Grafting Reactions onto Polyorganophosphazenes. V. Photostabilization of Poly[bis(4-benzylphenoxy)-phosphazene] by Light-Induced Grafting Copolymerization of Acrylate Polymers Containing Pendant HALS Moieties

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SYNOPSIS

The light-induced grafting reaction of acrylate monomers containing hindered piperidine groups (HALS) onto poly[bis(4-benzylphenoxy)phosphazene] is described as a function of several different experimental parameters, i.e., type of photoinitiator (benzophenone or benzoin ethyl ether), monomer concentration, solvent composition, light intensity, and swelling of the polyphosphazene films. The obtained phosphazene-g-HALS-containing acrylate-grafted copolymers, irradiated with light of wavelength longer than 300 nm under accelerated photooxidative conditions to test the photostabilizing ability of the grafted HALS groups, showed that the hindered piperidine groups grafted onto the polyphosphazene matrix are able to considerably depress the damage caused to the poly[bis(4-benzylphenoxy)phosphazene] films during light exposure. The efficiency of this process seems to be related to the amount of HALS residues grafted onto the phosphazene substrates. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(organophosphazenes) (POPs), i.e., the polymers formed by $-P=N-$ skeletal units with two organic substituents "R" attached at the phosphorus,[1]
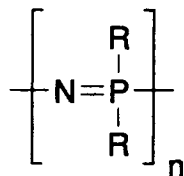
are particularly promising macromolecules[2] due to the wide range of practical applications offered by these materials. POPs, in fact, have been actively investigated over the last three decades as low-temperature elastomers,[3] self-extinguishing polymers,[4] fire-[5] and heat-resistant[6] macromolecules, bioma-

terials,[7] electric conductors or insulators,[8] ceramics,[9-11] catalysts,[12,13] membranes,[14] and photochemically relevant substrates.[15-17]

This last characteristic is of importance because of the transparency of the inorganic phosphazene skeleton up to 200–230 nm[18] and the great versatility[19] of the synthetic approach used for the preparation of these materials (i.e., the replacement of the reactive chlorines of the polydichlorophosphazene precursor with a great deal of different nucleophiles[20-22]) that allow the synthesis of phosphazene macromolecules containing selected chromophores appended to the inorganic backbone, showing predictable photochemical responses.[23] In this way, POPs able to act as heterogeneous phase polymeric photosensitizers,[24,25] polymeric photoinitiators,[26] materials for microelectronics,[27-33] etc., have been synthesized and characterized.

In the field of POP photochemistry, an increasingly important aspect is the instability of these materials to light exposure.[15,23] Several polymers of this class, in fact, show a remarkable capability to degrade or reticulate upon irradiation depending

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on the experimental conditions selected for photolysis. These phenomena are attributed mainly to the photochemical modifications undergone by the chromophores appended to the phosphorus along the inorganic skeleton while exposed to light under photolytic and/or photooxidative conditions, as demonstrated for phenoxy-,[34] β-naphthoxy-,[35] 4-methylanilino,[35,36] 4-isopropylphenoxy-,[37] 4-sec-butylphenoxy-,[38] 4-benzylphenoxy-,[39,40] or 4-benzoylphenoxy-substituted[41] POPs. In the light of these considerations, it may be concluded that the stabilization of POPs against light damage is a problem of paramount importance for the industrial development and the practical utilization of these substrates, if their mechanical properties and morphological aspects are to be preserved and their service lives are to be prolonged.

In the past, the photostabilization of selected POPs has been achieved following two different strategies, i.e., by the transfer of the excitation energy accumulated by irradiated chromophores appended to the phosphazene skeleton to suitable quenchers, in order to deactivate the reactive species on the polymer and diminish the overall photoreactivity of the system (this is the case of POPs substituted with 4-benzoylphenoxy groups[24] in which the excited triplet of the benzophenone was quenched using external[42] or internal[43] naphthalene groups) or by the synthesis of phosphazene macromolecules containing self-stabilizing chromophores (e.g., 2-hydroxybenzophenone[44] or HALS[45]) attached to the phosphorus atoms of the inorganic —P=N— skeleton.

In this article, we present a novel approach to the photostabilization of POPs as obtained by grafting acrylate polymers (i.e., the polyacrylate of 2,2,6,6-tetramethylpiperidin-4-ol [PAPH] and the polyacrylate of 1,2,2,6,6-pentamethyl-piperidin-4-ol [PAPMe]) containing hindered piperidine residues (HALS) onto a particular phosphazene substrate, the poly[bis(4-benzylphenoxy)phosphazene] (PBPP):
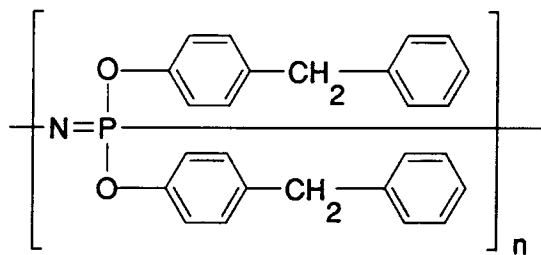
whose light sensitivity under direct[39] or photooxidative[40] irradiation and under light-induced grafting conditions[46-49] is currently well established.

It may be of importance to stress that the method for photostabilizing POPs presented in this article, although described for a specific polyphosphazene, lends it self nicely also in the case of other POPs containing alkyl radicals substituted in the aromatic phenol rings.

EXPERIMENTAL

All the solvents were C. Erba analytical grade, purified or dried according to the literature.[50] Hexachlorocyclophosphazene was a Shin Nisso Kako product purified by precipitation in n-hexane followed by repeated vacuum sublimations until a constant melting point of 113–114°C was reached.[1] Polydichlorophosphazene was obtained by the bulk thermal polymerization of hexachlorocyclophosphazene in evacuated sealed ampules at 250°C for several hours[20,21] and was freed of the unreacted trimer by sublimation at 65–70°C under reduced pressure.[51] 4-Hydroxydiphenylmethane was purchased from Aldrich and purified by vacuum sublimation.[39] Poly[bis(4-benzylphenoxy)phosphazene] (PBPP) was prepared by reacting polydichlorophosphazene with an excess of 4-hydroxydiphenylmethane sodium salt in an anhydrous xylene/dioxane mixture for 3 days, in accordance with the literature.[39,52] The purification and characterization of the polymer were reported elsewhere.[39] Benzophenone (BP) and benzoin ethyl ether (BEE) photoinitiators were analytical-grade Aldrich products used as received.

The acrylate monomers containing the hindered piperidine groups (HALS) (i.e., the acrylate of 2,2,6,6-tetramethyl-piperidin-4-ol [APH] and the acrylate of 1,2,2,6,6-pentamethyl-piperidin-4-ol [APMe]) were Ciba Geigy purified intermediates (GLC analyses 99.1 and 99.3%, respectively) and were used without further purification.

The corresponding HALS homopolymers (i.e., PAPH and PAPMe) were prepared as side products of the grafting process using the following experimental procedure: irradiation ($\lambda_{exc.} > 350$ nm, cutoff filters) for 45 min of an acetone solution of BEE ($C = 10^{-2}M$) containing 0.75M of APH or APMe and separation of the products by evaporation of the solvent and sublimation of the excess of monomer and photoinitiator. A successive characterization by gel permeation chromatography (GPC) gives a molecular weight of about 5000–7000 Daltons for these homopolymers.

The grafting procedures of PAPH and PAPMe onto the polyphosphazene matrices were as follows: films of PBPP (dimensions of 30 mm × 12 mm × 10 μ, as obtained by casting from CH_2Cl_2 solutions)

were supported on an aluminum frame and immersed in degassed (10^{-6} torr) methanol, acetone, or methanol/acetone mixtures, in the presence of the photosensitizer, until the swelling equilibrium was attained. They were successively irradiated at 25°C using a 150 W high-pressure mercury lamp (distance 20 cm) and cutoff filters to eliminate radiations of wavelengths below 350 nm; they were washed successively with methanol or methanol/acetone mixtures and eventually dried in a vacuum for 2 days.

The grafting yields, $G_g(\%)$, were obtained by IR spectroscopy, analyzing physical blends of PBPP and PAPH (or PAPMe), plotting the ratio between the optical density at 1735 cm^{-1} (attributed to the vibration of the acrylate ester moiety), and the extinction at 1610 cm^{-1} (assigned to the stretching of the aromatic ring of the side phenoxy substituents of PBPP) vs. the weight percentage of PAPH or PAPMe, respectively. This could be possible because the band at 1610 cm^{-1} of the polyphosphazene system is not affected, either in position or in intensity, by varying the amount of piperidine in the system, making also the reasonable assumption that the extinction coefficient of the band at 1735 cm^{-1} in the HALS-containing acrylate homopolymers and in the PBPP-g-PAPH and PBPP-g-PAPMe grafted copolymers is the same. The resulting equation used was

$$G_g(\%) = A_{1735}/A_{1610} \times 1/0.063$$

where 0.063 is the slope of the determined calibration plot.

The equilibrium swelling degree of PBPP films, $G_{se}(\%)$, immersed into methanol, acetone, or methanol/acetone mixtures, was determined gravimetrically, according to the expression

$$G_{se}(\%) = (W_{se} - W)/W \times 100$$

where W_{se} is the weight of the polymer film swollen in selected solvents until a constant weight is reached, and W, the initial weight of the phosphazene film.

Once prepared, the PBPP-g-PAPH- and PBPP-g-PAPMe-grafted copolymers were irradiated at 50°C in a Sairem Sepap 12.24 apparatus (Material Physico Chimique, France) equipped with four medium-pressure Hg lamps of 400 W each filtered by borosilicate glass bulbs ($\lambda_{exc} > 300$ nm) following the procedure previously reported[40] to test the photostabilizing ability of the grafted, HALS-containing acrylates. Similarly to the grafted copolymers, physical mixtures of the PAPH (or PAPMe) ho-

mopolymer blended with PBPP were also irradiated under comparable conditions to ascertain the photostabilizing ability of these last macromolecules for the polyphosphazene substrate.

The formation of nitroxyl radical formed by the HALS moieties during irradiation of PBPP-g-PAPH and PBPP-g-PAPMe copolymer films was detected by EPR spectroscopy using a Bruker EPR spectrometer Model ESP 300 and a benzene solution of the 2,2,6,6-tetramethylpiperidinyloxy free radical (TEMPO) as the reference standard.

The UV spectra were carried out with a Perkin-Elmer spectrophotometer Model 320, while the infrared analyses were performed with a Perkin-Elmer spectrophotometer Model 399. Molecular weight determinations were run by GPC using a Waters apparatus and polystyrene standards.

RESULTS AND DISCUSSION

Light-induced Grafting Copolymerization of PAPH and PAPMe onto PBPP

The first step in the grafting copolymerization of both organic and inorganic macromolecules onto polyorganophosphazenes implies the formation of active centers on the POP substrates.[46] According to the approach devised by Wisian Neilson et al.,[53-55] for instance, reactive grafting sites are obtained by the abstraction of labile protons present in the side poly(alkyl/aryl)phosphazene substituents by strong bases (e.g., alkyl or aryl lithium derivatives) to form phosphazene macroanions, from which the grafting copolymerization of polystyrene,[53] polysiloxane,[54] and poly(methyl methacrylate)[55] could be achieved. A second methodology, put together basically by our group[46-49,56-63] and adopted recently also by Allcock et al.,[64] first of all implies the formation of radical species on polyphosphazenes bearing alkyl residues in the side phenoxy substituents by hydrogen atom abstraction reactions using thermal[56,57,60] or photochemical[46-49,58,59,61-63] initiators or γ-rays.[65-68] Thus, the growth of organic polymeric branches from the phosphazene macroradicals could be obtained in the presence of styrene,[56,57] methyl methacrylate,[46,48,58,59,61] acrylamide,[68] N,N'-dimethylacrylamide,[46,48,62,63,68] acrylic acid, methacrylic acid, 4-vinylpyridine,[47,49,64] and glycidyl methacrylate[64] monomers.

The phosphazene-grafted copolymers obtained as above show considerably different surface[63,64] and bulk[56,57] properties with respect to the pristine macromolecules and present potential applications as compatibilizing agents for blends[46-48] or as biocom-

patible materials.[64-68] Expanding upon this research, we recently explored the grafting copolymerization reaction of acrylic monomers containing photostabilizing hindered piperidine groups (HALS), i.e., the acrylate of 2,2,6,6-tetramethyl-piperidin-4-ol (APH) and the acrylate of 1,2,2,6,6-pentamethylpiperidin-4-ol (APMe):

CH_2=CH
|
COO

CH_2=CH
|
COO

APH

APMe
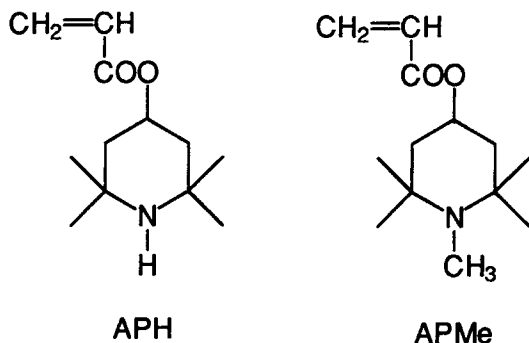
onto a light sensitive POP, the poly[bis(4-benzyl-phenoxy)phosphazene] (PBPP) with the aim of improving the light stability of this macromolecule. The grafting was achieved by selectively irradiating ($\lambda_{exc.}$ > 350 nm) benzophenone (BP) or benzoin ethyl ether (BEE) photoinitiators dissolved in monomer/methanol mixtures (sometimes containing variable amounts of acetone), in the presence of swollen films of poly[bis(4-benzylphenoxy)-phosphazene].

The IR characterization of the obtained grafted copolymers (see PBPP-g-PAPH in Fig. 1) shows the presence in these substrates of a new band at 1735 cm^{-1}, assigned to the stretching of the ester moiety in the copolymer; this band increases with the time exposure of the PBPP film to indicate that the grafting process depends on the irradiation time.

The mechanism proposed for this reaction implies the light-induced abstraction of hydrogen atoms from the methanol solvent and/or from the polyphosphazene matrix either by the excited triplets of the BP photoinitiator[47,59] or by the photofragmentation radicals coming from BEE,[47] to form phosphazene macroradicals and solvent radicals in accordance with previous literature; from the first species, the growth of organic polymeric chains from the main polyphosphazene substrates (grafting) can take place, while from the second ones, a simultaneous homopolymerization reaction of the HALS-containing acrylates originates.

The grafting percentages, G_g(%), of PAPH and PAPMe onto PBPP vs. irradiation times for experiments carried out in neat methanol using BP as a photosensitizer are reported in Figure 2. This picture shows that the grafting percentage of PAPH onto
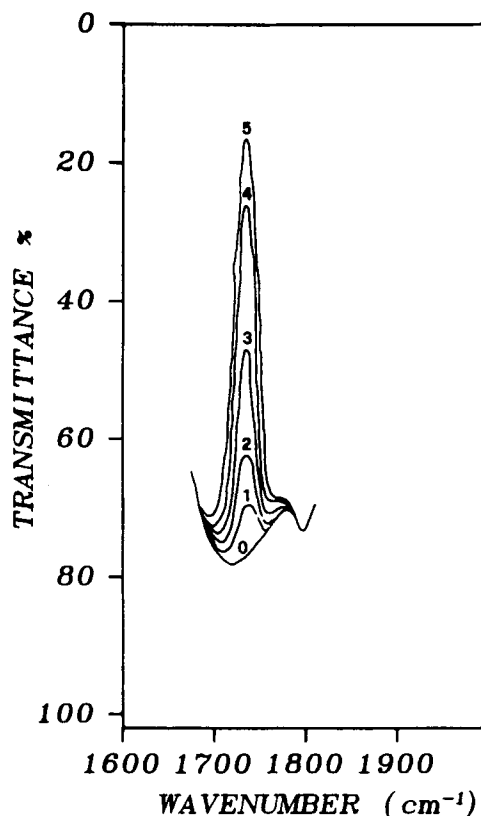

Figure 1 IR transmittance spectra of PBPP-g-PAPH at various irradiation times: (curve 0) $t = 0$, G_g(%) = 0; (curve 1) $t = 45$ s, G_g(%) = 0.75; (curve 2) $t = 1$ min, G_g(%) = 1.5; (curve 3) $t = 3$ min, G_g(%) = 3.1; (curve 4) $t = 6$ min, G_g(%) = 6.8; (curve 5) $t = 10$ min, G_g(%) = 10.4, obtained using BEE ($C = 10^{-2}M$) as a photoinitiator, APH ($C = 0.75M$) as a grafting monomer, and acetone solvent.

PBPP increases with the irradiation time, apparently reaches a plateau after 90 min of illumination, and seems not to increase any more for longer light exposure. From this picture, it also appears that the grafting process of PAPMe onto PBPP is considerably more efficient than is the corresponding process involving PAPH.

The possible explanation of the first point deals with the fact that the APH monomer is rapidly consumed during the grafting reaction onto PBPP, while its diffusion from the methanol solution toward the polyphosphazene matrix is strongly delayed by the enhanced viscosity of the solution, which increases constantly during irradiation due to the simultaneous formation of PAPH homopolymer. The second observation may be accounted for by considering the swelling capability of the PBPP films in pure methanol and in methanol containing 0.75M of acrylate HALS monomers. As reported in Table I, in fact, the initial swelling percentage of PBPP films in methanol (4.8%) is only
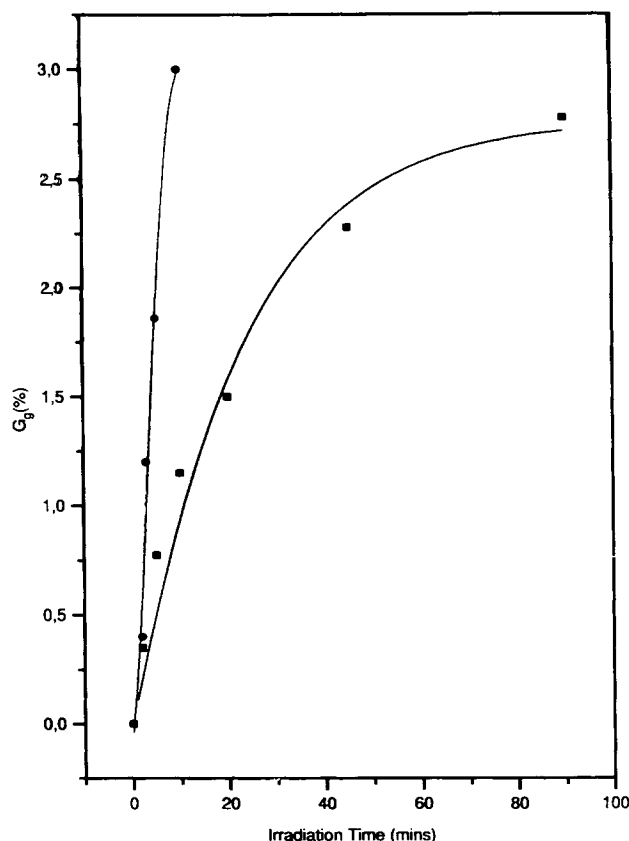
Figure 2 Percentage of (■) PAPH and (●) PAPMe grafted onto PBPP at various irradiation times, using methanol solvent, BP (C = 2.5 × $10^{-2}M$) photoinitiator, and APH and APMe monomers (C = 0.75M).

moderately increased by the addition to the reaction medium of 0.75M of APH (5.2%), probably because this compound is solid in nature, while it is dramatically increased (10.6%) when the same quantity of APMe, which is liquid and can act as a solvent for the polyphosphazene film, is added. This would therefore result in a strong difference in the

penetration ability of the two monomers into the PBPP swollen films, bringing about the already observed difference in their grafting yield onto the polyphosphazene matrix. This fact is in agreement also with previous results on the grafting processes of different vinyl polymers onto variable phosphazene films.[46-48,58,59,61,63]

The addition of acetone solvent in the reaction mixture deeply influences the grafting process of the acrylate polymers containing HALS groups onto PBPP. This is shown in Figure 3 where the grafting yield of PAPH onto PBPP is reported vs. the acetone content in the reaction mixture. In this figure, the initial grafting percentage G_g(%) for the formation of PBPP-g-PAPH-grafted copolymers in methanol is remarkably enhanced by the addition of increasingly high amounts of acetone in the reaction mixture, up to the percentage of 40–45% v/v of this solvent being attained in the system; for this methanol/acetone composition, the highest grafting percentage is observed. A further increase of the acetone content in the system results in a strong depression in the yield of the grafting process of PAPH onto PBPP, which falls to zero when the acetone percentage is above 90% v/v.

These facts can be accounted for by considering the role played in the overall grafting process by two different parameters, i.e., the ability of different composition media in swelling the immersed PBPP films and the efficiency of the benzophenone photoinitiator in starting the grafting process in these solvents.

In neat methanol, or in methanol containing low acetone concentrations, in fact, the swelling of the PBPP films is not so high as to favor the penetration of both monomer and photoinitiator into the polyphosphazene matrix, to enhance the grafting values G_g(%), and to improve the process yield; for these reasons, relatively low G_g(%) values are ob-

Table I Equilibrium Swelling Percentages of PBPP Films in the Presence of Methanol/Acetone or Methanol/Acetone/Monomer Mixtures

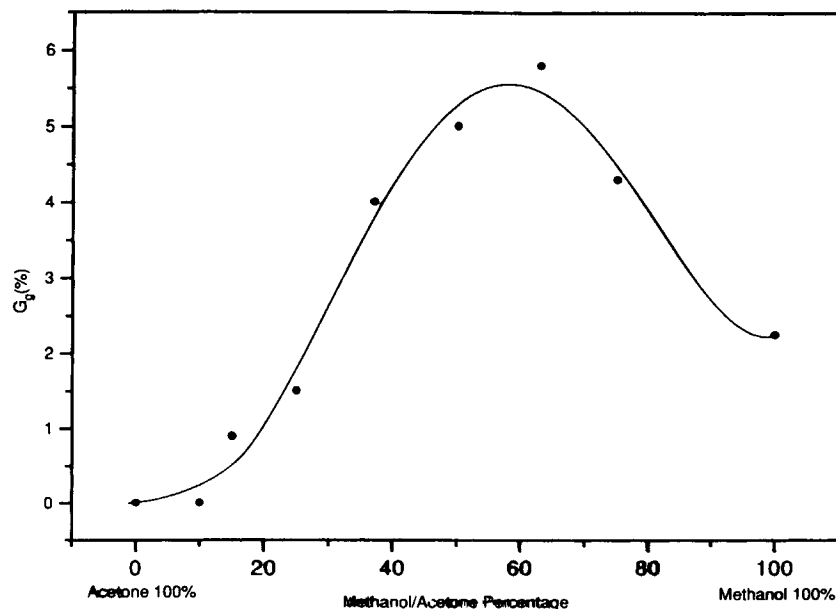| Reaction Medium Composition			Swelling Percentages	
Methanol Percentage	Acetone Percentage	Methanol + Acetone	Methanol + Acetone + 0.75M of APH	Methanol + Acetone + 0.75M of APMe
100	0	4.8	5.2	10.6
75	25	7.9	8.6	13.2
63	37	9.9	10.7	14.8
50	50	11.4	12.7	16.3
37	63	12.5	14.5	18.0
25	75	14.8	16.3	19.4
0	100	17.3	20	22

Figure 3 Percentages of PAPH grafted onto PBPP at different methanol/acetone ratios, using APH $(C = 0.75M)$ monomer and BP $(C = 2.5 \times 10^{-2}M)$ photoinitiator. Irradiation time, 45 min.

tained in these conditions. These phenomena, however, are more feasible when increasing the acetone content in the system, at least, until 40–45% of acetone percentage in the reaction mixture is attained, and allow the enhancement of the yield of the grafting process. A further increase of the acetone percentage in the grafting media results in a decrease of the relative concentration of the methanol in the system and in an increased difficulty of the BP photoinitiator in the production under illumination of the radicals necessary to sustain the grafting process. In this way, the efficiency of the BP photoinitiator is greatly reduced and the grafting process depressed. Other factors, such as the deactivation of the excited benzophenone triplets by energy-transfer processes to the acetone solvent, must be ruled out due to the large difference in the relative energy of the benzophenone and the acetone triplets[69] that makes the energy transfer process between these two species impossible.

The swelling of the polyphosphazene matrix, therefore, and the efficiency of the benzophenone photoinitiator seem to have contrasting effects on the overall grafting reaction of PAPH onto PBPP depending on the relative percentage of methanol and acetone in the system.

An efficient grafting reaction of PAPH onto PBPP in neat acetone could be restored only when the BEE photoinitiator is used instead of BP to initiate the process, as reported in Figure 4 where the $G_g(\%)$ values are plotted vs. irradiation times. We attributed such a high yield of the grafting reaction of PAPH onto PBPP to the different photoinitiation mechanism active for BEE (photofragmentation reaction) compared to that operative for benzophenone (photoinduced hydrogen abstraction reactions)[69,70] and to the high swelling of the PBPP films in the presence of neat acetone (see Table I) that facilitates the penetration of both monomer and photoinitiator into the polyphosphazene matrix.

Two other parameters were found to play a certain role in determining the overall grafting efficiency of PAPH onto PBPP, i.e., the percentage of APH monomer present in the reaction mixture and the intensity of the light used to induce the grafting process. As far as the first factor is concerned, Table II shows that a strong increase of the $G_g(\%)$ values is obtained for the grafting process when increasingly high amounts of APH monomer are present in the reacting system during light exposure. As for the influence of light intensity (see Fig. 5), the overall grafting percentage of PAPH onto PBPP (curve "a"), as measured in methanol/acetone mixtures 50/50 by volume, under standard illumination conditions (vide supra), is drastically reduced when a gray filter that abates 50% of the incident light is used during irradiation (curve "b").
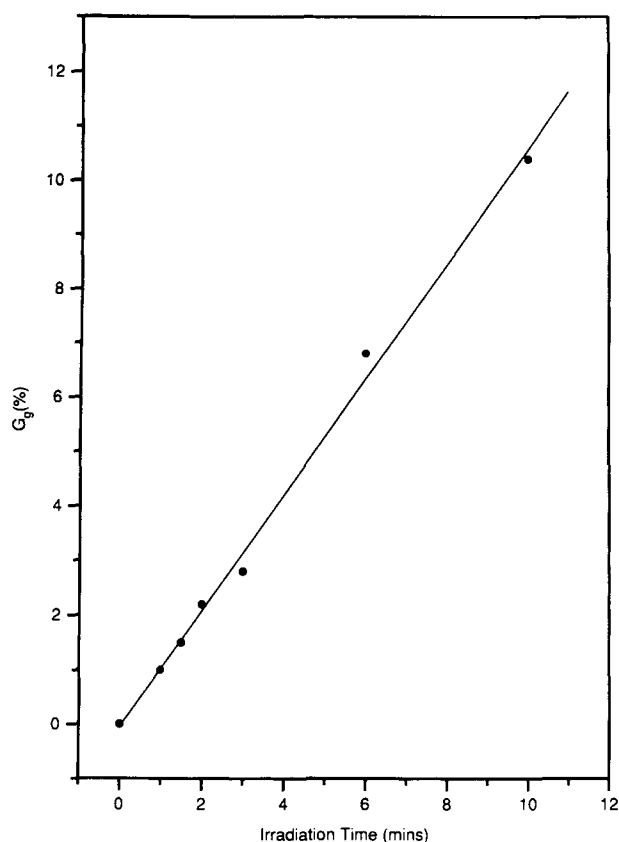
Figure 4 Percentages of PAPH grafted onto PBPP at different irradiation times using APH (C = 0.75M) monomer, BEE (C = $10^{-2}M$) photoinitiator, and acetone as a solvent.

Table II   Grafting Yield G_g (%) of PBPP-g-PAPH Formation at Different APH Concentrations[a]

Monomer Concentration (M)	G_g (%)
0.5	0.31
0.75	1.49
1	2.1

[a] Experiments carried out in methanol, using benzophenone (C = 2.5 × $10^{-2}M$) photoinitiator, irradiating the solution for 20 min.

Photooxidation and Photostabilization of PBPP-g-PAPH- and PBPP-g-PAPMe-Grafted Copolymers

The photochemical behavior of PBPP under direct photochemistry[39] or under photooxidation conditions[40] has already been investigated. The mechanism of this process implies primarily (see Scheme I) the splitting of a hydrogen atom from the methylene group of the phosphazene diphenylmethane moiety to form the macroradical **1** that evolves following different fates depending on the experimental conditions used for photolysis. In fact, this species can induce the crosslinking of the POP forming insoluble films by coupling reactions that are particularly feasible when photolysis is carried out in an argon atmosphere (pathway "a"); alternatively, when the irradiations are carried out in air, **1** can uptake molecular oxygen (pathway "b") forming the hydroperoxide **2**, whose breaking, thermal and/or photochemical, brings about the formation of the radical **3**. From these species, coupling reactions with other radicals (**1** or **3**, for instance) can induce the reticulation of the polymer films, β-

scission can lead to the formation of benzophenone and benzaldehyde residues on the phosphazene matrix, and the uptake of a hydrogen atom gives rise the formation of the phosphazene macroalcohol **4**. It is important to stress that the benzophenone moieties deriving from the oxidative evolution of the phosphazene diphenylmethane units are able to absorb light themselves during irradiation abstracting
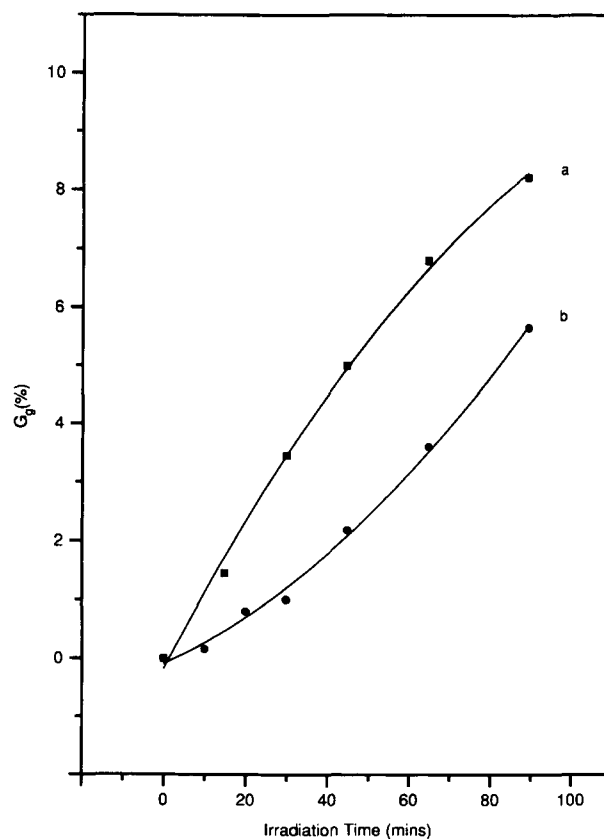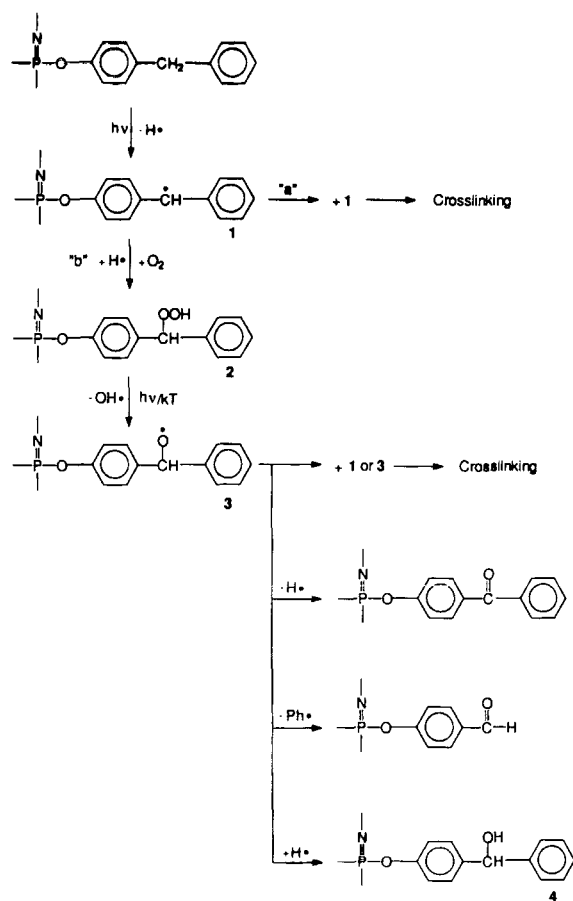

Figure 5 Percentages of PAPH grafted onto PBPP at different irradiation times using (curve a) a 150 W high-pressure mercury lamp and cutoff filters at 350 nm (irradiation distance = 20 cm) and (curve b) an additional gray filter that abates 50% of the impinging light. APH monomer (C = 0.75M); methanol/acetone mixtures 50/50 by volume.


Scheme 1

hydrogens from the 4-benzylphenoxy units of the phosphazene matrix, thus regenerating the macroradical **1** and sustaining the overall photooxidation process of PBPP.

The IR spectra of PBPP films irradiated under photooxidative conditions[40] ($\lambda_{exc} > 300$ nm) basically show the formation of a peak at 3550 cm^{-1} (assigned to the stretching of the hydroxylic groups), the growth of a broad band at 3400 cm^{-1} (attributed to the formation of hydroperoxide moieties), and the onset of a new band at 1660 cm^{-1} (originated by the presence of benzophenone groups in the irradiated PBPP film[71]) (see Fig. 6, curves 1–3). In the UV spectrum of these films, moreover, we can observe the formation of a strong absorption at 330–340 nm, a wavelength range where the benzophenone group is known to present the absorption maximum of its n–π^* transition[69] (see Figs. 7 and 8, curves "7").

The grafting of PAPH and PAPMe onto PBPP, carried out according to the above-illustrated procedures, introduces hindered piperidine groups (HALS) both in the bulk and in the surface[63] of the polyphosphazene films. These groups are well-known, long-term photostabilizing agents for poly-

mers (polyolefins in particular).[72,73] The action mechanism of HALS in preventing polymer degradation has been extensively examined and reviewed.[72-75] It is now well established that the principal feature of this reaction is represented by the ability of HALS (and of their transformation products) to interfere with the polymer chain oxidation process, either by scavenging radicals or by disarming initiators. Under photooxidative conditions, sterically hindered amines (**1**) are converted into the corresponding nitroxyl radicals[76,77] (**2**):
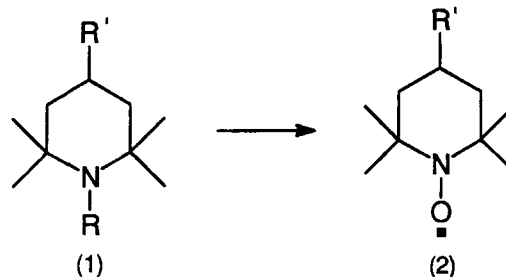
where R = H or CH$_3$, which are thought to be the true stabilizing species involved[78,79] in the photostabilization process.
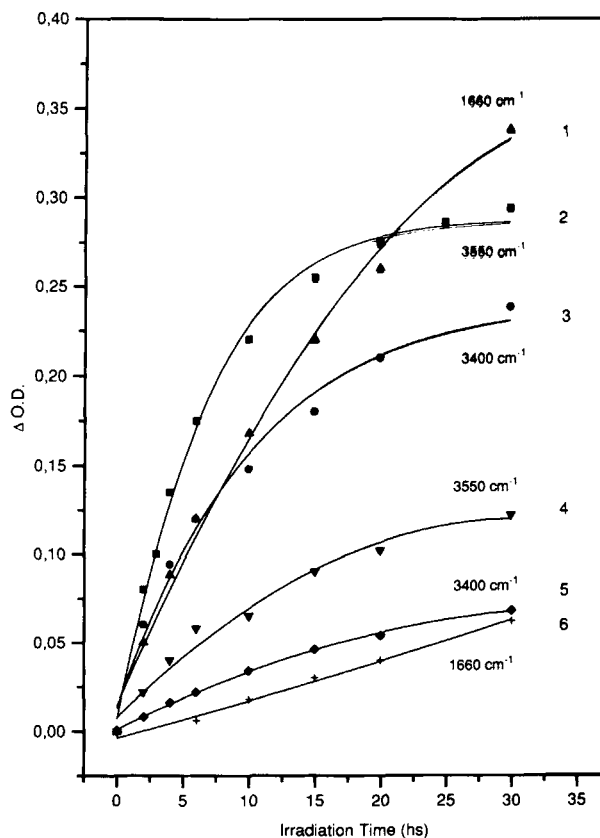

Figure 6 IR optical density variations of films of PBPP and PBPP-g-PAPH (1.49% w/w) copolymers at different wavenumbers and at various irradiation times.
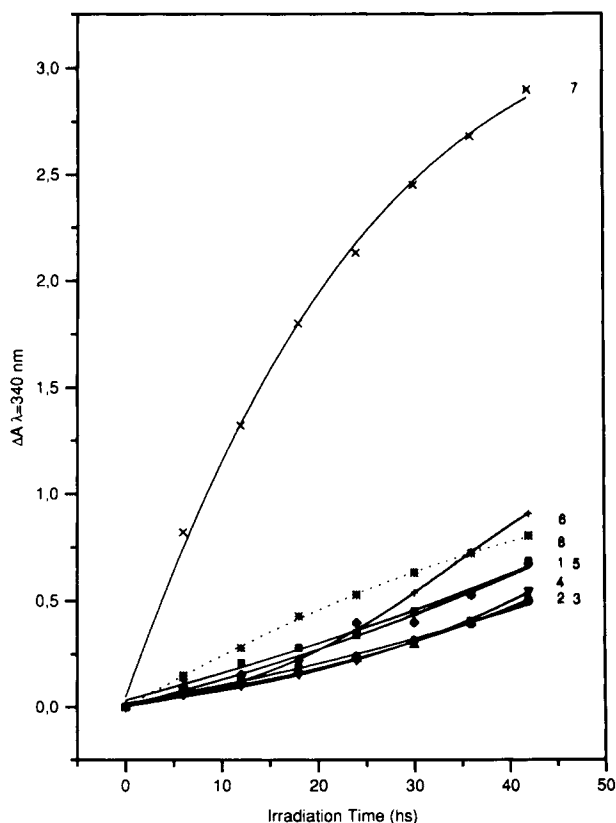
Figure 7 Optical density variations at 340 nm for different irradiation times of (curve 1) PBPP-g-PAPH (5.05% w/w), (curve 2) PBPP-g-PAPH (2.75% w/w), (curve 3) PBPP-g-PAPH (1.49% w/w), (curve 4) PBPP-g-PAPH (1.15% w/w), (curve 5) PBPP-g-PAPH (0.75% w/w), (curve 6) PBPP-g-PAPH (0.31% w/w), (curve 7) PBPP, and (curve 8) PBPP/PAPH (1.49% w/w) physical blend.

Figure 8 Optical density variations at 340 nm for different irradiation times of (curve 1) PBPP-g-PAPMe (6.5% w/w), (curve 2) PBPP-g-PAPMe (4.4% w/w), (curve 3) PBPP-g-PAPMe (3.1% w/w), (curve 4) PBPP-g-PAPMe (1.86% w/w), (curve 5) PBPP-g-PAPMe (1.20 w/w), (curve 6) PBPP-g-PAPMe (0.39 w/w), and (curve 7) PBPP.

It has been reasoned that the same species can be also formed in the case of PBPP-g-PAPH- and PBPP-g-PAPMe-grafted copolymers under irradiation and that they can induce the same photostabilization effects on PBPP, i.e., a phosphazene substrate that is known to be particularly sensitive to photooxidation processes. The first point has been proven by EPR spectroscopy carried out onto PBPP-g-PAPH- of PBPP-g-PAPMe-grafted copolymer films irradiated for 42 h. In the photooxidized films, in fact, the presence of nitroxyl radicals was detected in an amount that depends on the percentage of the grafted HALS moieties (see Table III).

The second point was demonstrated when PBPP-g-PAPH copolymer films, containing 1.49% of grafted HALS moieties, were irradiated under conditions comparable to those used for the PBPP photooxidative studies.[40] An oxidative pattern, qualitatively similar to that found for the irradiation of
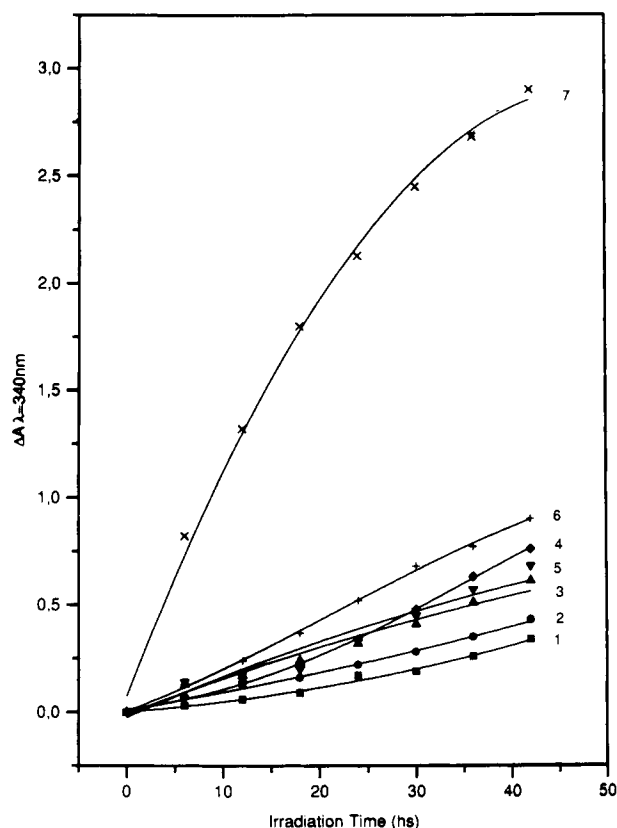
PBPP, was observed with the growth of new bands at 3550, 3400, and 1660 cm^{-1} in the IR spectrum (see Fig. 6, curves 4–6) and the onset of a new absorption at 330–340 nm in the UV region (see Figs. 7 and 8).

However, the optical density variations measured both in the IR and in the UV spectra are quanti-

Table III EPR Determination of Nitroxyl Radicals Formed on Irradiated PBPP-g-PAPH- and PBPP-g-PAPMe-grafted Copolymers

Percentage of Grafted PAPH	Percentage of Grafted PAPMe	Concentration of Nitroxyl Radicals (mol/kg × 10⁶)
0.31		261
1.49		1240
2.75		2632
	1.2	867
	1.80	955

tatively much lower than those measured during the photooxidation of neat PBPP to indicate that the HALS groups grafted onto the polyphosphazene matrix are really effective in the photostabilization of these substrates. It can be observed, moreover, that the entity of this phenomenon appears to be related to the amounts of HALS groups grafted onto the polyphosphazene system, i.e., the more elevated the quantity of HALS grafted onto the PBPP films, the higher the observed photostabilization effect (exceptions to this trend are found only in the case of heavily loaded PBPP-g-PAPH-grafted copolymers). These facts are reported in Figures 7 and 8, curves 1–6, which show the optical density variations measured at 340 nm in the UV spectra of the irradiated PBPP and PBPP-g-PAPH (Fig. 7) and PBPP and PBPP-g-PAPMe (Fig. 8) films containing HALS groups grafted in an amount between 0.3 and 6% w/w.

In both figures, the upper curve (curve "7") refers to the optical density variations measured during the photooxidation of PBPP itself, to indicate the great amount of benzophenone groups formed during this process in the polyphosphazene matrix. The lower curves (curves 1–6), on the contrary, refer to the formation of benzophenone moieties in polyphosphazene films containing variable amounts of grafted HALS groups. The comparison shows that the presence of HALS groups grafted onto the polyphosphazene system does stabilize the PBPP polymer against light damage by consistently reducing the formation of hydroperoxides and carbonyl groups even for long time exposures.

It may be worthwhile stressing that the photostabilization of PBPP induced by grafting PAPH onto this polymer, using benzophenone as a photoinitiator, is more pronounced than that obtained by simply blending PAPH homopolymers with PBPP. This is reported in Figure 7 (dotted curve 8) for a mixture of PBPP blended with PAPH (1.49% w/w) irradiated for 42 h, to be compared with the photostabilization curve 3 that refers to the photostabilization of a PBPP-g-PAPH-grafted copolymer film containing the same amount of HALS groups. Contrary to this observation, in the case of PBPP-g-PAPH-grafted copolymers obtained using BEE as a photoinitiator, the photostabilization effects observed appear to be comparable to those measured for PBPP/PAPH blends of similar composition.

These facts are not unexpected considering the different swelling degree of PBPP films in the two grafting processes (see Table I). In fact, the experiments involving the BP photoinitiator were carried out in methanol or in methanol containing a low

quantity of acetone, i.e., a reaction medium with a relatively low swelling capability for the polyphosphazene substrate, while the grafting reactions using the BEE photoinitiator were performed in neat acetone, i.e., a solvent that showed a high tendency to swell PBPP films. In the first case, the low penetration of both monomer and photoinitiator into the polyphosphazene matrix limits the grafting process to occur only in the proximity of the surface of the POP films; in the second one, the monomer and the photoinitiator molecules are allowed to penetrate deeply into the bulk of the POP substrate, thus distributing the majority of the grafted HALS residues all over the mass of the PBPP films. Similar findings were also reported for the light-induced grafting copolymerizations of poly(N,N'-dimethylacrylamide) onto PBPP and onto poly[bis(2,2',2''-trifluoroethoxy)phosphazene].[63] As the HALS groups involved in the photostabilization process are mainly those grafted close to the surface of the PBPP films,[72,73] an enhanced photostabilization effect for the PBPP-g-PAPH-grafted copolymers prepared using BP and a reduced efficiency of the same process for the copolymers prepared in the presence of BEE, in comparison to the photostabilization obtained with PBPP/PAPH physical blends, appears to be reasonable.

CONCLUSION

The light-induced grafting reaction of acrylate polymers containing pendant HALS groups (2,2,6,6-tetramethyl-piperidine and 1,2,2,6,6-pentamethyl-piperidine) leads to the preparation of phosphazene-grafted copolymers that contain very efficient photostabilizing groups, both in the bulk and on the surface of the polymer films.

The mechanism of the grafting process was investigated as a function of different experimental variables. For instance, the grafting of PAPMe onto PBPP was found to be more efficient than that of the PAPH, probably due to the enhanced capability of the former monomer to swell the phosphazene films efficiently with respect to the swelling capability of the second one. The swelling phenomena also play an important role in the grafting reaction when methanol/acetone mixtures of different compositions are used during light exposure. Equally important in determining the final yield of the grafting reaction are the type of photoinitiator (BP or BEE) used in this process, possibly due to the difference in the photoinitiating mechanisms for these two compounds and the intensity of the light

used to induce the grafting of the HALS-containing acrylate polymers onto PBPP.

The HALS residues contained in the grafted phosphazene copolymers proved to be very efficient in inducing the photostabilization of PBPP films under accelerated photooxidative degradation tests, delaying the formation of both hydroperoxide and carbonyl groups on PBPP films in a way the clearly depends on the total amount of grafted HALS groups. Finally, the comparison between the photostabilization effects induced onto PBPP by grafting HALS onto the polyphosphazene substrate or by simply blending HALS acrylate homopolymers with PBPP demonstrate the high efficiency of the first process with respect to the second one.

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