Functionalization of Polyorganophosphazenes. VII. Photooxidative Stabilization of Aryloxy-Substituted Polyorganophosphazenes Induced by Grafting HALS Groups Through Anhydride Moieties

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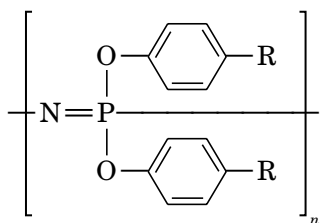
ABSTRACT: In this article, the general procedure for stabilizing polyorganophosphazenes against the damage induced in these substrates by photooxidation reactions under accelerated conditions is explored. This method is based on the preventive grafting of succinic anhydride groups onto selected polyphosphazenes induced by light excitation, followed by the reaction of the functionalized phosphazene substrates with amino-terminated HALS groups. HALS moieties, in fact, are able to strongly inhibit the photooxidation of phosphazene films under accelerated conditions even when randomly attached to the polyphosphazene materials in very low amounts. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **65:** 217–231, 1997

Key words: polyorganophosphazenes; light-induced-grafting; maleic anhydride; HALS; photooxidation; photostabilization

INTRODUCTION

Phenoxy-substituted phosphazene polymers,

where R may be H, CH_3, C_2H_5, iso-C_3H_7, *sec*-C_4H_9, and C_6H_5-CH_2, are a class of polyorganophosphazenes (POPs) that have attracted considerable attention during the past 2 decades due to their good mechanical properties,[1] fiber and film-forming capability,[2] and flame and heat resistence[3] and for their ease in undergoing functionalization reactions to produce, for instance, Rose Bengal-based photosensitizers for the heterogeneous-phase generation of singlet oxygen,[4] adhesive materials,[5,6] polymers supporting epoxide units,[7] oxidized film surfaces containing free carboxylic functions,[8] heparinized phosphazene film surfaces for biomedical applications,[9,10] and polyphosphazene copolymers containing grafted polystyrene,[11] methyl methacrylate,[12] *NN'*-di-

methylacrylamide,[13] glycidyl methacrylate,[14] 4-vinylpyridine,[14,15] acrylic and methacrylic acids,[15] vinyl acetate,[16] or succinic anhydride (SA) groups.[5,17-19]

This last functionalization of aryloxy-substituted phosphazene macromolecules was accomplished using the radical-induced solution grafting reaction of maleic anhydride (MA) onto these macromolecules to form phosphazene copolymers that have the following chemical structure:
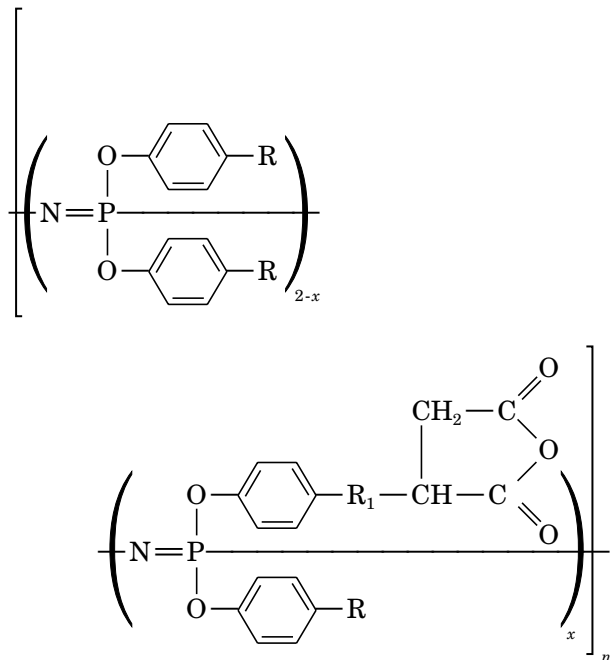
where "x" represents the percentage of grafted anhydride groups, R is as before, and R_1 may be CH_2, CH_3CH, $CH_3—C—CH_3$, $CH_3—C—C_2H_5$, and C_6H_5CH in which variable amounts of SA residues are present in the material as side pendant groups. It was found, moreover, that this grafting reaction is always accompanied by a strong decrease in the molecular weight of the polyphosphazene substrate due to the concurrent onset of skeletal degradative phenomena that may be an important drawback for the overall grafting process.[17,18]

It is interesting to observe that all the above-reported chemical modifications of the phosphazene structures derive from the chemical reactivity of the alkyl group present in the *para* position of the phosphazene side substituents. The same group, moreover, also seems to be responsible for the photooxidative phenomena that have been observed by irradiating, for instance, poly[bis(4-benzylphenoxy)phosphazene] (PBPP)[20] and poly-
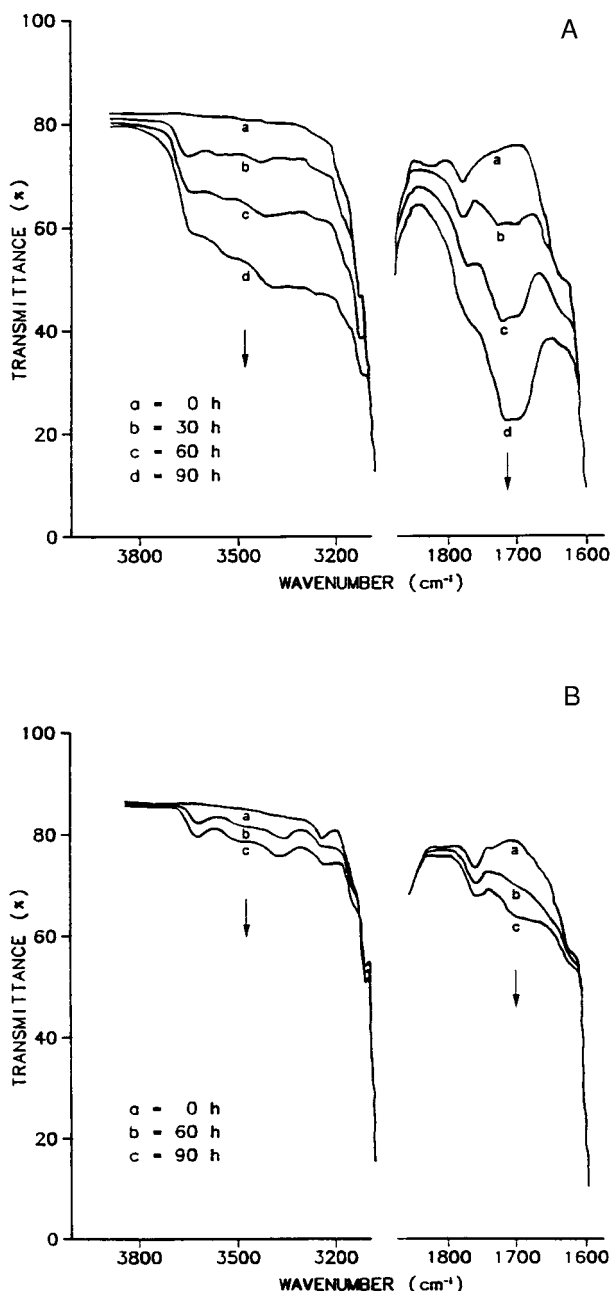
Figure 1 IR spectral variations of a film of PMPP: (A) pristine material; (B) polymer containing 0.4% w/w of T10 HALS groups under accelerated photooxidative conditions.

[bis(4-isopropylphenoxy)phosphazene] (PiPP)[21] films under accelerated conditions.

Starting from the two, above-reported, considerations (i.e., the molecular weight decrease observed during the grafting process of MA groups onto aryloxy-substituted POPs and the presence of photooxidative phenomena in these materials),

we undertook investigations on a series of phosphazene polymers in order to

(a) Study the photooxidative processes of these polymers in films;

(b) Use the light to induce the grafting reaction of MA onto selected POPs in the presence of suitable photosensitizers, with the aim of minimizing the risk of phosphazene chain degradability, thus preserving both the molecular weight and the mechanical properties of the polymer for longer service periods;

(c) Exploit the reactivity of the grafted SA groups to react with amino-terminated HALS groups, as HALS moieties are known to be very effective photostabilizers for polyolefins[22–25] and POPs[26,27]; and

(d) Investigate the photooxidative stabilization effect induced by the presence of these hindered piperidine moieties on the polyphosphazene substrates.

The POPs selected for this work have the following chemical structure:

**PMPP**   **PEPP**

PiPP   **PsBPP**

PBPP
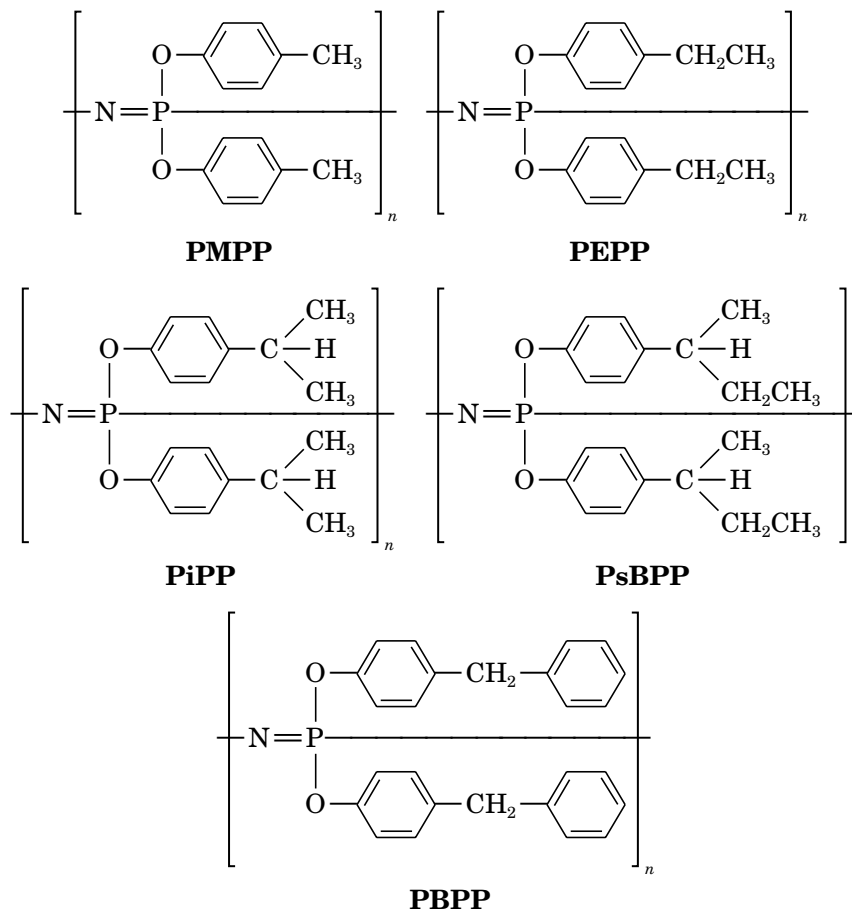
in which an alkyl or an alkylaryl group is always present in the *para* position of the phenoxy side substituents.

EXPERIMENTAL

The 4-methylphenol, 4-ethylphenol, 4-isopropylphenol, 4-*sec*-butylphenol, and 4-benzylphenol used were Aldrich products, purified by vacuum sublimation or distillation prior to use or dried by azeotropic distillation from xylene solutions. Maleic anhydride (MA), succinic anhydride (SA), benzoin ethyl ether (BEE), and NaH 60% oil dispersion (Aldrich) were used as received. Tetrahydrofuran (THF), dioxane, methanol, ethanol, toluene, xylene, and *n*-heptane were Carlo Erba analytical-grade solvents, purified or dried according to the literature.[28] HALS residues grafted onto the SA–anhydride-containing poly[bis(4-methyl-

phenoxy)phosphazene] were Ciba Geigy intermediates, of the following structure:

NH—(CH$_2$)$_6$—NH$_2$ T10

NH—(CH$_2$)$_2$—NH$_2$ T12
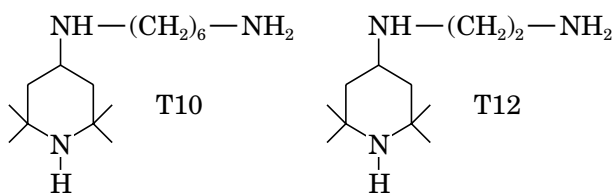
used as received.

The poly[bis(4-methylphenoxy)phosphazene] (PMPP),[4,29] poly[bis(4-ethylphenoxy)phosphazene] (PEPP),[17,29] poly[bis(4-isopropylphenoxy)phosphazene] (PiPP),[30–32] poly[bis(4-sec-butylphenoxy)phosphazene] (PsBPP),[5] and poly[bis(4-benzylphenoxy)phosphazene] (PBPP)[33,34] were prepared by reacting polydichlorophosphazene, (NPCl$_2$)$_n$, with the appropriate 4-alkylphenate (as obtained by the reaction of the corresponding phenol with NaH 60% oil dispersion) in the presence of phase-transfer catalysts.[35] The polymers obtained were purified by repeated precipitations from distilled THF in water, methanol, and n-heptane, in this order, and vacuum-dried for a few days. The final yields ranged around 60%, as calculated starting from the original polydichlorophosphazene.

The hexachlorocyclophosphazene, (NPCl$_2$)$_3$, was purchased from Shin Nissho Kako, and was, in turn, purified by repeated precipitations from hot hexane followed by vacuum sublimations until the melting point of 113°C was reached.[36] The product was successively polymerized in Pyrex ampules sealed under vacuum at 250°C for several hours, was freed of the residual, unreacted trimer by vacuum sublimation, according to literature,[35,37–39] and then reacted with suitable phenate groups.

The grafting reaction of MA onto POPs was carried out by dissolving 50 mg of selected POPs in 1 mL of toluene, in the presence of MA (17 mg = 1.73×10^{-4} mol), and by irradiating this mixture with light of wavelengths longer than 350 nm (cutoff filters), using a Pyrex cell 10 mm thick, and in the presence of BEE as a photosensitizer (17 mg = 7.1×10^{-5} mol). The functionalized phosphazene copolymers prepared according to this procedure were purified by precipitation in chilled methanol and quick-dried in a vacuum. The quantitative determination of the grafted anhydride groups was performed by infrared spectroscopy, using POP-g-SA-grafted copolymer films deposited onto KBr pellets, as previously reported.[5,17–19] Free-standing films of anhydride-functionalized phosphazene copolymers, POP-g-SA, as obtained by casting from CH$_2$Cl$_2$ solutions, were successively swollen in anhydrous toluene and then reacted with the above-described, amino-terminated, HALS groups, T10 and T12, according to the literature.[18,40]

The photooxidation[20,21] and the photostabilization experiments of polyphosphazene films were carried out at 50°C under accelerated weathering conditions in a Sairem-Sepap apparatus (Material Physico Chimique, France) equipped with four medium-pressure mercury lamps of 400 W each, filtered by a borosilicate glass bulb (λ_{exc} > 300 nm) simulating the outdoor sun exposure.

The measurements of the intrinsic viscosity [η] of tetrahydrofuran polyphosphazene solutions at 20°C, before and after the light-induced grafting of MA groups, were carried out using a suspended level Desreux-Bischoff-type viscosimeter.

For the light-induced grafting experiments, Hanau 150 W, high-pressure mercury lamp was used for irradiation, equipped with cutoff filters at wavelengths longer than 350 nm. The UV and IR characterizations of both pristine and modified phosphazene films were carried out using a 320 and a 399 Perkin-Elmer spectrophotometer, respectively. NMR characterization of the polymers was performed using a Bruker 200 AC (^{13}C-NMR) and a Varian FT 80 (^{31}P-NMR) spectrometer as previously reported.[5,17,18]

The gas chromatographic/mass spectrometric data were obtained using a Carlo Erba spectrometer Model QMD 1000 using a PS 264 capillary column of 30 m in length (temperature from 100 to 280°C; 10°C/min, He 1 mL/min).

RESULTS AND DISCUSSION

Photooxidation of Aryloxy-substituted Polyphosphazenes Under Accelerated Conditions

The photooxidation of PBPP[20] and of PiPP,[21] i.e., of aryloxy-substituted phosphazene polymers containing secondary and tertiary hydrogen atoms in the *para* position of the phenoxy substituents, have been already reported. In these studies, it was proved that films of POPs irradiated under accelerated conditions with light of wavelength longer than 300 nm undergo considerable photooxidation processes that induced the yellowing of the phosphazene films and the onset of photoreticulation and insolubilization phenomena. In this
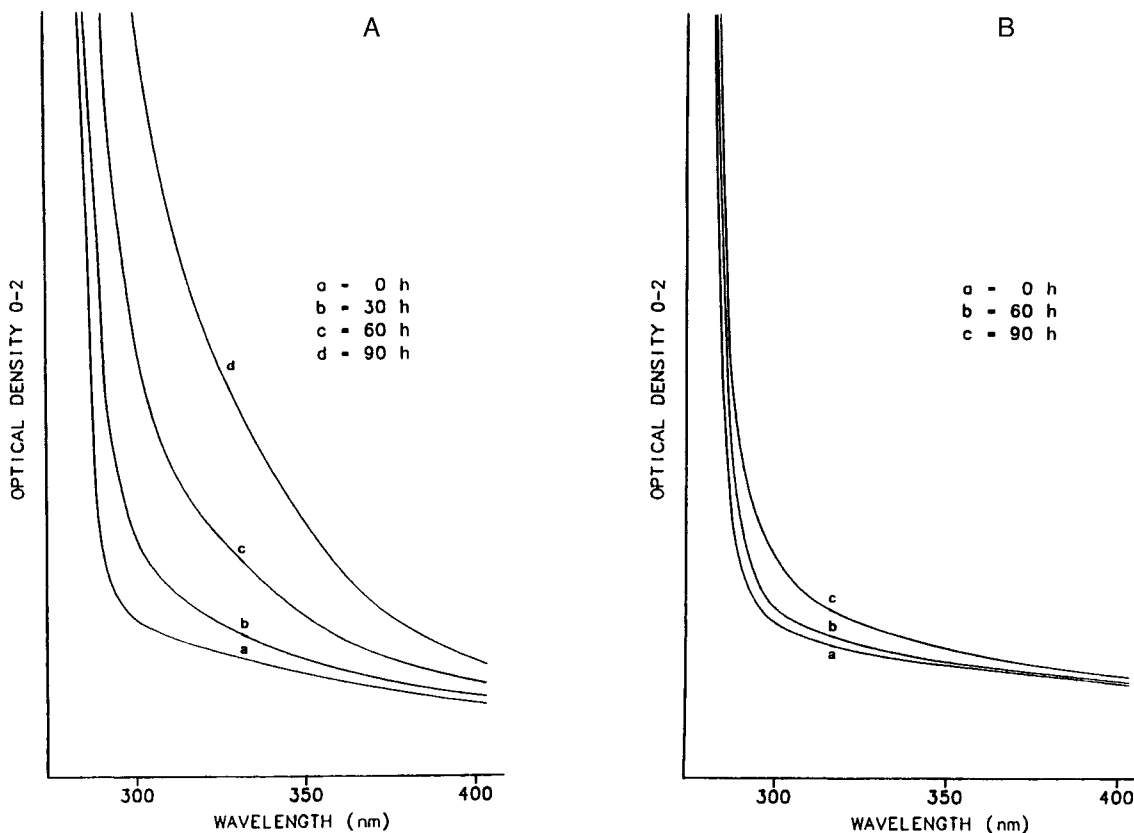
Figure 2   UV spectral variations of a film of PMPP: (A) pristine material; (B) polymer containing 0.4% w/w of T10 HALS groups under accelerated photooxidative conditions.

article, we present the results of our investigations on the photooxidation experiments of PMPP (i.e., a polymer that bears primary hydrogen atoms only) films (7 μ thick) carried out under accelerated conditions.

The corresponding spectral (IR and UV) optical density variations are reported in Figure 1(A) and (B) and in Figure 2(A) and (B), respectively. The IR spectrum of the original PMPP film [Fig. 1(A), curve a] and that of the PMPP films irradiated for 30, 60, and 90 min [Fig. 1(A), curves b, c, and d, respectively], indicated[41] that several new bands are formed under light exposure at 3650–3100 cm^{-1} (ν alcoholic and/or hydroperoxidic groups), 1780 cm^{-1} (ν C=O peracids), 1725 cm^{-1} (ν C=O of aromatic esters or benzoic acid dimers), and 1700 cm^{-1} (ν C=O of benzaldehyde carbonyl groups). Moreover, the UV spectrum of the same films shows a general increase in the optical density coupled with the shifting of the absorption toward the visible (up to about 450 nm), suggesting the formation of oxidation products of the 4-methylphenoxy substituents along the phosphazene skeleton.

All these facts can be rationalized in terms of reaction Scheme 1. In this scheme, PMPP films, irradiated under accelerated conditions, may decompose, releasing hydrogen or methyl radicals as a primary step, forming the macroradicals (**1**) and (**6**), respectively. These reactions may be followed by oxygen uptake with the formation of the hydroperoxides (**2**) and (**7**), from which the photochemical cleavage of the hydroperoxide moieties leads to the formation of the phosphazene macroradicals (**3**) and (**8**), respectively. The release from (**8**) of benzoquinone molecules[31,32] to form the phosphazene macroradical (**9**) may account for the yellowing of the phosphazene films upon irradiation. On the contrary, the macroradical (**3**) can be stabilized by reacting with a hydrogen radical to form the macroalcohol (**4**), whose successive modification by oxidation reactions produces phosphazene-supported benzaldehyde groups (**5**). Further oxidation steps from this product led to the formation of peracids, benzoic acids dimers, or aromatic esters, as confirmed by the signals observed in the IR spectra, already discussed in previous publications.[20,21]
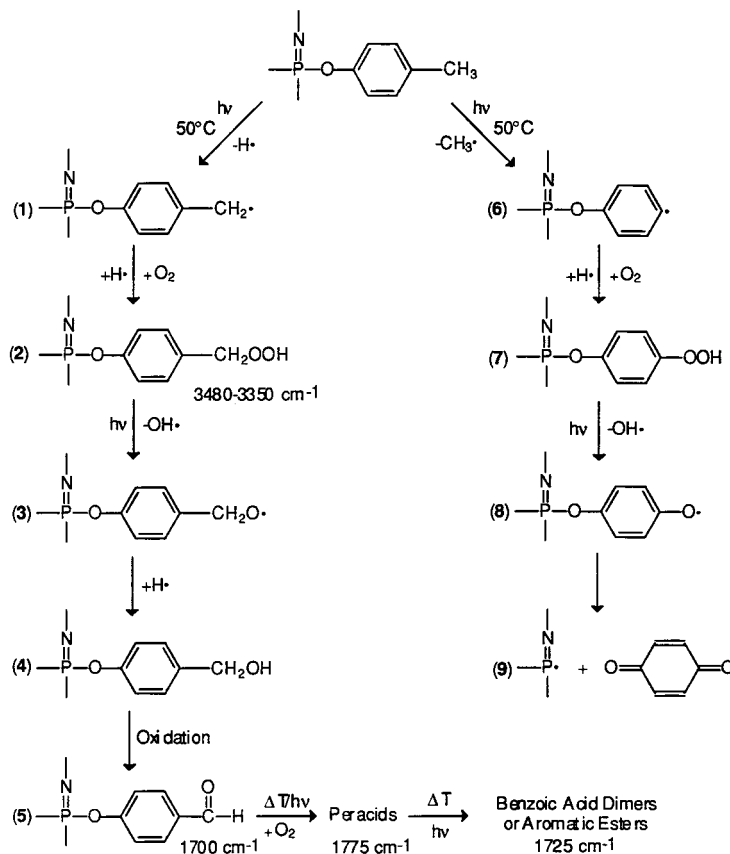
Scheme 1

The coupling reactions of the phosphazene macroradicals (**1**), (**3**), (**6**), (**8**), and (**9**) may reasonably account for the observed extensive cross-linking of the phosphazene films. It may be worth stressing that the proposed mechanism for the oxidative modifications of PMPP is in agreement with previous results concerning the photooxidation of PBPP[20] and PiPP[21] and that it is supported by experimental findings coming from the thermal[42] and photochemical[43] modification of organic polymers containing methyl–phenyl moieties.

Light-induced Grafting Reactions of Maleic Anhydride onto Aryloxy-substituted Phosphazene Polymers

During the last decade, the possibility of functionalizing phosphazene macromolecules through the introduction of anhydride[5,17–19] or ester[44] groups has been deeply investigated in our institute by exploiting the chemical reactivity of the alkyl groups present in the *para* position of the phenoxy side substituents of selected POPs.

The functionalized POPs prepared show very important modifications to their chemical reactivity (especially toward —OH- and —NH₂-terminated organic substrates[17,18,40]) accompanied by changes in physical properties, e.g., solution viscosity, molecular weight, and crystallinity. In particular, we explored the functionalization reaction of PsBPP,[5] PEPP,[17] PMPP,[18] PiPP,[19] and PBPP,[19] whose thermally induced grafting of MA does form the corresponding phosphazene-grafted copolymers containing variable percentages of grafted SA groups, but, concurrently, brings about the strong modification of the polymer solution viscosity and the collapse of the molecular weight. These phenomena were preferentially observed at high reaction temperatures and/or with long reaction times.

To overcome this problem and to introduce anhydride residues into the phosphazene substrates without modifying the molecular weight of these materials, we decided to investigate the photochemical grafting of MA onto several different aryloxy-substituted POPs at room temperature and in the presence of suitable photoinitiators.

The measurements were carried out by dissolv-

ing 50 mg of five different phosphazene polymers (PMPP, PEPP, PiPP, PsBPP, and PBPP) in aerated toluene at room temperature (20°C) in the presence of MA as an unsaturated monomer and BEE as a photoinitiator and irradiating the solution at $\lambda_{exc} > 350$ nm (cutoff filter) for variable periods of time (sometimes, the diffusive degassing of the system to eliminate molecular oxygen and to maximize the grafting effect was also adopted).

The NMR (^{13}C and ^{31}P) and IR spectroscopic characterization data for one of the exploited phosphazene substrates, PiPP, are reported in Tables I and II. In the same tables, moreover, the NMR and IR characterization data of the same phosphazene polymer functionalized with anhydride groups using thermal peroxides initiators[40] are presented for comparison purposes.

As can be seen from these tables, the reported experimental findings for PiPP samples functionalized with two independent methods are almost superimposable (see, in particular, the two ^{13}C-NMR peaks at 169.62 and 171.47 ppm and the two IR bands at 1785 and 1870 cm^{-1}, attributed to the carbonyl functions of the anhydride groups). We have to conclude, therefore, that the grafting reactions of MA onto PiPP carried out using both the thermal or the photochemical initiation procedure led to the preparation of the same functionalized polymers, whose structure for the thermally initiated grafting reactions, already assigned in previous publications,[5,17–19,40] is reported below:

Table I   NMR Characterization Data Obtained for the Thermally and the Photochemically induced Grafting Reactions of MA onto PiPP

| Thermally Functionalized PiPP	Photochemically Functionalized PiPP
^{13}C-NMR	
C(1): 149.51	149.66
C(4): 143.28	143.14
CH(5): 39.82	39.75
CO(6): 169.67	169.62
CO(7): 171.46	171.47
CH$_2$(8): 27.41	28.13
CH(9′): 33.20	33.24
CH$_3$(10,10′): 23.98	23.96
^{31}P-NMR	
−19.02	−19.1

Table II   IR Characterization Data for the Thermally and the Photochemically Induced Grafting Reactions of MA onto PiPP

IR (cm^{-1})	
Thermally Functionalized PiPP	Photochemically Functionalized PiPP
3040 ν CH aromatic	3040
2960–2870 ν CH alifatic	2960–2870
1870, 1785 ν C=O	1870, 1785
1610–1510 ν C—C aromatic	1610–1510
1250–1200 asymmetric ν of skeletal —P=N—	1250–1200
945 (ν P—O—Ph)	945
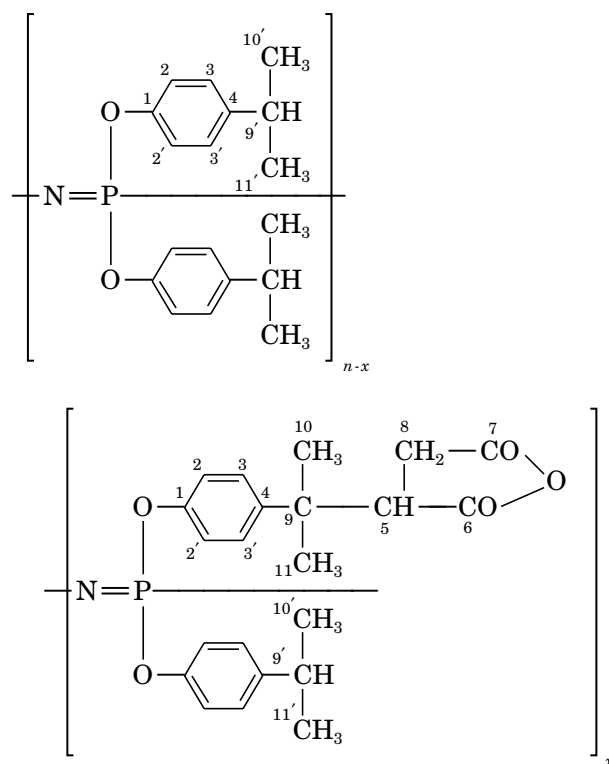
Due to the considerable complexity found in the mechanism of the thermally induced grafting reaction of MA onto POPs,[5,17–19] a reaction that was found to depend on several different experimental parameters, we decided to expand our studies on the light-induced grafting process of MA onto POPs by investigating the influence of the MA and the BEE concentration in the system, the molecular oxygen, and the type of phosphazene phenoxy substituents on the overall grafting yield of anhydride groups.

The influence of the MA and BEE content in
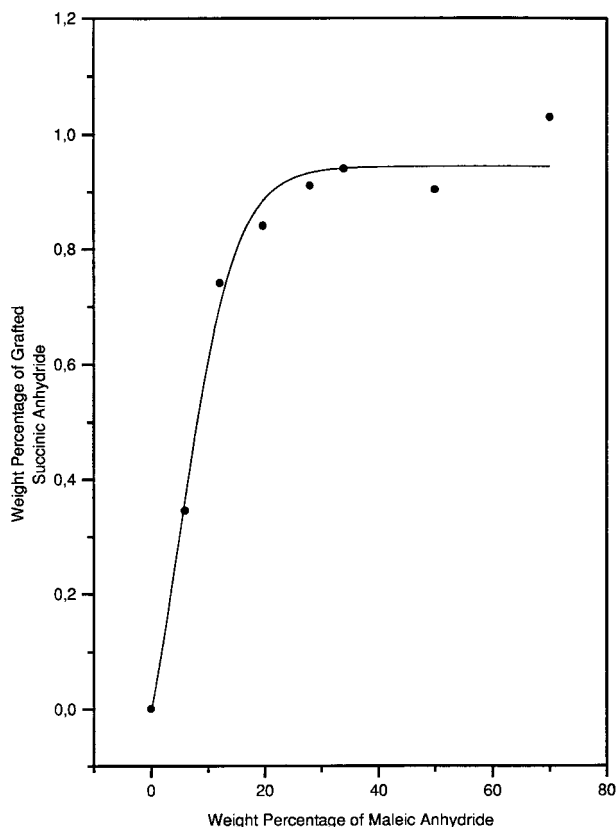
Figure 3 Influence of the weight percentage of MA on the weight percentage of SA grafted onto PsBPP in aerated solutions, after 80 min of irradiation.

the reaction mixture on the total yield of grafted succinic anhydride groups is illustrated in Figures 3 and 4 where we plotted the weight percentage of grafted MA vs. the weight percentage MA and BEE in the system, respectively, for the light-induced grafting reaction of MA onto PsBPP. As can be seen from these figures, the initial quantity of grafted SA constantly increases following the increase of MA or BEE concentrations in the reaction mixture, until a plateau is obtained. After this point, no further enhancement of the grafting yield is observed even after considerable additions of MA or BEE to the reaction mixture.

It may be interesting to observe that the comparison between the thermally[5] and the photochemically induced grafting reactions of MA onto PsBPP reveals that this latter process appears to be considerably less efficient than the former, the amount of the final SA residues grafted photochemically being roughly one-third of the corresponding groups thermally attached to the polyphosphazene substrate.

The effect of the molecular oxygen present in

the irradiated mixture for the light-induced grafting reaction of MA onto POPs was measured for aerated and deaerated toluene solutions of PEPP and PsBPP, and the corresponding results are reported in Figures 5 and 6. These figures show that molecular oxygen plays an important role in the photochemical grafting of anhydride groups onto POP substrates, in the sense that the presence of oxygen molecules leads to the observed strong decrease in the grafting efficiency of SA onto PEPP and PsBPP. According to our previous findings on the thermally induced grafting of MA onto PEPP[17] and on the reported negligible influence of molecular oxygen on the reactive excited states of photoinitiators that are reactive following a photofragmentation process,[45] this quenching effect has to be attributed to radical reactions that take place in the solution between oxygen itself and solvent or initiator radicals, which substract chemical species active in the grafting process, thus depressing the overall grafting yield.

Once again, the amount of SA residues grafted
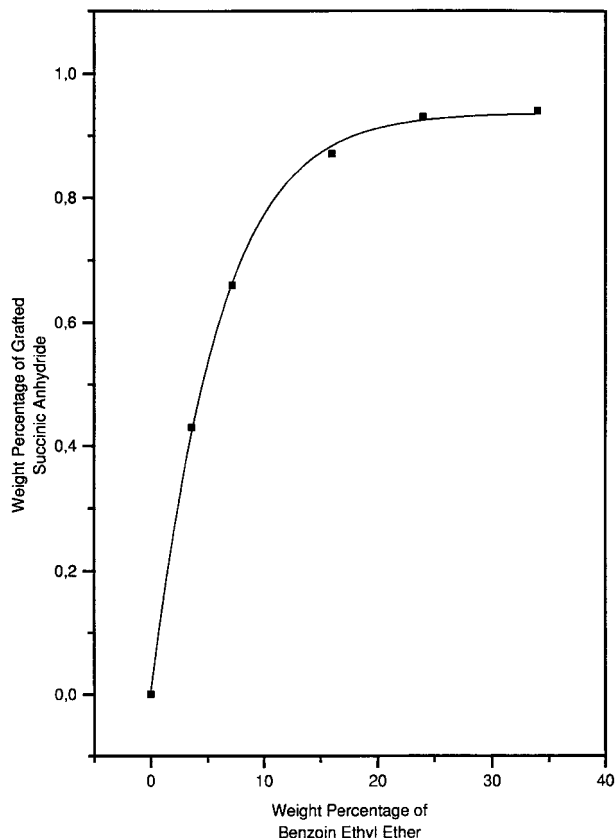
Figure 4 Influence of the weight percentage of BEE on the weight percentage of SA grafted onto PsBPP in aerated solutions, after 80 min of irradiation.
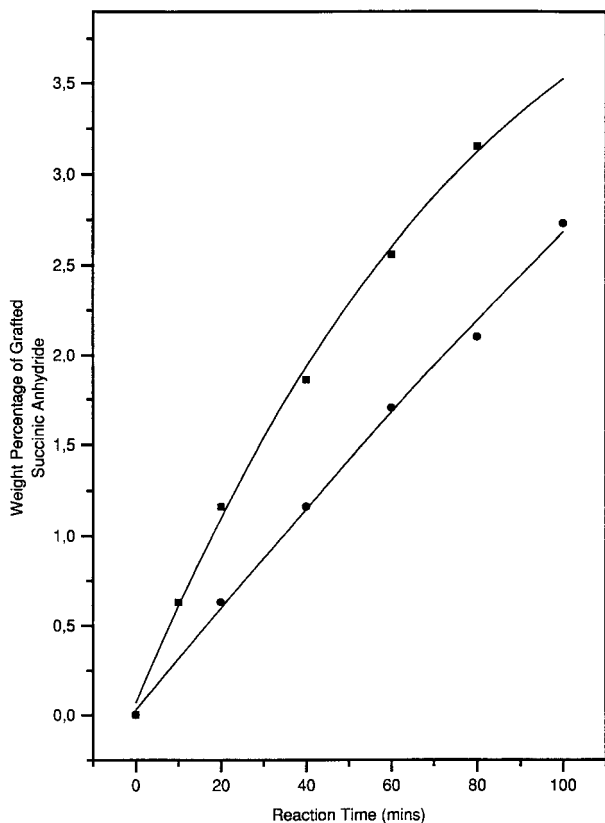
Figure 5 Influence of the reaction time on the weight percentage of SA grafted onto PEPP: (●) aerated solutions; (■) degassed solutions (10^{-2} Torr).

photochemically in these POPs is about one-third of the quantity of anhydride moieties grafted by thermal methods.[17] The influence of the nature of the phosphazene phenoxy substituents on the overall grafting of MA groups onto MA onto PMPP, PEPP, PiPP, PsBPP, and PBPP was investigated by dissolving these polymers in toluene, in the presence of BEE as a photoinitiator, and irradiating the resulting solutions with light of wavelengths longer than 350 nm, in the absence of oxygen and at room temperature.

The corresponding results are reported in Figure 7. As can be seen from this figure, each curve is characterized by the constant enhancement of the amount of the grafted SA groups with an increase in the reaction time. Moreover, the alkylphenoxy substituents present in the POPs exploited for the light-induced grafting reaction have a strong influence on the overall grafting yield of SA on these substrates, the experimentally measured reactivity order being as reported below:

PEPP > PiPP > PsBPP > PBPP > PMPP

It may be interesting to stress that the above-reported reactivity trend for the light-induced grafting reaction of MA onto different POPs closely parallels the reactivity sequence found for the same grafting process initiated thermally, using peroxide groups (benzoyl peroxide, for instance).[19] It should be mentioned, moreover, that aerated toluene solutions of the phosphazene macromolecules exploited for this work showed no intrinsic viscosity modifications for irradiations of 80 min under the above-reported experimental conditions, indicating that the light-induced grafting reaction of MA onto these substrates does not modify the molecular weight of the irradiated POPs, even for long illumination times.

As far as the mechanism of the light-induced grafting reaction of MA groups onto POPs is concerned, it may be observed that the interaction between UV light and MA is reported to induce, among others, the following types of reaction:

1. The photodimerization process of MA mol-
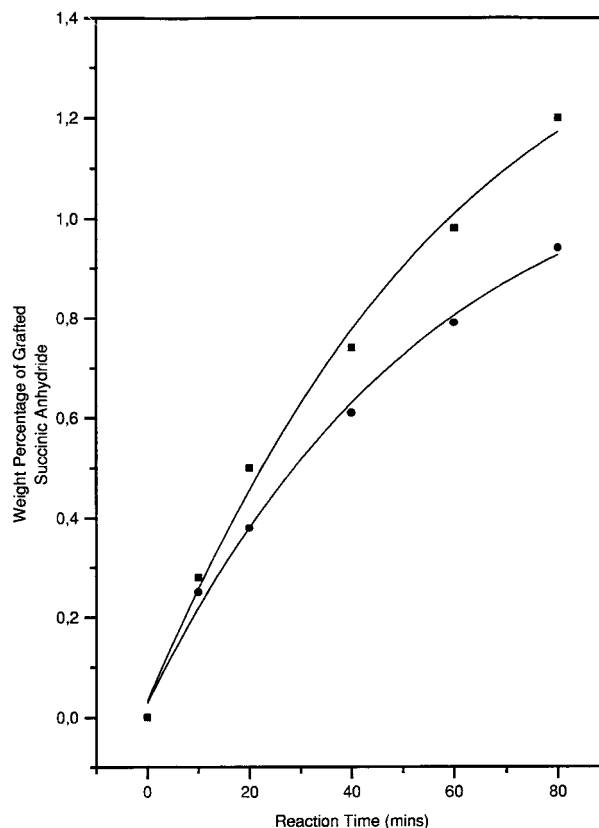
Figure 6 Influence of the reaction time on the weight percentage of SA grafted onto PsBPP: (●) aerated solutions; (■) degassed solutions (10^{-2} Torr).
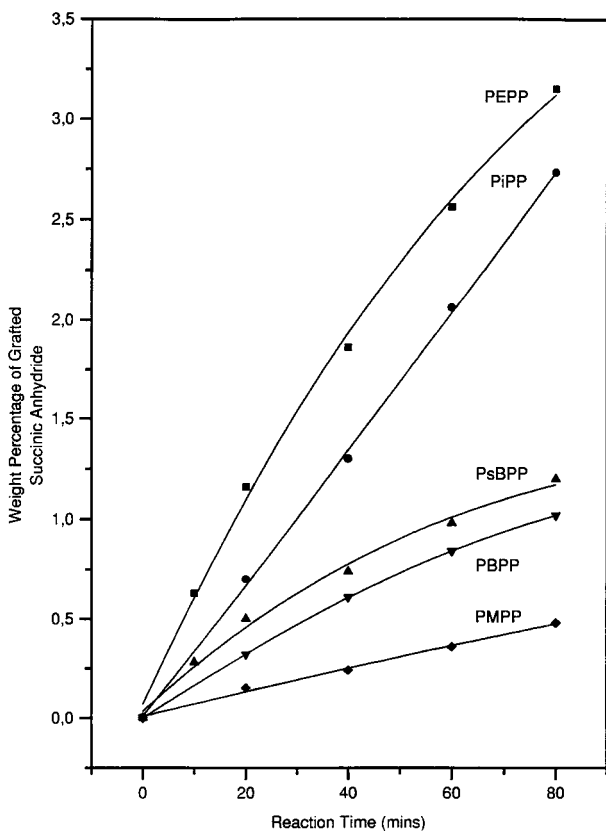
Figure 7 Influence of the phosphazene side substituents on the weight percentage of grafted SA in degassed solutions (10^{-2} Torr).

ecules when dissolved in carbon tetrachloride.[46–48]

2. The homopolymerization processes of MA induced by UV irradiation, sometimes in the presence of suitable sensitizers.[49–52]

3. The light-induced copolymerization processes of MA with styrene,[53–55] 2-vinylnaphthalene,[56] vinyl acetate,[57] cyclohexene,[58] and other unsaturated monomers.

4. The [2 + 2] photoaddition of MA to the aromatic ring of benzene, followed by the [4 + 2] thermal addition of a second anhydride molecule to the functionalized benzene, to eventually form a 2 : 1 adduct between these two species[59–61]; similar reactions have also been observed for the photochemical reaction that takes place between MA and benzene-containing organic macromolecules (polystyrene,[62,63] for instance) after 25–50 h of light exposure, depending on the type of irradiated substrate;
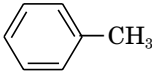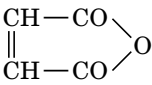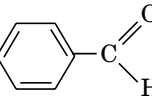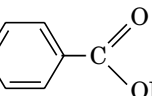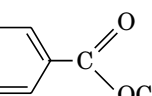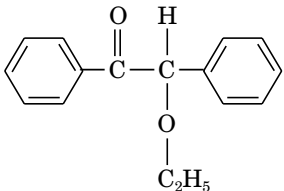
5. The photochemical addition of MA to or-

ganic polymers containing unsaturated double bonds, e.g., 1,2- or 1,4-polybutadiene,[64] which is a process that efficiently occurs only if an olefinic structure is present in the polymer structure, to indicate that a cycloaddition reaction is, at least in part, responsible for the process, although additional evidence points toward the contribution of a chain mechanism. In principle, almost all these processes are possible in our reaction mixture containing the phosphazene polymer, the MA, the BEE photoinitiator, and the aromatic solvent.

To shed some light on the mechanism of the light-induced grafting reaction of MA onto POPs in the presence of the BEE photoinitiator, we carried out a series of photochemical experiments designed to obtain additional information about this process. We first irradiated the toluene solution of BEE and MA, not containing phosphazene substrates, using the same reaction conditions previously exploited for the grafting process of MA onto POPs (i.e., $\lambda_{exc} > 350$ nm, cutoff filters, and room temperature), and we analyzed the obtained reaction mixture by gas chromatography/mass spectrometry to identify the products formed in this reaction. A list of these substances is reported in Table III.

From this table, it is evident that, besides the original toluene solvent, unreacted MA, and residual BEE, the other identified products are benzaldehyde, benzoic acid, and ethylbenzoate, mainly derived from the primary photofragmentation of the BEE photoinitiator, followed by further addition or oxidation modification reactions. Another product formed, i.e., the 1 : 1 adduct between the toluene solvent and MA, was identified in an extremely low quantity and it was not possible to attribute its structure on the basis of the mass spectrometric fragmentation pattern. Moreover, no 2 : 1 adducts between MA and toluene were detected.

A second series of photochemical experiments, carried out utilizing PsBPP dissolved in toluene or xylene solvents ($\lambda_{exc} > 350$ nm) containing only MA molecules but not the BEE photoinitiator, showed that no grafting reactions of MA onto the polymers took place under these experimental conditions; this suggests that charge-transfer (CT) complexes between aromatic solvents and MA, if present, are completely unable to promote

Table III Gas Chromatographic/Mass Spectrometric Identification of the Reaction Products Obtained by Irradiating BEE and MA in Toluene with Light of $\lambda_{exc} > 350$ nm, at Room Temperature

| Identified Products	Chemical Structure	m/z
Toluene		91
Maleic anhydride		98
Benzaldehyde		99
Benzoic acid		122
Ethylbenzoate		150
Benzoin ethyl ether		240
1 : 1 adduct MA/toluene	Not identified	183

the light-induced grafting reaction of MA onto the polyphosphazene substrate.

In the light of these considerations it may be concluded that

(a) The above-reported photochemical reactions of MA, i.e., processes (1), (2), and (3), must be ruled out as possible reactions that contribute to the light-induced grafting of MA onto POPs because of the lack of the formation of MA dimers, homopolymers, and copolymers, respectively; in our photochemical experiments, furthermore, no unsaturated polymers containing olefinic bonds were present in the reaction mixture; this makes the previously reported reaction (5) impossible under our conditions.

(b) The photoreaction (4) must be also discarded because no 2 : 1 MA/toluene adduct molecules were detected in the reaction mixture by GC/MS measurements.

(c) The CT complexes between MA and aromatic solvents are ineffective in contributing toward the photochemical initiation of the MA grafting process under our experimental conditions.

(d) The reactivity order found for the thermally induced grafting process of MA onto different aryloxy-substituted phosphazene polymers[19] is completely similar to that found for the corresponding photochemical reaction of MA onto the same series of POPs, suggesting that the same thermodynamic (the presence in the polyphosphazene of substituents that bear primary, secondary, and tertiary labile hydrogen atoms) and the steric (accessibility of the anhydride radicals toward the phosphazene macroradicals) factors are operative in both reactions; furthermore, these data are in agreement with the results reported by Ciardelli and co-workers[65] on the reactivity of primary, secondary, and tertiary hydrogen atoms in polyolefins, and

(e) The IR and NMR spectroscopic findings for both the thermally and the photochemically induced grafting reaction of MA onto PiPP clearly indicated that these reactions led to the formation of macromolecules having identical structure.

Therefore, the only reasonable explanation that can be put forward to account for the observed experimental findings on the light-induced grafting process of MA onto POPs deals with a reaction mechanism similar to that previously hypothesized for the same process induced thermally onto both polyphosphazene substrates[5,17–19,66] and organic macromolecules,[67,68] which is reported in Scheme 2.

Following the proposed scheme, the primary photochemical event of the grafting process is the photofragmentation reaction of the BEE photoinitiators (Norrish Type I cleavage[45]) to form benzoyl and ethoxybenzyl radicals that are able to abstract hydrogens from the alkyl radicals of the phosphazene phenoxy substituent, forming phosphazene macroradicals from which, eventually, the grafting of MA molecules can take place. The obtained macromolecules, which contain a grafted SA radical, may abstract hydrogens from the sol-
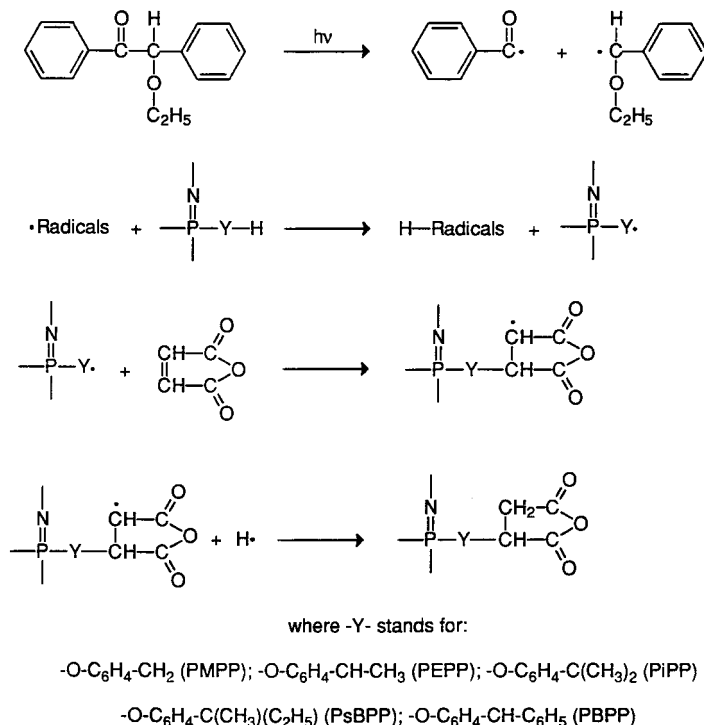
Scheme 2

vent, impurities, or the polymer itself, to finally stabilize the functionalized POPs.

It may be worth considering that the use of benzophenone as a photosensitizer to initiate the light-induced grafting of MA onto POPs gave very poor results, the grafting process being accessible in a reasonable yield in the presence of BEE only. This is not unexpected, due to the fact that benzophenone is a photoinitiator active by a hydrogen abstraction mechanism, whose reactive state (T_1) can be effectively quenched by low-lying excited triplets of suitable quenchers (e.g., MA[62]) by physical energy transfer processes. BEE, on the contrary, is a photoinitiator that produces radicals via a photofragmentation process and is, therefore, able to form the reactive species responsible for the initiation of the light-induced grafting of MA onto POPs quite efficiently. Similar results have previously been achieved in the case of the light-induced grafting of 4-vinylpyridine onto PBPP sensitized by BP and BEE.[15]

Grafting Reactions of Hindered Amines Light Stabilizers (HALS) onto Anhydride Functionalized POPs

The attachment of HALS groups to polyphosphazene substrates was achieved by treating SA-con-

taining phosphazene films, obtained as reported above, with toluene solutions of amino-terminated HALS molecules (T10 and T12 Ciba Geigy intermediates). Toluene solvent, in fact, is able to swell the polyphosphazene films, thus allowing the photostabilizer molecules to penetrate inside the polymer bulk and to react with the anhydride units present in these systems, according to the reaction sequence in Scheme 3.

The formation of HALS-containing phosphazene macromolecules is supported by infrared spectroscopic data, since in the spectrum of these
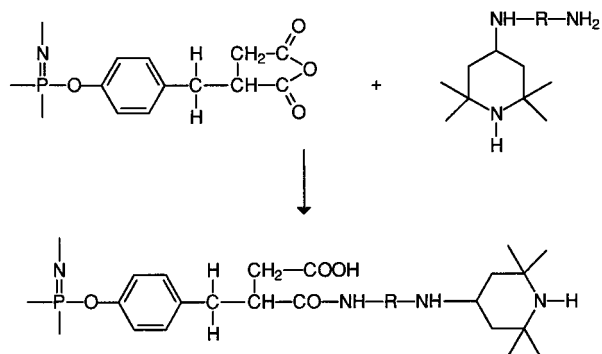
Where R stands for $(CH_2)_2$ or $(CH_2)_6$

Scheme 3

substrates we can find bands at 1640 cm^{-1} (ν —CO—NH—) and at 3400–3200 cm^{-1} (ν —NH—) attributed to the attached piperidine groups, while the bands at 1870 and 1785 cm^{-1}, assigned to the stretching of anhydride carbonyl groups,[5,17,18] completely disappeared. It must be stressed, furthermore, that an approach to the photooxidative stabilization of an acrylonitrile–EPDM–styrene terpolymer by grafted HALS groups through anhydride moieties, similar to that above described for phosphazene materials has been previously reported.[69]

Photooxidative Stabilization Experiments of Poly[bis(4-methylphenoxy)phosphazene] Containing Grafted HALS Groups

The problem of the photochemical stabilization of POPs has already been explored in our institute by considering the possibility of deactivating the excited states of reactive chromophores attached to the phosphazene backbone (e.g., benzophenone) by energy-transfer processes using both free[70] and phosphazene-bonded[71] quencher substrates. Alternatively, the photooxidative stabilization process of PBPP[20] was achieved by light-induced grafting acrylate polymers containing HALS groups onto the phosphazene matrices.[26]

Expanding upon this research, we decided to investigate the photooxidative stabilization effects of selected POPs containing HALS groups in their structure grafted through anhydrided residues (*vide supra*). In fact, films of phosphazene macromolecules containing variable quantities of grafted HALS stabilizers were irradiated under accelerated conditions and the corresponding results compared with the photooxidative processes of the pristine, unstabilized POPs.[20,21]

As an example, in Figures 1(B) and 2(B), we reported the IR and UV spectral variations of PMPP films containing 0.4% (w/w) of T10 HALS residues grafted onto the polymer. Both figures show that prolonged light exposure of functionalized phosphazene films led, from a qualitative point of view, to the formation of oxidation products that shift UV absorption toward the visible range of the spectrum. As proved by IR spectroscopy, moreover, the products seem to be very similar to those obtained by irradiation of PMPP original films (*vide supra*), i.e., hydroperoxides, alcohols, aldehyde groups, esters, peracids, etc. From a quantitative standpoint, however, the photooxidative phenomena observed in this polymer are strongly reduced when compared to those found for the pristine PMPP, as indicated by the much lower spectral variations measured for the irradiated, HALS-containing PMPP.

According to the well-known powerful stabilizing ability shown by HALS additives in the case of polyolefins,[72] we attribute the strong photostabilization effect observed in the case of PMPP to the HALS groups attached to this material through the grafted anhydride groups, which effectively inhibit the photooxidative action of the impinging light. It should be pointed out that photooxidative stabilization effects similar to those described for the functionalized PMPP were also obtained for other aryloxy-substituted phosphazene macromolecules, thus making this approach to the photostabilization of POPs quite generally valid.[25,72]

CONCLUSIONS

In this article, we described a general procedure to preserve POP films against damage deriving from the photooxidation of these polymers under accelerated conditions. This method is based on the two-step functionalization reaction of aryloxy-substituted POPs that, first of all, implies the attachment of succinic anhydride groups onto selected POPs, followed by the reaction of these functions with amino-terminated HALS moieties.

The first reaction was accomplished quite easily by dissolving a selected polymer in a toluene solvent in the presence of MA and of the BEE photoinitiator and by selectively irradiating this last species with light at wavelengths longer than 350 nm (cutoff filters). This method has the great advantage of not bringing about any polymer degradation[5,17–19] during the light-induced grafting reaction of MA onto POPs.

The phosphazene-grafted copolymers obtained, POP-*g*-SA, were successively treated with —NH$_2$-terminated-Ciba Geigy HALS intermediates (T10 and T12) to open the anhydride ring and to support HALS moieties onto the polyphosphazene substrate. Films of HALS-containing phosphazene macromolecules were eventually irradiated under accelerated photooxidative conditions and the spectroscopic modifications undergone were compared with those previously observed for the pristine, unmodified, POPs. The experimental findings observed strongly indicate that these substrates are considerably less sensitive toward photooxidative phenomena than are the original, unmodified materials, even in the presence of low

amounts (0.4% w/w) of HALS residues randomly attached along the polyphosphazene skeleton.

REFERENCES

1. P. Potin and R. De Jaeger, *Eur. Polym. J.,* **27,** 341 (1991).

2. R. E. Singler, N. S. Schneider, and G. L. Hagnauer, *Polym. Eng. Sci.,* **15,** 321 (1975).

3. E. J. Quinn and R. L. Dieck, *J. Fire Flammab.,* **7,** 358 (1976).

4. G. Facchin, F. Minto, M. Gleria, R. Bertani, and P. Bortolus, *J. Inorg. Organomet. Polym.,* **1,** 389 (1991).

5. M. Gleria, F. Minto, M. Scoponi, F. Pradella, and V. Carassiti, *Chem. Mater.,* **4,** 1027 (1992).

6. M. Gleria, F. Minto, M. Scoponi, F. Pradella, and V. Carassiti, *Ital. Pat.* MI 000,119 (1992).

7. G. Fantin, A. Medici, M. Fogagnolo, P. Pedrini, M. Gleria, R. Bertani, and G. Facchin, *Eur. Polym. J.,* **29,** 1571 (1993).

8. H. R. Allcock, R. J. Fitzpatrick, and L. Salvati, *Chem. Mater.,* **4,** 769 (1992).

9. T. X. Neenan and H. R. Allcock, *Biomaterials,* **3,** 78 (1982).

10. H. R. Allcock and T. X. Neenan, U.S. Pat. 4,451,647 (1984) (to Research Corp.); *Chem. Abstr.,* **101,** 97663h, (1984).

11. M. Gleria, A. Bolognesi, W. Porzio, M. Catellani, S. Destri, and G. Audisio, *Macromolecules,* **20,** 469 (1987).

12. F. Minto, M. Scoponi, L. Fambri, M. Gleria, P. Bortolus, and F. Pradella, *Eur. Polym. J.,* **28,** 167 (1992).

13. F. Minto, M. Scoponi, M. Gleria, F. Pradella, and P. Bortolus, *Eur. Polym. J.,* **30,** 375 (1994).

14. H. R. Allcock, C. J. Nelson, and W. D. Coggio, *Chem. Mater.,* **6,** 516 (1994).

15. F. Minto, M. Gleria, P. Bortolus, L. Fambri, and A. Pegoretti, *J. Appl. Polym. Sci.,* **56,** 747 (1995).

16. F. Minto, L. Fambri, and M. Gleria, *Macromol. Chem. Phys.,* **197,** 3099 (1996).

17. M. Gleria, F. Minto, G. Fontana, R. Bertani, and G. Facchin, *Macromolecules,* **28,** 4399 (1995).

18. G. Fontana, F. Minto, M. Gleria, G. Facchin, R. Bertani, and G. Favero, *Eur. Polym. J.,* **32,** 1273 (1996).

19. F. Minto, G. Fontana, R. Bertani, G. Facchin, and M. Gleria, *J. Inorg. Organomet. Polym.,* **6,** 367 (1996).

20. M. Scoponi, F. Pradella, V. Carassiti, M. Gleria, and F. Minto, *Makromol. Chem.,* **194,** 3047 (1993).

21. M. Scoponi, F. Pradella, M. Gleria, and F. Minto, *J. Inorg. Organomet. Polym.,* **6,** 325 (1996).

22. B. Rånby and J. F. Rabek, *Photodegradation, Photo-oxidation and Photostabilization of Polymers,* Wiley, London, 1975.

23. J. F. Rabek, *Photostabilization of Polymers. Principles and Applications,* Elsevier, London, 1990.

24. J. Sedler and A. Zahraduickova, in *International Conference on Advances in the Stabilization and Controlled Degradation of Polymers,* Lucerne, Switzerland, 1985–86, Vol. 1, p. 227.

25. F. Gugumus, *Polym. Degrad. Stab.,* **40,** 167 (1993).

26. M. Gleria, F. Minto, R. Scrima, and V. Borzatta, *J. Appl. Polym. Sci.,* **61,** 1675 (1996).

27. F. Minto, V. Borzatta, and M. Gleria, *J. Inorg. Organomet. Polym.,* **6,** 171 (1996).

28. A. I. Vogel, *A Textbook of Practical Organic Chemistry,* Longman, London, 1970.

29. R. E. Singler, G. L. Hagnauer, N. S. Schneider, B. R. LaLiberte, R. E. Sacher, and R. W. Matton, *J. Polym. Sci. Polym. Chem. Ed.,* **12,** 433 (1974).

30. L. Goldfarb, N. D. Hann, R. L. Dieck, and D. C. Messersmith, *J. Polym. Sci. Polym. Chem. Ed.,* **16,** 1505 (1978).

31. M. Gleria, F. Minto, P. Bortolus, W. Porzio, and A. Bolognesi, *Eur. Polym. J.,* **25,** 1039 (1989).

32. M. Gleria, F. Minto, P. Bortolus, W. Porzio, and S. V. Meille, *Eur. Polym. J.,* **26,** 315 (1990).

33. H. R. Allcock, M. N. Mang, A. A. Dembek, and K. J. Wynne, *Macromolecules,* **22,** 4179 (1989).

34. F. Minto, M. Gleria, M. Scoponi, F. Pradella, and P. Bortolus, *J. Inorg. Organomet. Polym.,* **2,** 405 (1992).

35. P. E. Austin, G. H. Riding, and H. R. Allcock, *Macromolecules,* **16,** 719 (1983).

36. H. R. Allcock, *Phosphorus–Nitrogen Compounds,* Academic Press, New York, 1972.

37. H. R. Allcock and R. L. Kugel, *J. Am. Chem. Soc.,* **87,** 4216 (1965).

38. H. R. Allcock, R. L. Kugel, and K. J. Valan, *Inorg. Chem.,* **5,** 1709 (1966).

39. H. R. Allcock and R. L. Kugel, *Inorg. Chem.,* **5,** 1716 (1966).

40. G. Fontana, Thesis, University of Padova, Italy, March 21, 1995.

41. R. M. Silverstein, C. G. Bassler, and T. C. Morrill, *Spectrophotometric Identification of Organic Compounds,* Wiley, New York, 1974.

42. T. Dyakonov, J. Drbohlav, I. J. Goldfarb, and W. T. K. Stevenson, *Polym. Degrad. Stab.,* **46,** 371 (1994).

43. N. A. Weir, *J. Appl. Polym. Sci.,* **17,** 401 (1973).

44. M. Gleria, F. Minto, F. Doriguzzi, R. Bertani, G. Facchin, and E. Tondello, to appear.

45. P. K. T. Oldring, Ed., *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints. Photoinitiator for Free Radical and Cationic Poly-*

merization, Sita Technology, London, U.K., 1991, Vol. 3.

46. P. Boule and J. Lamaire, *Tetrahedron Lett.,* 865 (1976).

47. I. R. Dunkin and J. G. MacDonald, *J. Chem. Soc. Chem. Commun.,* 772 (1979).

48. D. Todd and M. Pickering, *J. Chem. Ed.,* **65,** 1100 (1988).

49. D. Bryce-Smith, A. Gilbert, and B. Vickery, *Chem. Ind. (Lond.),* 2060 (1962).

50. J. L. Lang, W. A. Pavelich, and H. D. Clarey, *J. Polym. Sci. Part A,* **1,** 1123 (1963).

51. N. G. Gaylord and S. Maiti, *J. Polym. Sci. Polym. Lett. Ed.,* **11,** 253 (1973).

52. N. G. Gaylord, in *Ultraviolet Light Induced Reactions in Polymers,* S. S. Labana, Ed., ACS Symposium Series, Washington, DC, 1976, Vol. 25, Chap. 1, p. 1.

53. M. Raetzsch, G. Schicht, and W. Jahn, *Acta Polym.,* **33,** 377 (1982).

54. M. Raetzsch, G. Schicht, M. Arnold, J. Barton, and I. Capek, *Chem. Zvesti,* **38,** 823 (1984); *Chem. Abstr.,* 102, 62631q (1985).

55. G. A. Miner, W. E. Meador, and C. K. Chang, *Langley Res. Cent., NASA, Hampton, VA,* NAS. 1.15:4166, NASA-TM-4166, L-16703, (1990); *Chem. Abstr.,* **115,** 280632a (1991).

56. T. Li, B. Luo, S. Li, and G. Chu, *Chin. J. Polym. Sci.,* **8,** 170 (1990); *Chem. Abstr.,* **114,** 186128y (1991).

57. X. Li, G. Chen, S. Li, A. Qin, and S. Yu, *Macromol. Rapid Commun.,* **9,** 195 (1988).

58. T. Li, J. Pan, and Z. Zhang, *Makromol. Chem.,* **190,** 1319 (1989).

59. W. M. Hardham and G. S. Hammond, *J. Am. Chem. Soc.,* **89,** 3200 (1967).

60. N. J. Turro, *Modern Molecular Photochemistry,* Benjamin/Cummings, Menlo Park, CA, 1978, p. 453.

61. W. L. Dilling, *Chem. Rev.,* **83,** 1 (1983).

62. P. Hrdlovic and I. Lukac, *J. Polym. Sci. Polym. Symp.,* **47,** 319 (1974).

63. P. Hrdlovic, L. Zahumensky, I. Lukac, and P. Slama, *J. Polym. Sci. Polym. Chem. Ed.,* **16,** 877 (1978).

64. S. Tazuke and H. Kimura, *J. Polym. Sci. Polym. Chem. Ed.,* **15,** 2707 (1977).

65. G. Ruggeri, M. Aglietto, A. Petragnani, and F. Ciardelli, *Eur. Polym. J.,* **19,** 863 (1983).

66. B. C. Trivedi and B. M. Culberstone, *Maleic Anhydride,* Plenum Press, New York, 1982.

67. S. Cimmino, L. D'Orazio, R. Greco, G. Maglio, M. Malinconico, C. Mancarella, E. Martuscelli, R. Palumbo, and G. Ragosta, *Polym. Eng. Sci.,* **24,** 48 (1984).

68. G. De Vito, N. Lanzetta, G. Maglio, M. Malinconico, P. Musto, and R. Palumbo, *J. Polym. Sci. Polym. Chem. Ed.,* **22,** 1335 (1984).

69. J. L. Hahnfeld and D. D. Devore, *Polym. Degrad. Stab.,* **39,** 241 (1993).

70. M. Gleria, F. Minto, L. Flamigni, and P. Bortolus, *Polym. Degrad. Stab.,* **22,** 125 (1988).

71. F. Minto, L. Flamigni, P. Bortolus, and M. Gleria, *J. Inorg. Organomet. Polym.,* **1,** 53 (1991).

72. F. Gugumus, *Polym. Degrad. Stab.,* **44,** 299 (1994).