

Grafting Reactions onto Poly(organophosphazenes). IV. Light-Induced Graft Copolymerization of Organic Polymers Containing Free Acid or Basic Functionalities onto Poly[bis(4-benzylphenoxy)phosphazene]

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SYNOPSIS

The light-induced graft copolymerization of acrylic acid, methacrylic acid, and 4-vinylpyridine onto poly[bis(4-benzylphenoxy)phosphazene] films to prepare new grafted phosphazene copolymers containing acid and basic functionalities is reported. The process was carried out in monomer/methanol mixtures in the presence of benzophenone or benzoin ethyl ether as photosensitizers by selective excitation of these last species. The yield of the grafting processes was evaluated as a function of the monomer concentration in the reaction medium, type of photoinitiator, and characteristics of the grafted organic monomers. The acid functions inserted in poly[bis(4-benzylphenoxy)phosphazene]-*g*-poly(meth)acrylic acid grafted copolymers, and the basic groups of the poly[bis(4-benzylphenoxy)phosphazene]-*g*-poly-4-vinylpyridine substrates were allowed to interact with basic and acid dyes, respectively, to form permanently colored polymeric films. The photoactivity of these films as substrates for the photosensitized production of singlet oxygen was tested. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The grafting of organic (or inorganic) macromolecules onto poly(organophosphazenes) (POPs) is one of the most intriguing topics in recent phosphazene research¹⁻¹⁵ because it provides an easy and elegant method of modifying both the bulk^{1-4,15} and the surface^{9,11,12,15} properties of phosphazene materials. Correspondingly, the chemical and physical characteristics of the grafted organics are also greatly changed. For example, the flame resistance of polystyrene (PS) is claimed to be considerably improved by grafting this macromolecule onto polydichlorophosphazene¹ or poly[bis(4-isopropylphenoxy)_x(2,2',2''-trifluoroethoxy)_{2-x}phosphazene] copolymers.^{2,3} The biocompatibility of poly[bis(phenoxy)phosphazene] (PPP) and poly[bis(2,2',2''-trifluoro-

ethoxy)phosphazene] (PTFEP) is remarkably enhanced by the surface grafting of hydrophilic polymers induced by γ -rays¹¹ or chemical¹⁶ treatment. The surface hydrophilicity of poly[bis(4-isopropylphenoxy)phosphazene] (PIPP), poly[bis(4-secbutylphenoxy)phosphazene] (PsBPP), poly[bis(4-benzylphenoxy)phosphazene] (PBPP), and PTFEP, is dramatically increased by grafting poly-*N,N'*-dimethylacrylamide (PNNDMAA) onto films of these materials.¹⁵

In the frame of this work, a relatively new¹⁷ phosphazene material was considered, that is PBPP. This polymer shows interesting thermal,^{18,19} photooxidative,¹⁸ and photochemical²⁰ characteristics due to the presence of diphenylmethane residues attached to the inorganic phosphazene skeleton. These groups can be converted easily into benzophenone moieties both by chemical²¹ and photochemical^{18,20} oxidation, thus considerably enhancing the photochemical reactivity of the modified polymer.²²⁻²⁴ Moreover,

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PBPP shows relatively good mechanical and thermal properties and a moderate degree of crystallinity¹⁹ that make it very suitable for undergoing photoinduced modifications.²⁵ The secondary hydrogen present in the methylene group of the side benzylphenoxy substituent can be easily removed with the formation of reactive radicals able to efficiently interact with organic vinyl monomers and induce their grafting reactions onto the polyphosphazene matrix.^{14,15}

Therefore PBPP is a good candidate for grafting processes, and in this article we report the light-induced grafting reactions of acrylic acid (AAM), methacrylic acid (MAAM), and 4-vinylpyridine (4-VPM) monomers onto PBPP films carried out in the presence of benzophenone (BP) or benzoin ethyl ether (BEE) as photoinitiators, selectively excited with a light of $\lambda > 350$ nm. The resulting graft copolymers are very interesting materials that contain side organic branches emerging from the PBPP matrix with free, reactive, acid, or basic functionalities, susceptible of undergoing further derivatization reactions. These groups can be reacted with basic or acid dyes, respectively, thus anchoring the dyes onto the grafted phosphazene copolymers to produce permanently colored phosphazene films with interesting photochemical responses.²⁶⁻²⁸ The new materials formed in this way can be exploited, for instance, in the heterogeneous-phase generation of singlet oxygen, with the possible practical application of the process in continuous reactor systems.

EXPERIMENTAL

Materials

PBPP, $[\text{NP}(\text{O}-\text{C}_6\text{H}_4-\text{CH}_2-\text{C}_6\text{H}_5)_2]_n$, was prepared and purified according to the literature.^{17,20} AAM, and MAAM, and 4-VPM (Aldrich) were purified from the stabilizers by vacuum distillation. BP and BEE, rose bengal (RB), erythrosine B, crystal violet, toluidine blue, methylene blue (MB), phenosafranin, and thionin (Aldrich) were used as received. All solvents were C. Erba analytical grade products and were purified or dried according to standard procedures²⁹ when necessary.

Equipment and Characterization Procedures

UV spectra were obtained with a Perkin-Elmer spectrophotometer model 322. Phosphorescence quenching experiments were run with a Perkin-Elmer spectrofluorimeter model MPF 44. IR charac-

terization was performed with a Perkin-Elmer IR spectrophotometer model 399.

The grafting process was carried out by irradiation with a high pressure mercury lamp HBO 150 W coupled with a cutoff filter (350 nm). The experiments with the colored grafted phosphazene copolymers for the generation of singlet oxygen were performed with the same equipment, using a Bausch & Lomb high-intensity monochromator.

Grafting Procedures

Films of PBPP deposited on glass slides, partially swollen in monomer/methanol mixtures containing free BP (concn = $2.5 \times 10^{-2} M$) or BEE (concn = $2.1 \times 10^{-2} M$), were degassed to 10^{-6} torr by several freeze-pump-thaw cycles and irradiated with a light of $\lambda > 350$ nm, thus selectively exciting the photosensitizer.^{12,15} The grafted copolymers obtained were thoroughly washed with methanol to eliminate the excess of monomer, the homopolymer formed, and the sensitizer, then dried in vacuum for 2 days and weighed.

The grafting G_g (%) and swelling G_s (%) percentages were determined gravimetrically.^{15,30}

Chemical Modification of Grafted Polyphosphazene Films

Films of PBPP-*g*-PAA and PBPP-*g*-P4-VP grafted copolymers (30 mm \times 10 mm \times 30 μm) were immersed in 6 mL of a methanol solution of different dyes (concn = 2×10^5) and stirred for periods of time varying from 0.1 up to 5 h. Both the colored films and the original dye solution were successively analyzed by UV spectroscopy to determine the kinetics of the dye adsorption.

Heterogeneous-Phase Generation of Singlet Oxygen by RB Supported onto PBPP-*g*-P4VP Grafted Copolymers

The quantum efficiency of the heterogeneous phase generation of singlet oxygen was measured following the oxidation reaction of 1,3-diphenyl-isobenzofuran (DPIBF)³¹ photosensitized by free and by phosphazene-supported RB.³² The procedure implies the immersion of a PBPP-*g*-P4-VP film functionalized with attached RB in an oxygen-saturated methanol solution of DPIBF (concn = $4.2 \times 10^{-3} M$), followed by the irradiation of the dye at 562 nm. The optical density decrease at 415 nm, indicative of the disappearance of the DPIBF, was compared to that measured by irradiating a methanol solution of free

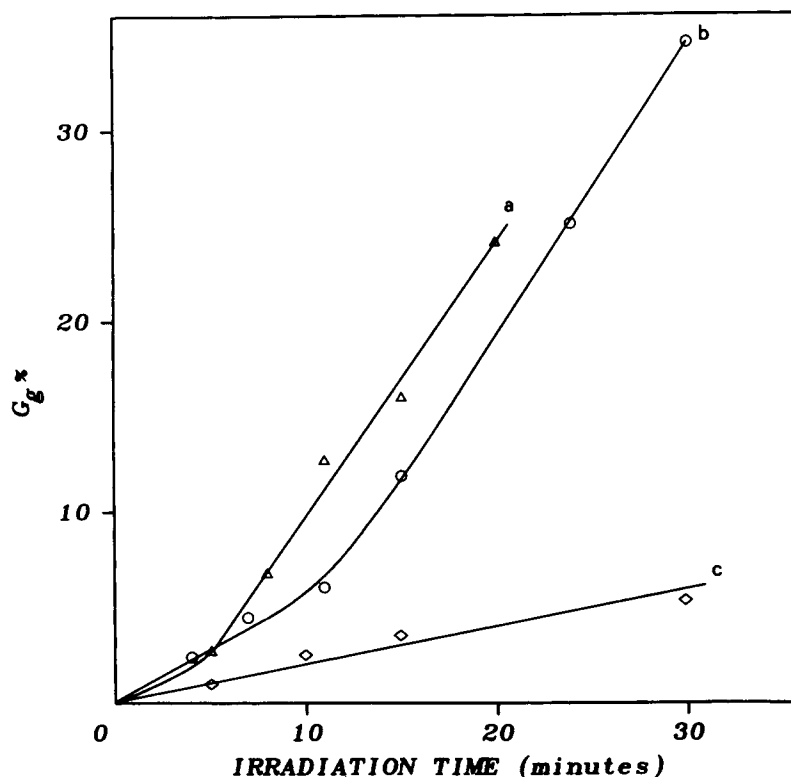


Figure 1 Percentage of: (a) polyacrylic acid (benzophenone photoinitiator), (b) polymethacrylic acid (benzophenone photoinitiator), and (c) poly-4-vinylpyridine (benzoin ethyl ether photoinitiator) grafted onto poly[bis(4-benzylphenoxy)phosphazene] films at monomer/methanol ratio of 37/63 v/v.

RB (concn = $7.6 \times 10^{-6} M$) of the same optical density of the RB-supported phosphazene film.³²

A similar procedure was used to test the quantum efficiency of the singlet oxygen formation using films of PBPP-*g*-PAA supporting MB irradiated at 577 nm.

RESULTS AND DISCUSSION

Grafting Reactions of PAA, PMAA, and P4-VP onto Poly[bis(4-benzylphenoxy)phosphazene]

The irradiation of BP or BEE dissolved in a mixture of methanol and organic vinyl monomers, in the presence of swollen films of PBPP leads to the formation of PBPP grafted copolymers. The mechanism of these reactions, already discussed in previous papers,^{12,15,33,34} implies the primary formation of radicals by the irradiated photoinitiators. These radicals are able to remove hydrogens from the polyphosphazene matrix and/or from the reaction mixture, thus generating highly reactive sites that start both the grafting and the homopolymerization processes.

Figure 1(a,b) shows the grafting kinetics of AA and MAA onto PBPP sensitized by benzophenone. In the same conditions no grafting or homopolymerization of 4-VP were observed. In all cases, the reaction medium was composed of a monomer/methanol mixture of 37/63 in volume.

The results obtained with 4-VPM are in partial agreement with the data reported by Feng and Rånby,³⁵ who found a very low grafting yield of 4-VPM onto poly(ethylene terephthalate) fibers when the reaction is photoinitiated by benzophenone. This was attributed both to a low yield of radical formation in 4-VPM and to a slow propagation rate that, for this vinyl monomer, is lower than for the acrylic or methacrylic species.

To test the above hypotheses first we measured the rate of interaction between excited BP and 4-VPM. To this end we obtained the quenching rate constant from the Stern-Volmer plots of BP phosphorescence quenching by methanol, styrene, and 4-VPM in acetonitrile. The values obtained are $4.75 \pm 0.05 M^{-1}$ for quenching by CH_3OH , and $2.1 \pm 0.1 \times 10^5 M^{-1}$ for both styrene and 4-VPM. H-abstraction is responsible for the quenching of BP by

Table I Swelling Percentage, G_s (%), of PBPP Films Immersed in Monomer/Methanol Mixtures

Monomer Percentage (v/v)	PBPP/AAM	PBPP/MAAM	PBPP/4-V-PM
17	2.5	2.7	7.3
25		2.9	
30	4.7	4.3	
37	5.2	7.4	21
43	6.4		
50	9.8	8.2	27

CH_3OH ; the process occurs³⁶ with a rate constant $k_q = 3.0 \times 10^5 \text{M}^{-1} \text{s}^{-1}$. By comparing the slopes of the Stern-Volmer plots with styrene, 4-VPM, and CH_3OH , $k_q = 1.31 \times 10^{10} \text{M}^{-1} \text{s}^{-1}$ is obtained for the two vinyl monomers. This value is typical of a triplet energy transfer process controlled by diffusion.³⁶ This is justified by the triplet energy values (E_T) reported in the literature for BP ($E_T = 69.2$ kcal/mol in a polar solvent,³⁷ as the reaction medium is) and styrene ($E_T = 60.8 - 64.9$ kcal/mol³⁸). The same slope of the Stern-Volmer plots obtained for styrene and 4-VPM points to an E_T value for 4-VPM $\leq E_T$ value for styrene. In this case the BP triplet is deactivated by 4-VPM with the formation of the 4-VPM triplet, an electronically excited species that does not polymerize. Given the values of k_q and the concentrations of 4-VPM and CH_3OH in the reaction mixture, triplet energy transfer from excited BP by

far prevails on the H-abstraction and radical formation so that the grafting process cannot occur.

Figure 1(c) reports the grafting of 4-VPM when BEE is used as a photoinitiator. The photolysis of BEE gives free radicals that start the grafting of 4-VPM. The grafting is remarkably smaller than for acrylic monomers, which could be attributed to a lower propagation rate as reported.³⁵ The high chain transfer constant of 4-VPM, the formation of H bonds with water, hydroperoxides, or other impurities possibly present in the reaction medium, and the stabilization of radicals on the pyridinic ring by resonance³⁹ are all phenomena that could contribute to depressing the reactivity of 4-VPM and to reducing the light induced grafting to low levels.

Two other parameters are important in determining the grafting process of vinyl-type polymers onto PBPP, i.e. the relative percentage of monomers (AAM, MAAM, or 4-VPM) present in the reaction medium and the swelling degree of the polyphosphazene film. In previous articles^{33,34} these parameters proved to have contrasting influence in the determination of the G_g (%) of the organic polymers onto POPs. At low monomer concentrations, it was found that the swelling of the POP films, which facilitates the penetration of both monomer and photoinitiator into the phosphazene matrix, is the dominant process that contributes to an easy grafting onto the polyphosphazene. At increasing monomer concentrations, the quenching of the photoinitiator excited triplet, and the consequent reduction of free radicals able to start the grafting, prevails. The best

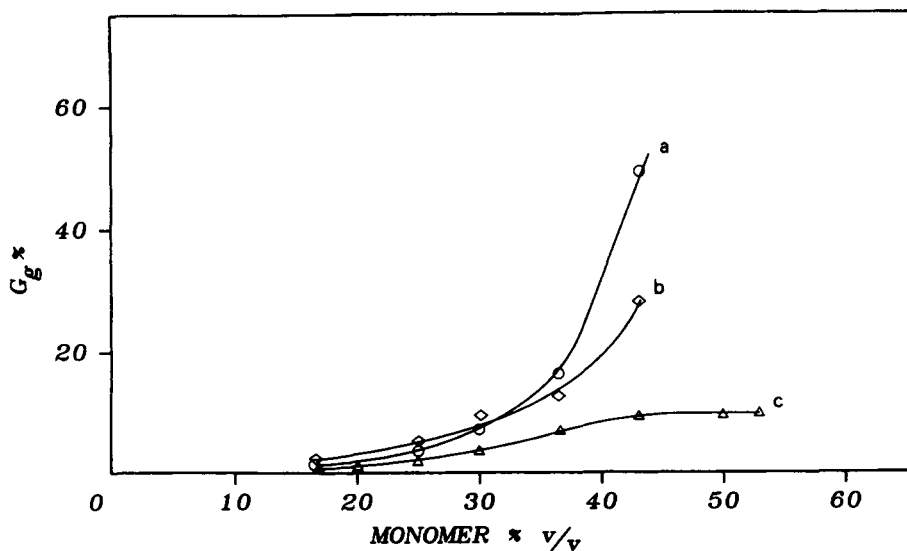


Figure 2 Percentage of: (a) polyacrylic acid, (b) polymethacrylic acid, and (c) poly-4-vinylpyridine grafted onto poly[bis(4-benzylphenoxy)phosphazene] films at various monomer/methanol ratios; (a, b) after 15 min; (c) after 45 min.

compromise between these processes was obtained with 20–30% of monomer in the system.

In the case of the grafting processes of PAA and PMAA onto PBPP, the increase of AAM and MAAM concentrations in the reaction media leads to a remarkable swelling of the polyphosphazene films, as reported in Table I.

Figure 2 shows that the enhanced swelling of the polymeric matrix favors the grafting of the vinyl monomers onto the PBPP films and increases the final G_g (%) values of the process.

However, in contrast to what was previously observed for PBPP-*g*-PMMA grafted copolymers,³³ no decrease of the grafting percentage of PAA and PMAA onto PBPP was observed at high monomer concentration. This indicates that, even with AAM and MAAM percentages higher than 50% v/v, the swelling of the POP film remains the prevailing process with respect to the quenching of the excited BP photoinitiator.

As far as the grafting of P4-VP onto PBPP is concerned [see Fig. 2(c)], after an initial increase at relatively low 4-VPM percentages, the G_g (%) values reach a plateau value at about 45% v/v of monomer in the system. This suggests that at these percentages the quenching of the excited BEE by the pyridine monomer starts to become significant.

Characterization of Phosphazene Grafted Copolymers

The PBPP-*g*-PAA, PBPP-*g*-PMAA, and PBPP-*g*-P4-VP grafted copolymers obtained were characterized by IR spectroscopy and by chemical modification of the acid and basic functionalities in the vinyl polymers grafted onto the polyphosphazene matrix.

The IR spectrum of the PBPP-*g*-PAA grafted copolymer is characterized by a broad intense band located at 3400–2500 cm^{-1} (stretching of the —OH groups in the carboxylic function⁴⁰), by a peak at 1715 cm^{-1} (stretching of the carbonyl group⁴¹), (see Fig. 3) and by the presence of the typical PBPP absorptions at 1610 and 1500 cm^{-1} (ν C=C of the aromatic ring), 1200 cm^{-1} (ν asymmetric of —P=N— backbone) and 960 cm^{-1} (ν of the P—O—Ph side substituents). Similar results (1710 cm^{-1} , stretching of the carbonyl group) are obtained in the IR spectra of PBPP-*g*-PMAA grafted copolymers. In the case of the PBPP-*g*-P4-VP system, besides the above mentioned phosphazene absorptions, the IR spectrum of the grafted films shows a new band at 1560 cm^{-1} , whose intensity is related to the grafting irradiation times: this band is

attributed^{39,40} to the stretching of the —C=N— group of the grafted VP polymer. All these findings strongly support the occurrence of the grafting of the PAA, PMAA, and P4-VP, respectively, onto PBPP films.

Further evidence of these facts comes from dyeing experiments carried out on the PBPP grafted copolymers. In fact, the light-induced grafting reactions of PAA, PMAA, and P4-VP onto PBPP lead to the preparation of polyphosphazene films that contain free carboxylic (acid) and pyridinic (basic) functions. This allows the coloring of these new materials by interaction, for instance, with basic or acid dyes, respectively.

Thus PBPP-*g*-PAA and PBPP-*g*-PMAA grafted substrates were allowed to interact with MB, thionin, toluidine blue, phenosafranin, and crystal violet methanol solutions; PBPP-*g*-P4-VP was treated with RB and erythrosine B to give permanently colored films. The process was carried out by immersing the grafted POP films into a dye solution for different periods of time (up to 5 h) and its progress was followed by the UV-vis spectrophotometry of both solution and film. It should be stressed that

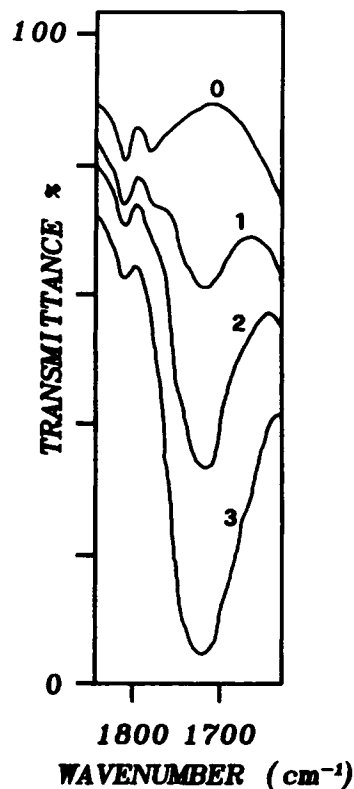
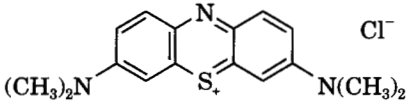
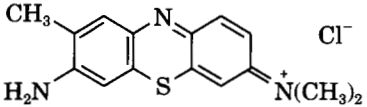
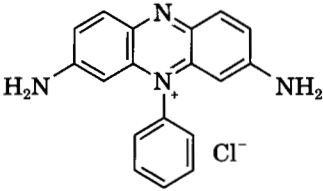
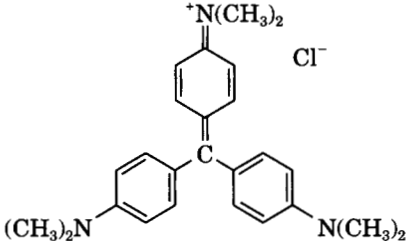
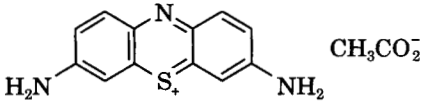
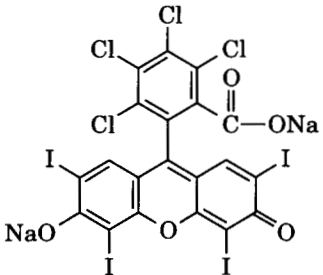
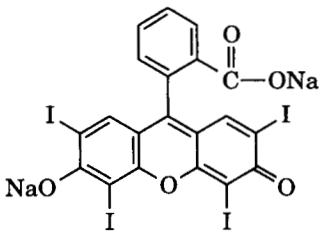


Figure 3 Infrared transmittance variations of PBPP-*g*-PAA copolymer films at various irradiation times: (0) $t = 0$ min; (1) $t = 1$ min 30 s; (2) $t = 5$ min; (3) $t = 8$ min.

Table II Spectral Characteristics of Grafted PBPP Films Colored with Basic or Acid Dyes

Absorption of Colored, Grafted Phosphazene Films	λ (nm) of Free Dyes in Methanol	Formula of Dyes
PBPP- <i>g</i> -PAA/methylene blue 667 (max), 615 (shoulder)	652 (max) 605 (shoulder)	
PBPP- <i>g</i> -PAA/toluidine blue, after 20 min 638 (max), 595 (shoulder), after 240 min 595 (max), 638 (shoulder)	626 (max)	
PBPP- <i>g</i> -PAA/phenosofranin 525 (max)	525 (max)	
PBPP- <i>g</i> -PAA/crystal violet 607 (max), 560 (shoulder)	588 (max) 550 (shoulder)	
PBPP- <i>g</i> -PAA/thionin 563 (max), 605 (shoulder)	598 (max) 563 (shoulder)	
PBPP- <i>g</i> -P4-VP/rose bengal 572 (max), 530 (shoulder)	556 (max) 517 (shoulder)	
PBPP- <i>g</i> -P4-VP/erythrosin B 552 (max), 510 (shoulder)	530 (max) 495 (shoulder)	

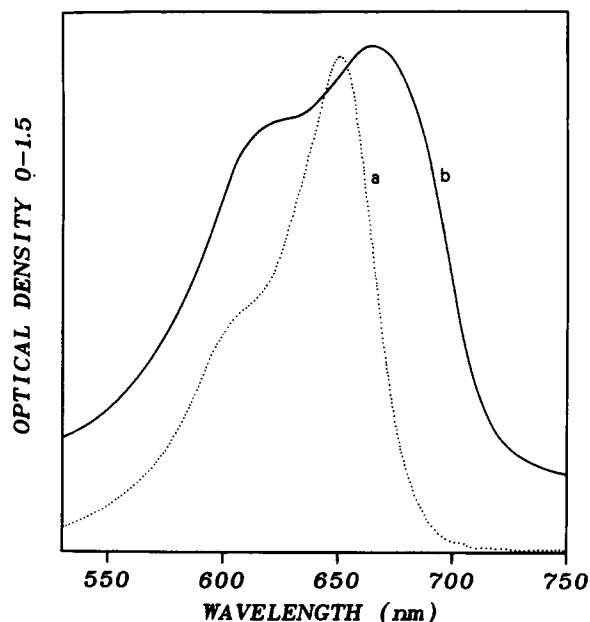


Figure 4 Absorption spectrum of: (a) methanol solution of methylene blue and (b) methylene blue attached to PBPP-*g*-PAA films.

original PBPP films do not interact with the examined dyes at all and that the grafted colored substrates do not release the dye when immersed in pure methanol at room temperature. This is an indication of quite a strong interaction between the dye and the grafted material but does not furnish any information on the nature of the interaction.

The spectral data of the free dyes and of the colored polymer films are reported in Table II.

The absorption spectra of the PBPP-*g*-PAA/methylene blue and PBPP-*g*-P4-VP/RB systems, as examples of polyphosphazene films colored with basic and acid dyes, respectively, are shown in Figures 4 and 5.

An inspection of the data in Table II and Figures 4 and 5 shows that the absorption spectra of the dyes free in solutions undergo considerable changes both in shape and in intensity when linked to the phosphazene grafted copolymers. In the case of MB, for instance, the original peak at 652 nm is greatly decreased and the shoulder at 600 nm increased when the dye is bonded to the PBPP-*g*-PAA. According to the literature,⁴² in fact, the long wavelength band in the spectrum of MB ($\lambda = 652$ nm) is attributed to a monomer form, and the shoulder at $\lambda = 600$ nm is assigned to the dimeric species formed in solution by aggregation phenomena. In diluted MB solutions, as well as for PBPP-*g*-PAA grafted copolymers immersed for short periods of time, the

monomer form prevails on the dimer, and the peak at 652 nm is more intense than the shoulder at 600 nm. By prolonging the time permanence of the phosphazene films in the MB solutions, the amount of dye linked to the acidic polyphosphazene matrix is enhanced; dimeric forms of the dye are therefore generated and the band at a long wavelength in the MB spectrum is reduced; that at the short wavelength is increased in intensity (see Fig. 4). Concurrently to these phenomena, remarkable bathochromic shifts of the absorption maxima of the two bands are observed.

Similar shifts in the absorption spectra are also detected in the case of free RB when the spectrum of this dye dissolved in methanol is compared to that of the same compound attached to the surface of PBPP-*g*-P4-VP grafted copolymer films (see Fig. 5).

It is interesting to note that in pentakis(phenoxy)(4-RB-methylene phenoxy)cyclophosphazene, a phosphazene trimer in which RB is chemically bonded to the cyclophosphazene structure,³² a similar bathochromic shift with respect to free RB was observed. This could suggest that a chemical bond is formed between RB and the grafted polymer.

The extent of the interaction increases as the grafting increases, as shown in Figure 6 where the decrease in the optical density of the MB solution is reported as a function of the immersion time for

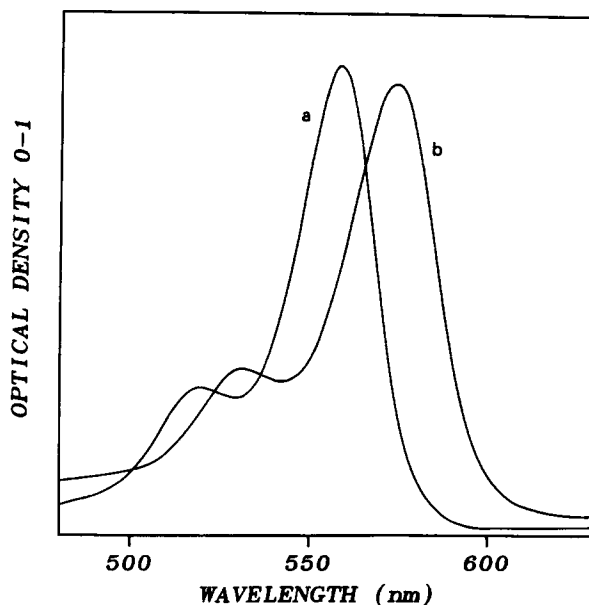


Figure 5 Absorption spectrum of: (a) methanol solutions of rose bengal and (b) rose bengal attached to PBPP-*g*-P4-VP films.

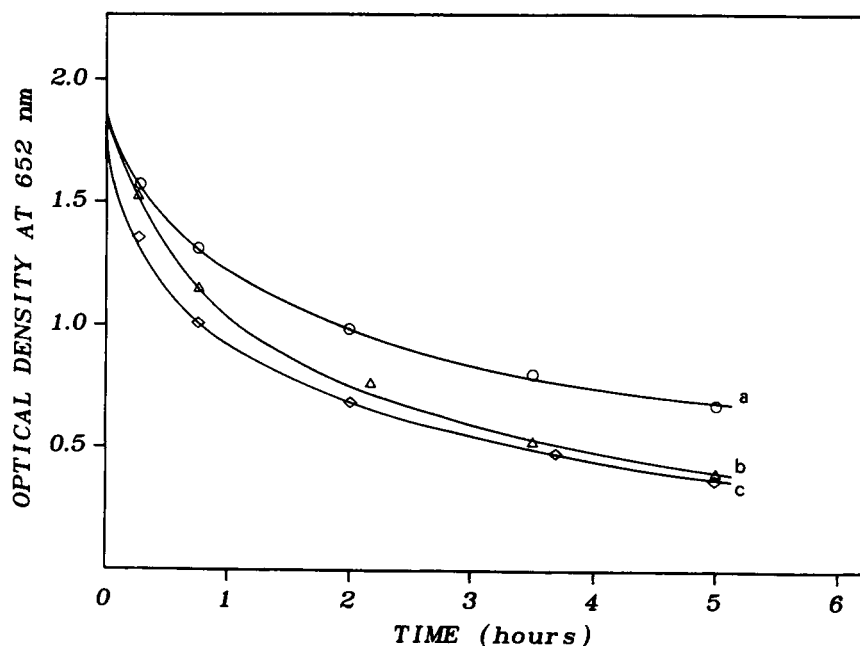


Figure 6 Optical density variations of a methanol solution of methylene blue at various immersion times of PBPP-*g*-PAA films containing: (a) 2.6% w/w of grafted PAA; (b) 15.9% w/w of grafted PAA; and (c) 24.0% w/w of grafted PAA.

three PBPP-*g*-PAA films containing different amounts of PAA.

As can be seen from this picture, the uptake of MB by the polyphosphazene film surfaces takes place immediately after the immersion of the polyphosphazene matrix into the dye solution; the rate of the process, however, slowly decreases as the permanence of the POP films in solution increases, until a plateau is reached after 5–7 h of immersion. The kinetics of the coloring of the phosphazene films depends on the absolute amount of free carboxylic functions grafted onto these substrates. In fact, the immersion of PBPP-*g*-PAA films containing 24.0% w/w of PAA in the MB solutions [see Fig. 6(c)] induces a very rapid decrease in the dye absorbance. The rate of this process, however, diminishes when polyphosphazene grafted copolymers containing 15.9% of PAA are used, and reaches the minimum value in the case of PBPP-*g*-PAA that bears only 2.6% of grafted PAA. These facts indicate that the higher the amount of PAA grafted onto the polyphosphazene, the more efficient the adsorption process of the dye in the system is.

Heterogeneous-Phase, Singlet Oxygen Generation

PBPP-*g*-P4-VP films dyed with RB were tested as heterogeneous phase photosensitizers for singlet

oxygen generation. This electronically excited form of oxygen shows unusual oxidizing features, especially toward allylic double bonds, cyclic aromatic compounds, heterocycles, and macromolecules.⁴³ The activity of RB supported on polymers has already been studied by Schaap et al.⁴⁴ who used styrene-divinylbenzene beads, and by ourselves through the functionalization of poly[bis(4-methylphenoxy)phosphazene] with this dye.³² Films of PBPP-*g*-P4-VP (24% w/w) colored with RB were immersed in oxygen saturated solutions of 1,3-diphenyl-isobenzofuran (DPIBF) and the system was irradiated at $\lambda = 562$ nm. A variation of the optical density at 415 nm was observed due to the disappearance of DPIBF following the reaction of this molecule with singlet oxygen.³¹

The quantum yield³¹ of the process, determined according to the above reported procedure (see Experimental) was found to be 0.44, in agreement with the value (0.43) reported by Schaap et al.⁴⁴ for the production of singlet oxygen photosensitized by RB supported on polystyrene-divinylbenzene beads.

For the same reaction, photosensitized by MB attached to PBPP-*g*-PAA films, a quantum efficiency of 0.25 was measured.

Moreover, it should be pointed out that the processes of heterogeneous phase photogeneration of $^1\text{O}_2$ by RB or MB bonded to the surface of PBPP-*g*-P4-VP or PBPP-*g*-PAA grafted copolymer films,

respectively, may have potential applications in continuous flow reactors. Investigations in this direction are in progress.

CONCLUSIONS

The light-induced grafting reactions of PMAAs and P4-VP onto PBPP leads to the preparation of grafted copolymers that contain free carboxylic and pyridinic groups. During these processes, PAA and PMAA were found to be more reactive than P4-VP, which could be grafted onto PBPP using BEE only instead of benzophenone as a photoinitiator. Similarly to the results reported previously,^{12,15,34} the grafting reactions of organic substrates onto POPs proved to be influenced also by the concentration of the vinyl monomer present in the reaction medium.

The chemical modification of POPs, by grafting polymers containing free acid and basic functionalities onto these substrates, was used successively to introduce additional reactivity in the polyphosphazenes. In fact, PBPP-*g*-PAA, PBPP-*g*-PMAA, and PBPP-*g*-P4-VP were reacted with basic and acid dyes, respectively, to form colored phosphazene films. One of these materials, i.e. PBPP-*g*-P4-VP treated with RB, was exploited for the photosensitized, heterogeneous-phase generation of singlet oxygen by the selective irradiation of the dye linked to the POP surface. The quantum yield of this process, measured following the oxidative disappearance of DPIBF,³¹ was found to be 0.44, a value comparable to that previously reported in the literature for the singlet oxygen produced by irradiation of RB attached to styrene-divinylbenzene beads.⁴⁴ The same held true when the sensitized production of singlet oxygen was attempted using the MB dye attached to PBPP-*g*-PAA films.

The authors are indebted to the Progetto Finalizzato Chimica Fine e Secondaria II del Consiglio Nazionale delle Ricerche for financial support.

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Received March 22, 1994

Accepted November 4, 1994