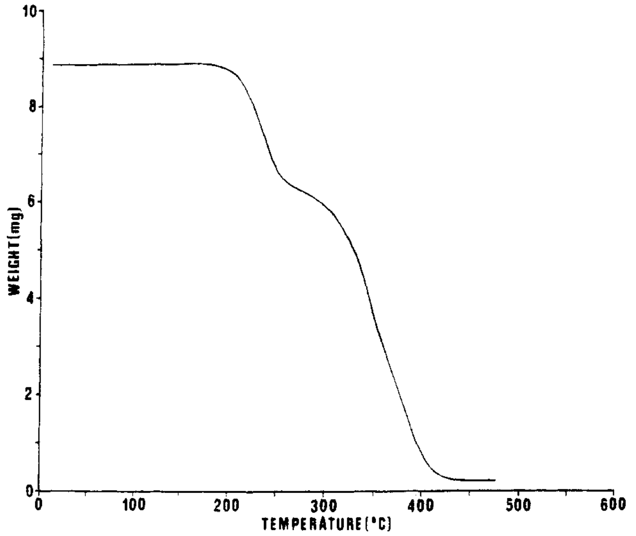

Figure 1. Typical TGA scan for styrene–(α-ethoxyvinyl)pentafluorocyclotriphosphazene copolymers.

pared to (α-methylvinyl)phosphazene[3] copolymers.

In summary, we have developed a new series of novel copolymers involving a vinylphosphazene and traditional organic monomers. Significant alterations of copolymerization behavior of vinylphosphazene monomers may be affected by the nature of the substituent on the olefinic center. The nature of the effect of the phosphazene on the vinyl ether center in I has been elucidated by a consideration of the Q and e values for this system.

Acknowledgment. We thank Dr. G. A. Stahl of Phillips Petroleum Co. for a copy of the Mortimer–Tidwell program and D. E. Brown for adapting it to our computer. This work was supported, in part, by the Office of Naval Research.

Registry No. $N_3P_3F_5C(OC_2H_5){=}CH_2$, 80297-67-2; $(N_3P_3F_5(OC_2H_5){=}CH_2)\cdot$(styrene) (copolymer), 80297-68-3; $(N_3P_3F_5C(OC_2H_5){=}CH_2)\cdot$(MMA) (copolymer), 99798-90-0; styrene, 100-42-5.

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Photochemical Behavior of Poly(organophosphazenes). 4. Photosensitization Properties of Poly[bis(4-benzoylphenoxy)phosphazene]

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ABSTRACT: The reaction between poly[dichlorophosphazene] $(NPCl_2)_n$ and 4-hydroxybenzophenone leads to the formation of poly[bis(4-benzoylphenoxy)phosphazene] $[NP(OC_6H_4COC_6H_5)_2]_n$. This polymer proved to be an efficient triplet-state energy donor in heterogeneous-phase photosensitization experiments since the two benzophenone moieties supported at the phosphorus atoms of the phosphazene chain are able to transfer the absorbed energy to suitable acceptors, so inducing their photoreactions. The polymer may be recovered from the reaction mixture simply by filtration and reused for successive experiments.

Introduction

The possibility of anchoring metallic or metallorganic catalysts,[1] synthetic reagents,[2] enzymes,[3] etc. on polymeric substrates is a subject of current research. It has been found, in fact, that these molecules still maintain their catalytic activity when supported on polymeric matrices,[4] offering, on the other side, significant advantages in the separation and purification procedures of reaction products.[5]

In the last two decades, a great deal of work has been done also in supporting organic photosensitizers on insoluble polymeric substrates.

In 1973 Neckers and Blossey[6] reported the synthesis of polystyrene supporting Rose Bengal, a dye largely used in the photosensitized generation of singlet oxygen. Successively, two other molecules have been considered as possible polymer-supported photosensitizers, i.e., aceto-

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phenone and benzophenone;[7,8] the reasons for this choice are[9] (i) the favorable absorption spectra of these molecules, (ii) the energy of their lower excited triplet state $E^T = 73$ and 65.5 kcal/mol, respectively, and (iii) the high efficiency with which this state can be populated by light absorption, via intersystem crossing from the corresponding singlet.

However, it was found that the photosensitizers of the above class supported on vinylic matrices (polystyrene or styrene–divinylbenzene copolymers) exhibit a variable degree of inconvenience[8] due to (a) photodecarboxylation reactions, and (b) intramolecular hydrogen abstractions from the polymeric organic backbone. These processes strongly depress the photosensitization efficiency of the polymeric materials and make them of little use for routine photosensitization experiments.[8,10]

To overcome the above mentioned problems, fluorinated vinyl polymers as support for photosensitizers have been synthesized.[11] However, the synthesis of these materials requires a rather complicated, time-consuming, multistep procedure, and this fact seems to be a serious drawback to their practical use.

To circumvent both the loss of photosensitizing properties of the carbonylic groups in vinylbenzophenone polymers and copolymers and the long, noneconomic preparation of poly[(fluorovinyl)benzophenone], we have adopted a different synthetic approach. We used as polymeric support for the photosensitizer the inorganic backbone of a class of macromolecules not previously considered in this field: the poly(organophosphazenes). The skeleton of these polymers, formed by alternate phosphorus and nitrogen atoms, is completely inorganic in nature: this fact makes impossible any intramolecular hydrogen abstraction from the chain induced by light absorption.

In this paper we report the synthesis of a novel phosphazene-supported benzophenone derivative, poly[bis(4-benzoylphenoxy)phosphazene] (BzPOP) $[NP(OC_6H_4COC_6H_5)_2]_n$, and investigate its characteristics as a triplet energy donor.

Experimental Section

The solvents used for the preparation and purification procedures were all Carlo Erba analytical grade. Benzene, triethylamine (TEA), and 2-methyltetrahydrofuran, anhydrified by refluxing on metallic sodium, barium oxide, and $NaBH_4$, respectively, were distilled immediately before use. 4-Hydroxybenzophenone was an Aldrich product and was purified by vacuum sublimation, followed by successive precipitations from tetrahydrofuran/n-heptane mixtures.

Weight-average molecular weights ($\bar{M}_w$) of BzPOP were determined by a Sophica spectrogoniodiffusometer and by a Waters GPC apparatus. T_g determinations have been done with a Perkin-Elmer instrument Model DSC 2.

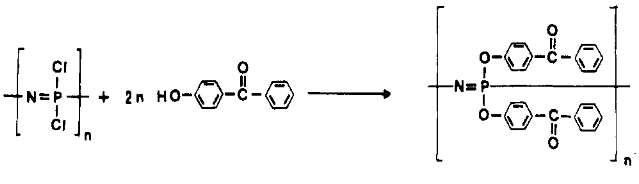
UV absorption spectra have been measured with a Perkin-Elmer 320 spectrophotometer. Phosphorescence emission was determined with a Perkin-Elmer MPF 44 spectrophotofluorimeter equipped with an accessory for measurements at 77 K. IR spectra were obtained with a Perkin-Elmer 399 spectrophotometer. The progress of the photosensitized reactions was followed by a Perkin-Elmer Sigma 3 gas chromatograph (column 2 $^1/_2$% SE 30 on chromosorb G).

The photosensitization experiments were performed with an Hanovia HBO 150-W high-pressure mercury lamp equipped with a cut-off filter that transmits >340-nm light.

Synthesis and Characterization of Poly[bis(4-benzoylphenoxy)phosphazene]

General Considerations. Poly(organophosphazenes) are a class of macromolecules whose main chain is formed by a sequence of P=N units, with the phosphorus atoms bearing two side substituent groups.[12] The structure of these polymers may be expressed by the formula $-[N{=}PR_2]_n-$, where the polymerization degree n can be very high (10 000–15 000) and R can be varied over a large number of organic molecules.

The synthesis of poly(organophosphazenes) is always achieved by nucleophilic substitution of the chlorine atoms of the poly[dichlorophosphazene] $(NPCl_2)_n$ precursor.[13] Correspondingly, the synthesis of BzPOP has been obtained by reacting poly[dichlorophosphazene] with 4-hydroxybenzophenone in the presence of TEA, according to the following reaction scheme:



Synthesis of Poly[bis(4-benzoylphenoxy)phosphazene]. All the preparative steps were performed under flux of dry nitrogen, using rigorously anhydrous solvents; moreover, dark conditions were also adopted during the synthesis in order to prevent photoreactions of the benzophenone groups with the solvents used for the preparation and the purification.

$(NPCl_2)_n$ (6 g, 5.17×10^{-2} mol, in repetitive units) dissolved in 100 mL of benzene was placed in a 1000-mL three-necked round-bottomed flask equipped with a mechanical stirrer and an efficient condenser. To this solution was added dropwise 41 g (0.207 mol) of 4-hydroxybenzophenone, dissolved in 150 mL of benzene plus 27 g of TEA, at room temperature. The reaction mixture was stirred for 24 h at room temperature and successively refluxed for 144 h. The obtained polymer was precipitated in an excess of n-heptane to isolate a white powder that does not dissolve in benzene. The polymer is slightly soluble in tetrahydrofuran (THF) and very soluble in dichloromethane (CH_2Cl_2). To eliminate the excess of unreacted 4-hydroxybenzophenone, the obtained polymer was purified by three successive dissolutions in CH_2Cl_2 and precipitation in n-heptane, followed by a Soxhlet extraction with benzene for 1 week. The triethylammonium salt formed during the reaction was eliminated by vigorous shaking of a suspension of polymer in water up to the negative test for chloride ions with $AgNO_3$.

A total of 15 g of polymer was obtained (theoretical, 21.95 g), with a yield of 63.3%. Elemental analysis (calculated values in parentheses) is as follows: C, 70.67 (71.03); H, 4.12 (4.10); N, 3.36 (3.18); Cl, 1.18 (0).

The chemicophysical characterization data of the synthesized polymer are the following: $T_g = 48$ °C; intrinsic viscosity, 1.15 dL/g in CH_2Cl_2; weight-average molecular weight $\bar{M}_w = 1.9 \times 10.^6$

Spectroscopic Considerations. The UV absorption spectrum of BzPOP is reported in Figure 1 together with the spectrum of hexakis(4-benzoylphenoxy)cyclotriphosphazene $[NP(OC_6H_4COC_6H_5)_2]_3$,[14] which can be considered as a cyclic oligomeric form of the polymer.[15] As already noted for other poly(organophosphazenes),[16,17] the high polymeric linear phosphazenes and the corresponding cyclic trimers have almost identical absorption spectra, which can be satisfactorily explained in terms of the absorption of the corresponding free organic substituent (in this case, the 4-hydroxybenzophenone). Two bands are clearly distinguishable in the absorption spectrum of the phosphazene-bonded benzophenone: the low energy one ($\lambda_{max} = 338$ nm, $\epsilon = 340^{18}$) is attributable to the n, π^* transition of the benzophenone carbonyl group. The high energy band ($\lambda_{max} = 258$ nm, $\epsilon = 32\,000$) is related to the

Table I

type photosensitized reactn	% prod. at photostationary state with free benzophenone	% prod. at photostationary state with phosphazene-supported benzophenone
trans → cis isomerization of stilbene	45	40
trans → cis isomerization of piperylene	55	57
cycloaddition of indene	*a*	*a*
valence isomerization of norbornardiene to quadricyclane	85	80

[a] Photoreaction has been observed but not quantitatively determined.

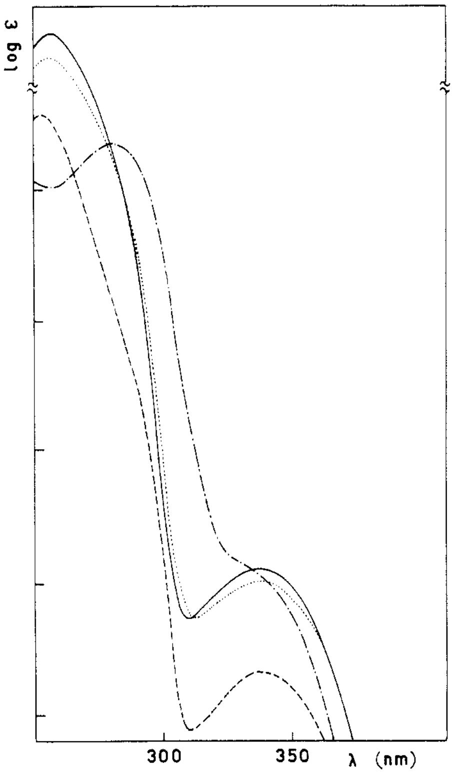


Figure 1. Absorption spectra of hexakis(4-benzoylphenoxy)cyclophosphazene (—), poly [bis(4-benzoylphenoxy)phosphazene] (···), 4-hydroxybenzophenone (–·–·–), and benzophenone (- - -) in methylene chloride.

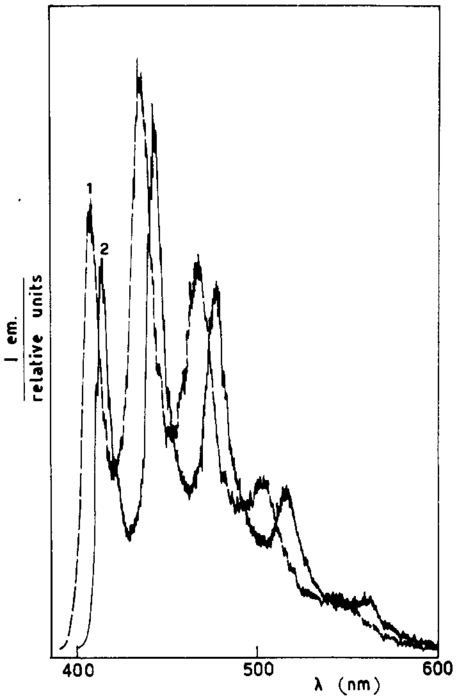


Figure 2. Phosphorescence emission spectra of poly[bis(4-benzoylphenoxy)phosphazene] in 2-MeTHF/methylene chloride (90/10) glass at 77 K.

π, π* absorption band of the benzophenone. In both bands, extinction coefficients of the polymer are slightly lower than that of the trimer. This fact can be attributed to a defective substitution of the chlorine atoms of the starting poly[dichlorophosphazene] by 4-hydroxybenzophenone, as revealed by elemental analysis data. In fact, in BzPOP with a chlorine content $\simeq 1.2\%$, there is, on average, one phosphorus atom bearing a chlorine every eighth fully substituted phosphorus atom. In Figure 1 are also reported the absorption spectra of the free chromophores, i.e., benzophenone and 4-hydroxybenzophenone. A comparison of the 4-hydroxybenzophenone spectrum with that of the polymer-bonded benzophenone shows strong differences in the energy of the π, π* transition, the energy of the *n*, π* being practically the same in the two molecular species. The π, π* band of 4-hydroxybenzophenone (λ_{max} 280 nm) is red-shifted with respect to the same transition of the phosphazene-bonded benzophenone (λ_{max} 258 nm). This phenomenon was already observed in the case of phenoxy-, β-naphthoxy-, and anilino-substituted polyphosphazenes[17,19] and was attributed to a nonplanarity of the aromatic π system and the lone pair(s) of the heteroatom bonded to the backbone phosphorus. The resulting lower conjugation of the *n* lone pair(s) with the π electrons of the aromatic system causes the hypsochromic shift in the spectrum of the phosphazene-bonded chromophore with respect to that of the free molecule. In agreement with this hypothesis, the spectrum of BzPOP and that of the corresponding cyclic trimer are, in fact, very similar to that of the free benzophenone unsubstituted (λ_{max} 253 nm in CH_2Cl_2). The benzophenonic nature of the excited states of BzPOP is confirmed also by the phosphorescence emission spectra in 2-MeTHF/CH_2Cl_2 glass, reported in Figure 2 together with that of benzophenone for comparison purposes. The spectrum of the polymer shows the same vibrational progression of 1600 cm^{-1}, the typical carbonyl stretching frequency of benzophenone. However, the 0–0 band of the polymer has an energy ($E_{0\text{-}0}$ = 24 050 cm^{-1}) slightly lower than that of the free benzophenone ($E_{0\text{-}0}$ = 24 500 cm^{-1}).

Photosensitization Experiments and Photochemistry. On the basis of the above mentioned spectroscopic characteristics of BzPOP, one may expect very similar properties of the excited state of both the free and the phosphazene-supported benzophenone chromophore. This was verified, in particular, for some photochemical reactions sensitized by triplet–triplet energy transfer in which BzPOP acts as a triplet energy donor. The reactions are (i) the trans $\rightleftarrows$ cis isomerization of 1,3-pentadienes (piperylenes) and stilbene, (ii) the dimerization of indene, and, (iii) the valence isomerization of norbornadiene to

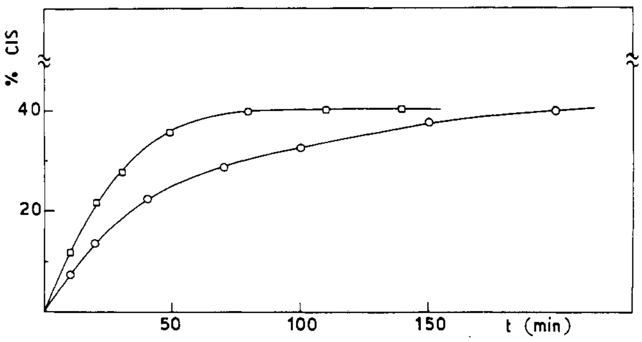


Figure 3. Rate of photostationary state attainment for the sensitized trans ⇄ cis isomerization of stilbene: (□) freshly prepared suspension of BzPOP; (○) suspension subjected to 20 irradiation cycles (see text).

quadricyclane. Some of the above reactions may find useful applications in organic synthesis (*cis*-stilbene is less stable than the trans isomer, and, at room temperature, the mixture of the two isomers contains 96% trans) or in chemical storage of solar energy (the conversion of norbornadiene to quadricyclane).[20]

As reported in Table I, the photostationary compositions obtained by irradiating free and polymer-bonded benzophenone are practically the same, confirming that the excited-state properties of the benzophenone moiety supported on the phosphazene skeleton are very similar to those of the free benzophenone.

Some experiments were carried out to verify the possibility of prolonged use of BzPOP as a photosensitizer. A benzene solution of *trans*-stilbene containing suspended BzPOP was irradiated up to the photostationary composition attainment (1-h irradiation). After that, the polymer was filtered, added to another solution of *trans*-stilbene, and subjected again to irradiation. After 20 of the above-mentioned cycles, the same photostationary composition of the first experiment was reached, but the rate of the process is reduced to 60% of the initial value, as shown in Figure 3. A spectrophotometric analysis of the final reaction mixture gave evidence that the loss of photosensitizing ability of BzPOP is not due to the release of the benzophenone moieties in solution owing to an homolytic scission of P–O or O–C bonds of the $[NP(OC_6H_4COC_6H_5)_2]_n$. In fact, no appreciable amount of free benzophenone or 4-hydroxybenzophenone was found in the irradiated suspensions. On the other hand, some chemical reactions did occur in the polymer, since the irradiated material, recovered by filtration, does not dissolve in CH_2Cl_2 as does the starting polymer.

To identify the photoreactions responsible for the loss of the photosensitizing properties, a film of BzPOP was deposited on a NaCl plate and irradiated for 90 h in air. The film was cast from a CH_2Cl_2 solutions of the polymer and pumped at 10^{-4} torr for 2 days in order to eliminate residual solvent molecules.

The main features of the IR spectrum of the irradiated polymer film are an increase of absorption in the region of 1700–1800 and 3400–3500 cm^{-1} together with a decrease of the band at 1660 cm^{-1}.

The increase of 1700–1800 cm^{-1}, already observed for the irradiation in air of other polymers, in particular polystyrene,[21] is related to the formation of carbonyl groups, whose nature is not fully identified so far, which should be formed in a photooxidative cleavage of the aromatic rings. The decrease of the strong absorption band at 1660 cm^{-1} (attributed to the stretching of the benzophenone carbonyl group) and the very feeble increase of the absorption in the region 3400–3500 cm^{-1} may be reasonably ascribed to the formation of benzpinacol moieties, which implies the disappearance of the carbonylic functions and the concurrent formation of hydroxylic groups.

It seems reasonable to conclude that the formation of benzpinacol, observed in the polymer film, may occur in the suspensions of the polymer too, and it is responsible for the cross-linking processes and the loss of photosensitizing properties of BzPOP.

Though in BzPOP vinyl hydrogens are absent, a photoreduction process of carbonylic functions causes, as in poly[vinylbenzophenone] (PVB), a loss of photosensitizing ability. However the mechanisms of the two processes are completely different, and they should occur with different rates. In PVB, the intermolecular (or intramolecular) hydrogen abstraction of the tertiary hydrogen of the vinyl chain leads to the reduction of the carbonyl. In BzPOP, the photoreduction is likely to occur through a self-quenching reaction of the benzophenone triplet and hydrogen abstraction from benzophenone ground state. This phenomenon has already been observed in concentrated solution of benzophenone dissolved either in benzene or in carbon tetrachloride; moreover the formation of benzpinacol occurs by irradiation of molten, degassed neat benzophenone.[22]

The quenching rate constant for benzophenone n, π^* triplet by isopropylbenzene (a model compound for the tertiary hydrogens of PVB) is $5 \times 10^5\ M^{-1}\ s^{-1}$,[9] while k_q for the quenching process $^3\phi_2(C{=}O) + \phi_2(C{=}O)$ is, in benzene, $1.5 \times 10^5\ M^{-1}\ s^{-1}$.[22] In the hypothesis that in a polymeric system the ratio of the k_q for the above-mentioned processes remains unaltered, one should expect a loss of photosensitizing properties 3–4 times lower in BzPOP with respect to that of PVB. An interaction between electronically excited benzophenone and benzophenone in the ground state occurs in solutions of PVB.[23] It has been shown that in poly(organophosphazenes) substituted with arylamino and aryloxy groups similar interactions occur between an excited chromophore and a neighboring pendant group in the ground state.[24-26] So, it is a reasonable hypothesis that the process occurring in concentrated benzophenone solutions occurs also in BzPOP films and suspensions.

Another possible source of cross-linking processes is probably connected to the presence of residual unreacted P–Cl bonds in the benzophenone-supporting phosphazene chain. This presence is intimately related to the substitution process of poly[dichlorophosphazene] by 4-hydroxybenzophenone. Since such processes are never driven to completeness, even if forcing reaction conditions[27] or phase-transfer catalysts[28] are used during the reaction, some unsubstituted chlorine atoms are still present in the final substituted phosphazene polymer. These residual P–Cl bonds, present in a very low amount, do not absorb light in our experimental conditions, since P–Cl chromophore in phosphazene materials is reported to absorb appreciably only at wavelengths lower than 240–250 nm;[29] these groups therefore are not suspected to participate in the photochemical process. Although inert from a photochemical point of view, these groups are still very reactive toward nucleophiles (especially water) and may participate in further substitution processes or in some secondary radical reactions during light irradiation, which might finally result in remarkable changes of the thermal, mechanical, and photochemical properties of the polymer.

Conclusions

In this paper we report the synthesis, the characterization, and the photoreactivity of a novel type of polymer-supported benzophenone: poly[bis(4-benzoylphenoxy)-

phosphazene] $[NP(OC_6H_4COC_6H_5)_2]_n$. This polymer, which has practically the same excited-state properties as the free benzophenone, is able to transfer, in the heterogeneous phase, triplet energy to several substrates, so inducing their photoreaction. During the irradiation, the polymer undergoes a progressive loss of photosensitizing efficiency, which is probably due to the formation of benzpinacol accompanied by cross-linking processes. However, on the basis of literature kinetic data, it is expected that the loss of photosensitizing ability of this polymer due to irradiation is lower than that of the homologous vinyl derivatives. The ease of preparation of polyphosphazene-bonded benzophenone, compared with the multistep procedure devised to synthesize fluorinated PVB, the high molecular weight normally obtained for phosphazene polymers ($\geq 10^6$),[30] which allows the preparation of macromolecules bearing a very large number of absorbing groups, and the stability of phosphazene chains toward free radical induced skeleton scissions, higher than that of carbon-backboned polymers,[29] are all factors indicative of the substantial improvement obtained with BzPOP.

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

Registry No. 1,3-Pentadiene, 504-60-9; stilbene, 588-59-0; indene, 95-13-6; norbornadiene, 121-46-0; quadricyclane, 278-06-8.

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