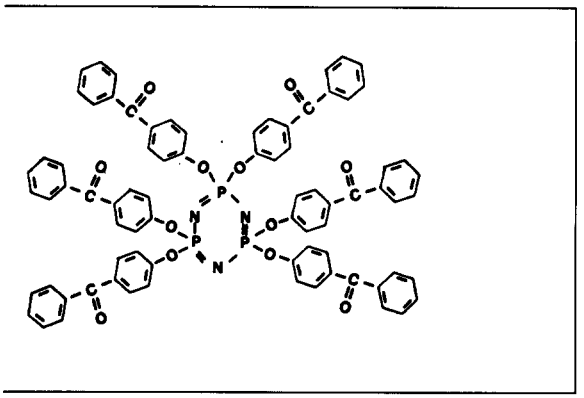
Given the success of this approach to the functionalization of PIPP, we decided to examine the photochemical behaviour of this polymer in the presence of macromolecular systems containing Bz chromophores.

The reactivity of polymeric systems containing photoreactive groups is a lively research area because of possible applications in the field of graphic arts and microelectronics [8]. Moreover, it has been reported that some Bz-containing homopolymers have a higher activity, for u.v. initiated polymerization of acrylic monomers, than the corresponding low molecular weight compounds [9, 10]. Energy migration along the polymer chain was claimed to explain these results.

We chose, as high molecular weight system, poly[bis(4-benzoylphenoxy)phosphazene], $[NP\text{-}(O\text{-}C_6H_4\text{-}CO\text{-}C_6H_5)_2]_n$, (BzPOP), and the corresponding cyclic trimer, hexakis(4-benzoylphenoxy)cyclophosphazene

$[NP\text{-}(O\text{-}C_6H_4\text{-}CO\text{-}C_6H_5)_2]_3$ (BzT), as the model compound of the above polymer.





Previous studies on these compounds [11, 12] demonstrated that Bz groups attached to cyclo- and polyphosphazene skeletons maintain the photochemical characteristics of free Bz. The compounds behave, in an inert solvent such as benzene or carbon tetrachloride, as triplet energy donors able to photosensitize typical triplet reactions [11], while they abstract hydrogen from suitable donors with formation of ketyl radicals [12].

We now report on the photochemistry of PIPP sensitized by BzT and BzPOP, both in solution and in film.

EXPERIMENTAL PROCEDURES

All the solvents were C.Erba RPE analytical grade. When necessary, they were purified by known procedures [13] or dried by refluxing over Na/Bz complex immediately prior to use.

PIPP, $[NP\text{-}(O\text{-}C_6H_4\text{-}4\text{-}C_3H_7iso)_2]_n$, BzT and BzPOP were synthesized and characterized as reported [5, 11, 14].

Films of these polymers for u.v. and i.r. characterization were cast on quartz or NaCl windows by slow evaporation of dichloromethane solutions and drying in vacuum for two days. u.v. Irradiation was performed with a 900 W xenon lamp coupled with filters to eliminate radiation of $\lambda < 340$ nm. u.v. and i.r. measurements were carried out with Perkin–Elmer Spectrophotometers, mod. 320 and 399 respectively. The quenching of BzT phosphorescence in CCl_4 was measured by a Perkin–Elmer MPF 44 A Spectrofluorimeter.

Viscosity measurements were run in a Desreux–Bischoff, suspended level type viscosimeter. X-ray diffraction experiments were carried out with a Siemens D-5000, computer-controlled diffractometer; DSC measurements were performed with a Perkin–Elmer 2 DSC apparatus.

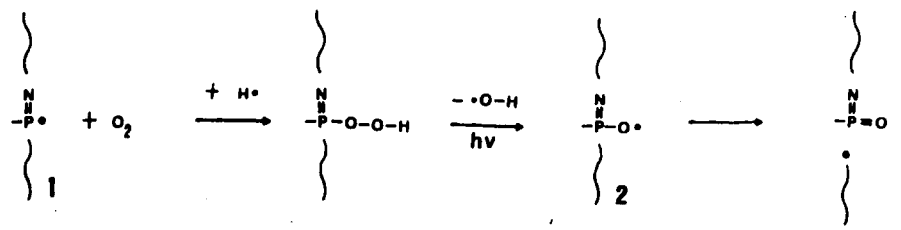
RESULTS AND DISCUSSION

Photochemistry of PIPP in solution, sensitized by BzT or BzPOP

The photochemistry of PIPP, sensitized by BzT and BzPOP, was first studied in solution. Figure 1 shows the absorption spectrum of BzT/PIPP (part A) and BzPOP/PIPP (part B) systems dissolved in CH_2Cl_2 and the optical density variations of these solutions due to irradiation. As can be seen from these spectra, the optical density of the solution increases between 300 and 360 nm during illumination. This result, which is in line with previous findings on the Bz-sensitized photochemistry of PIPP [12], is indicative of the formation LAT's [15] originate from rearrangement of ketyl radicals on the Bz moieties attached to the cyclic or polymeric phosphazene units.

In the presence of oxygen, remarkable degradation of PIPP is observed. The viscosity changes of PIPP solutions irradiated in presence of Bz, BzT and BzPOP (the concentration of the carbonyl compounds was such to ensure equal absorption of the incident light in the three experimental runs) are reported in Fig. 2. The flow-time ratio between irradiated (T) and unirradiated (T_0) solutions of PIPP in CH_2Cl_2 decreases dramatically under illumination, reaching 50% of the original value after five hr illumination.

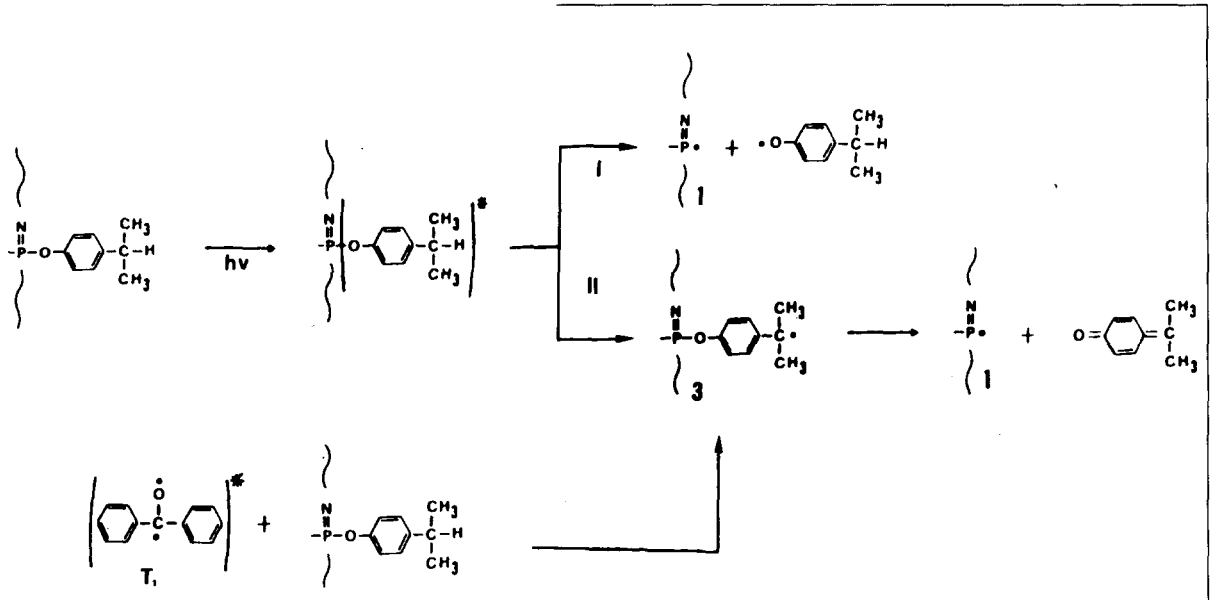
The degradation of polyphosphazene solutions in the presence of oxygen is a general phenomenon in the photochemistry of these macromolecules [7, 12, 16–18]. The degradation arises from the photochemical or thermal decomposition of hydroperoxide groups on the backbone phosphorus, as in the following scheme.



Scheme 1

The macroradical I originates directly from the photochemical homolysis of the phosphorus–oxygen bond in the direct photolysis of PIPP (see path I in Scheme 2) or from the successive reaction of the primary formed radical 3, as in Bz-sensitized photolysis of PIPP [7] (see path II in Scheme 2).

tion of the PIPP solutions in the viscometric experiments was 6.13 g/l, corresponding to 1.95×10^{-2} mol/l in PIPP repeat units, i.e. 3.9×10^{-2} mol/l in tertiary hydrogen of the cumyl moiety. The molarity of CH_2Cl_2 is 16,17, i.e. 500 times that of the isopropyl group tertiary hydrogens, and the oxygen concentra-



Scheme 2

The trend of the curves in Fig. 2 confirms that the Bz groups attached to the cyclo- or poly-phosphazene skeleton maintain, practically to the same extent, the excited state reactivity of free Bz: this result indicates very similar efficiencies of the radical I formation. The generation of this radical exclusively by abstraction of the tertiary hydrogen of the isopropyl group of PIPP by the electronically excited Bz group implies a similar frequency of the encounter between the excited Bz and the tertiary hydrogen of the cumene group. However, this is not plausible because of the mobility of a small molecule, free Bz, and of a macromolecule, BzPOP. Conformational motions of the polyphosphazene chain or migration of the absorbed light energy along the chain, as far as a Bz group in a position favourable for interaction with a cumyl group of PIPP, could explain the similar reactivity of the free Bz and BzPOP. Both these phenomena have been found in polymer solution [19–22]. An alternative explanation can however be proposed on the basis of the following observations.

Previous studies [12] have shown that light absorption by BzPOP in CH_2Cl_2 solutions leads to the formation of the Bz ketyl radical owing to hydrogen abstraction from the solvent. Moreover the phosphorescence of BzT in CCl_4 solutions is quenched by cumene and methylene chloride with rate constants $k_q = 1.4 \times 10^6$ and $2.5 \times 10^5\ M^{-1}\ sec^{-1}$ respectively, while oxygen quenches aromatic ketone triplet at a diffusional rate $k_q = 10^{10}\ M^{-1}\ sec^{-1}$ [23]. Experiments with BzPOP could not be performed because of the low solubility of the polymer in CCl_4. The concentration in air-equilibrated organic solvents is $\sim 2 \times 10^{-3}$ mol/l [24]. In a diffusion-controlled process, the Bz excited triplet will be deactivated mainly ($\sim 85\%$) by the dissolved oxygen and $\sim 15\%$ by CH_2Cl_2: the product $k_q[Q]$ is 2×10^7, 4.2×10^6 and $5.5 \times 10^4\ sec^{-1}$ for Q = oxygen, methylene chloride and hydrogen of isopropyl benzene respectively.

The quenching of Bz triplet by methylene chloride is further favoured by the so-called nearest neighbour static quenching, an effect observable at high quencher concentration. In such a case, at the moment of light absorption, the quencher is already in contact with the light-absorbing molecule and there is no need for mutual diffusion to observe the quenching of the excited species [25, 26].

On the basis of the above considerations, one can conclude that the main photochemical act of the triplet-excited Bz moiety of BzPOP in methylene chloride is hydrogen abstraction from the solvent. The radicals of the solvent so formed can then abstract hydrogen from the PIPP and induce photodegradation of the macromolecule in the presence of oxygen.

In our opinion the proposed mechanism well explains the similar efficiencies of Bz, BzT, in which energy migration cannot occur, and of BzPOP, in inducing PIPP degradation.

The intervention of the CH_2Cl_2 solvent molecules in the photosensitized degradation of PIPP solutions is confirmed by the experiments carried out in benzene. Compared with CH_2Cl_2, benzene is quite an inert solvent towards Bz triplet ($k_q = 10^4$ [27] and

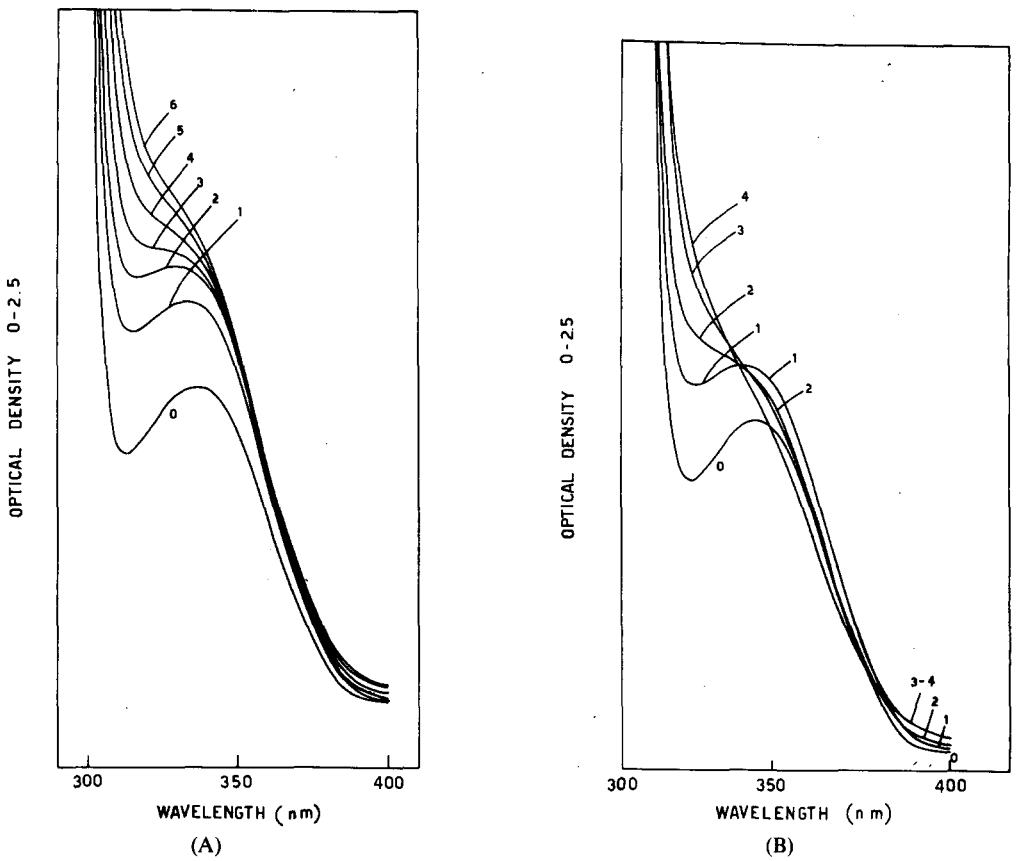


Fig. 1. Optical density variations of BzT/PIPP (part A) and BzPOP/PIPP (part B) systems in CH_2Cl_2 under u.v. irradiation. [PIPP] = 1.95×10^{-2} M, [BzT] = 9.6×10^{-2} M, [BzPOP] = 3.2×10^{-2} M (in repeat units). Part A: 0 ($t = 0$ hr); 1 ($t = 1$ hr); 2 ($t = 2$ hr); 3 ($t = 3$ hr); 4 ($t = 4$ hr); 5 ($t = 5$ hr); 6 ($t = 6$ hr). Part B: 0 ($t = 0$ hr); 1 ($t = 1$ hr); 2 ($t = 2$ hr); 3 ($t = 3$ hr); 4 ($t = 4$ hr).

2.5×10^5 mol^{-1} sec^{-1} for benzene and CH_2Cl_2 respectively). In the presence of Bz or BzT (BzPOP is not soluble in benzene [11]) the formations of LAT's under irradiation was easily observed (see Fig. 3) but, after 2 hr of irradiation, the optical density of the solution does not further increase. The viscosity of the solutions steadily increases with irradiation time and the formation of gel was evident when no further variation of the solution optical density was detected.

Extensive crosslinking and gel formation were observed in CH_2Cl_2 solutions also when the above described irradiations were carried out in an argon atmosphere.

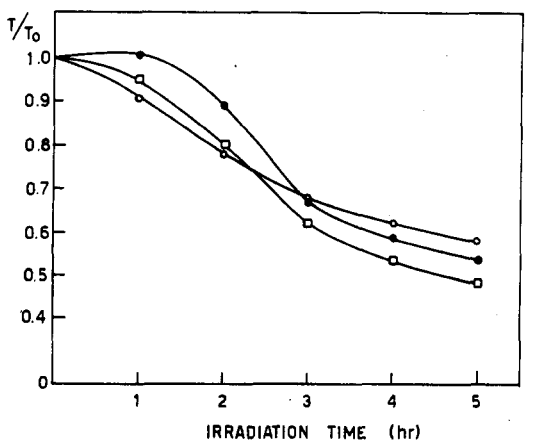


Fig. 2. Relative viscosity variations of PIPP in CH_2Cl_2 during Bz ($C = 2 \times 10^{-2}$ M) (□) BzT ($C = 9.6 \times 10^{-2}$ M (●), and BzPOP ($C = 3.2 \times 10^{-2}$ M in r.u.) (○) sensitized photochemistry.

Photochemistry in film

The Bz sensitized photochemistry of PIPP in film has been reported previously [7]. During photolysis, remarkable crosslinking has been observed accompanied, in the presence of air, by formation of hydroperoxides and carbonyls on the surface of the polymer films. Different behaviour however has been found for the photochemistry of PIPP films containing BzT and BzPOP.

Irradiation of both BzT/PIPP and BzPOP/PIPP systems in film, under experimental conditions similar to those used for the photochemistry of Bz/PIPP systems, shows no occurrence of photochemical reactions, as demonstrated by the absence of changes in the u.v. and i.r. spectra of these films.

It must be stressed that, while the i.r. spectra of the films are fully additive and no new bands due to the interaction of the components are detectable, the u.v. spectrum reported in Fig. 4 shows features greatly different from those of Bz/PIPP films. In fact, the

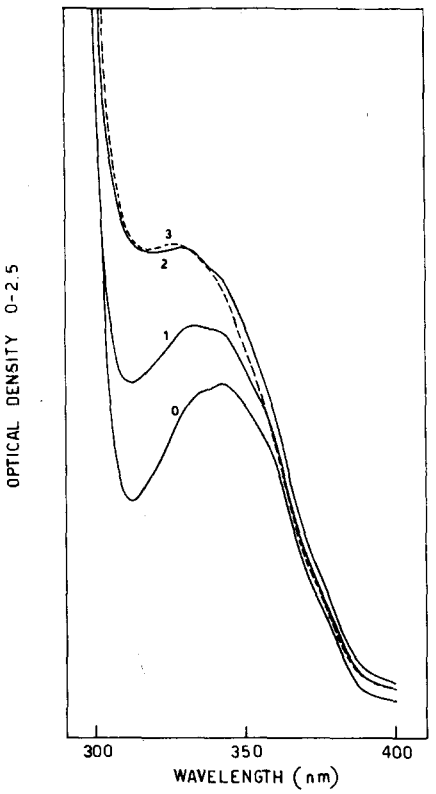


Fig. 3. Optical density variations of PIPP ($C = 1.95 \times 10^{-2}$ M in r.u.) in benzene, during BzT ($C = 9.6 \times 10^{-2}$ M) sensitized photochemistry in air. 0 ($t = 0$ hr); 1 ($t = 1$ hr); 2 ($t = 2$ hr); 3 ($t = 3$ hr).

n–π^* transition of the Bz moieties bonded to the cyclic and polymeric phosphazene substrates, located at 337 nm, disappears; two new bands at 280 and 292 nm, are formed, and a remarkable background absorption is detectable >300 nm. However, the original spectrophotometric characteristics of the BzT/PIPP system are restored by dissolving the film in CH_2Cl_2, as reported in Fig. 4, curve 3, so confirming the i.r. findings, i.e. that no irreversible chemical process occurs in the system. Parallel to this, the

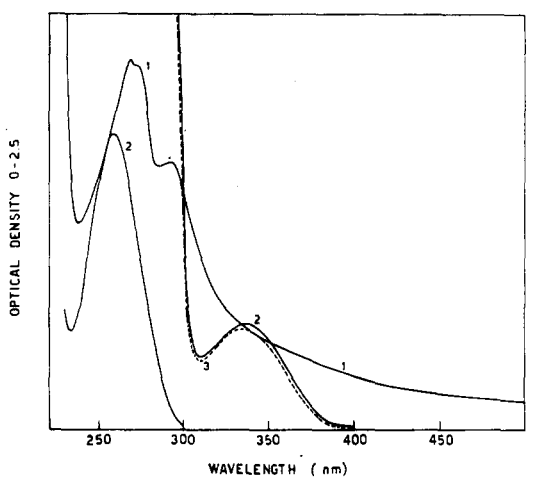


Fig. 4. Absorption spectrum of the BzT/PIPP system in film (1), in solution in CH_2Cl_2 (2), and in CH_2Cl_2 solution (3) obtained by dissolving in already cast film of this pair.

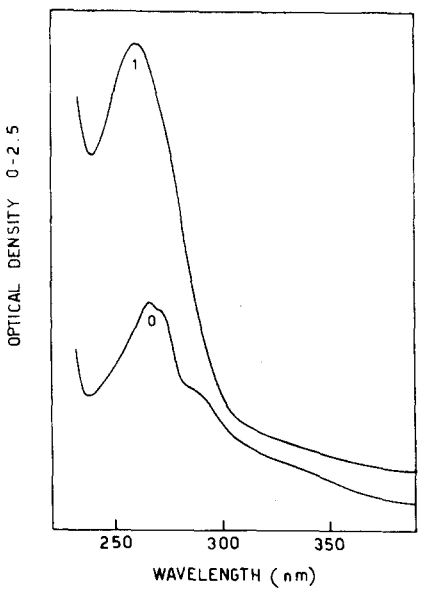


Fig. 5. Optical density variations of a film of BzT/PIPP, previously swollen in CCl_4, 0 ($t = 0$ hr); 1 ($t = 4$ hr).

original reactivity of BzT/PIPP and BzPOP/PIPP system is completely restored by dissolution of the films in CH_2Cl_2. Photochemical reactivity is also observed if the doped PIPP films are swollen with an inert solvent, e.g. CCl_4.

This last result is reported in Fig. 5, where the initial u.v. absorption of the BzT/PIPP films has been found to increase considerably after 4 hr irradiation when films have been swollen for few hours in CCl_4 prior to photochemistry, and in the i.r. spectrum of the same system (see Fig. 6) where formation of hydroperoxides (3700–3200 cm^{-1}) and carbonyls (1800–1700 cm^{-1}) is observed together with simultaneous disappearance of PIPP C—H (3000–2800 cm^{-1}) and Bz C=O (1690 cm^{-1}) bonds. Completely similar behaviour has been found also for the BzPOP/PIPP system.

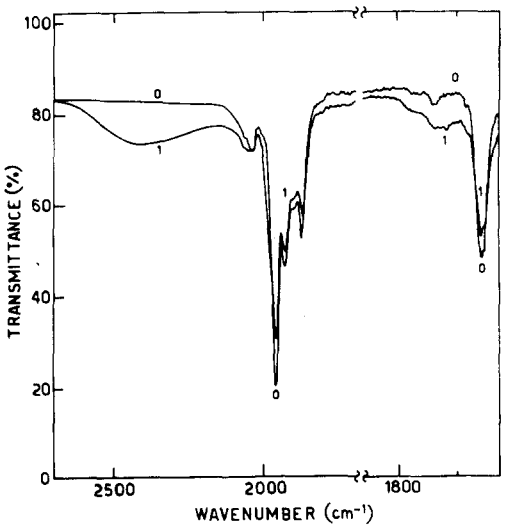


Fig. 6. i.r. Transmittance variations of PIPP films, previously swollen in CCl_4, during BzT sensitized photochemistry. 0 ($t = 0$ hr); 1 ($t = 4$ hr).

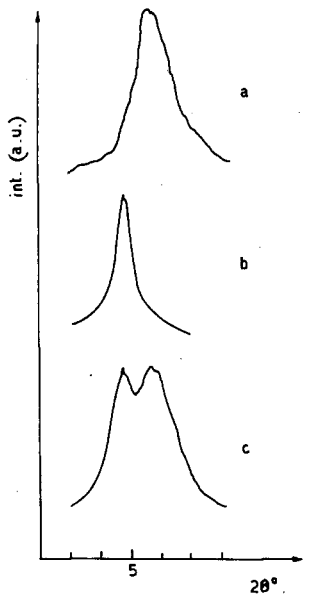


Fig. 7. X-ray diffraction spectra of cast films of PIPP (a), BzPOP (b) and 50% mixtures.

These findings on the photochemical behaviour of the BzT/PIPP and BzPOP/PIPP systems in films, may be interpreted on the basis of a lack of contact between Bz-containing cyclic or polymeric phosphazene systems in the solid state and PIPP, due to complete separation of the two crystalline phases. This separation would prevent the molecules from photoreacting in the same way as under homogeneous conditions. To support this interpretation, X-ray diffraction studies and DSC investigation have been carried out on the BzPOP/PIPP films.

*X-ray diffraction studies and DSC investigations of BzPOP are under way and will be reported elsewhere.

X-ray diffraction and DSC investigations

X-ray diffraction experiments were performed on cast films of BzPOP and PIPP and on films formed from 50% mixtures of these polymers. Figure 7 shows the spectra of the low 2θ angle region. A single peak for both pure polymers and two peaks for the mixture are observed.

Crystalline phases of PIPP have been extensively studied [4], while for BzPOP no structural data have been reported†. We were able to interpret the peaks in Fig. 7 (part A and B) in terms of equatorial reflections. The mixture spectrum (Fig. 7, part C) maps exactly the overlap of PIPP and BzPOP spectra. This fact is indicative of complete phase segregation, at least for the crystalline part of the polymers.

DSC examination of the same samples confirms these conclusions. The thermal behaviour of BzPOP* is characterized by a glass transition ($T_g = 50°$) and a melting ($T_m = 176°$) in the first heating cycle: quenching and subsequent DSC scan show a crystallization at $\sim 110°$. The thermal transition study of PIPP has been recently reported [3], viz. a glass transition ($T_g = 0°$), a phase transition ($T_a = 100°$), the mesophase transformation ($T_b = 140°$) and melting ($> 140°$). In Fig. 8, the DSC scan of the polymer mixture is shown. The glass transition and melting of BzPOP occur at the same temperatures as found for homopolymer (50° and 176° respectively). The behaviour of PIPP is complex, so that it is difficult to interpret completely the DSC run in the range of 90–150°, due to peak overlap. However the invariance of the behaviour of BzPOP in the mixture BzPOP/PIPP agrees with X-ray diffraction experiments, giving a strong indication of incompatibility of the two polymers.

CONCLUSIONS

According to the above reported findings, the photochemistry of PIPP, sensitized by Bz-containing

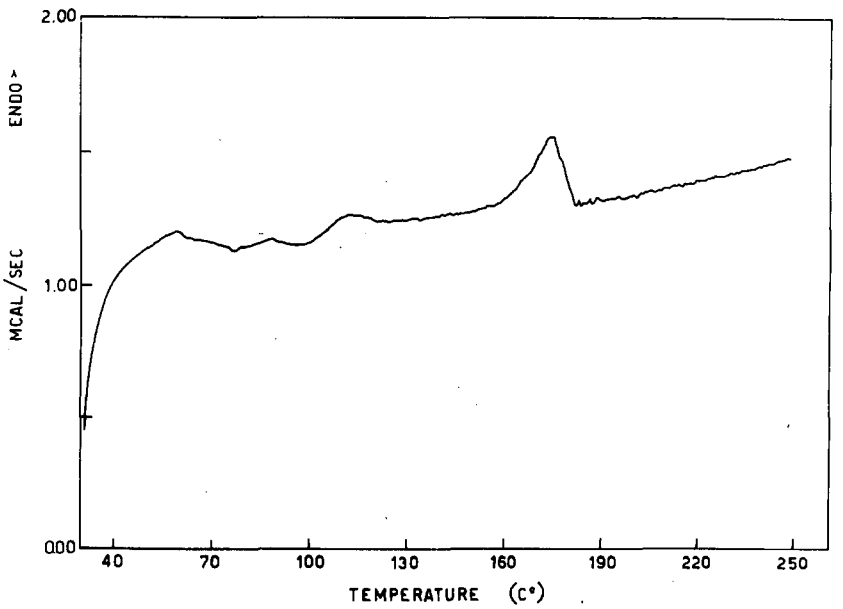


Fig. 8

cyclo- and polyphosphazenes, can take place only in homogeneous solution, while the same phenomena could not be observed in films. So the attempt to improve the surface functionalization of PIPP films by using Bz attached to the polyphosphazene skeleton as photosensitizer, failed.

In fact, X-ray diffraction studies and DSC measurements indicate that the intermolecular hydrogen abstraction reaction from isopropylic groups by excited Bz moieties cannot take place in films due to complete phase segregation of BzT or BzPOP and PIPP.

If it were possible to compatibilize Bz-containing phosphazene substrates with PIPP in the solid state, probably the photoreactivity of these systems would reappear. One possible way to achieve this aim might be a drastic decrease of molecular weight of both BzPOP and PIPP to be mixed. This could possibly be done by using low molecular weight polydichlorophosphazene in the substitution reaction with the sodium salts of 4-hydroxybenzophenone and 4-isopropylphenol.

The behaviour under irradiation of BzPOP/PIPP mixtures in the solid state suggests that photochemical studies can be valuable for checking miscibility and compatibilization of polymeric substrates. Research in this direction is under way and will be reported in a later paper.

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