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Functionalization of Poly(Organophosphazenes). IX. Light-Induced Grafting Reactions of Maleates onto Aryloxy-Substituted Poly(Organophosphazenes)

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FUNCTIONALIZATION OF POLY(ORGANOPHOSPHAZENES). IX. LIGHT-INDUCED GRAFTING REACTIONS OF MALEATES ONTO ARYLOXY-SUBSTITUTED POLY(ORGANOPHOSPHAZENES)

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Key Words: Poly(organophosphazenes); Functionalization; Light-Induced Grafting Reactions; Maleates; 1-Vinyl-2-pyrrolidone; Blends.

ABSTRACT

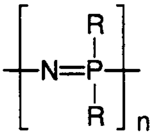
In this paper the light-induced grafting reaction of dimethyl maleate, diethyl maleate, dibutyl maleate and diethyl fumarate, onto aryloxy-substituted phosphazene polymers, to form polyphosphazene copolymers containing grafted succinate groups, is investigated by means of IR spectroscopy and the equilibrium swelling technique of polyphosphazene films. The importance of several different experimental factors that can influence the final succinate grafting yields is discussed, i.e. the type and concentration of the polyphosphazenes and of the unsaturated products, reaction time, the absence or presence of molecular oxygen or of the 1-vinyl-2-pyrrolidone monomer, and the concentration of the benzoin ethyl ether photoinitiator.

Furthermore, it is shown that the overall efficiency of the light-induced grafting process is lower than that previously measured for the reaction initiated thermally using peroxide species, and that the photochemical grafting reaction always occurs with no degradation of the phosphazene macromolecules.

The possibility of exploiting these new phosphazene substrates in blend technology has been considered.

INTRODUCTION

In the last two decades several research groups have shown a growing interest in the possibility of forming blends between poly(organophosphazenes), POPs, and conventional organic or inorganic macromolecules [1-18], with the aim of improving the flame resistance [1-8, 14, 15, 17, 18] and electrical conductivity [10-12] of these substrates. Moreover, attention has been paid to the formation of blends between poly(organophosphazenes) themselves containing different phosphorus substituents [1, 9, 14, 18].



$$\left[-N=\underset{R}{\overset{R}{P}}-\right]_n$$

During these investigations there was found to be general difficulty in achieving the complete miscibility between POPs and selected organic polymers, leading to phase separation of the two components. This could be due to the high molecular weight of polyphosphazene substrates [19] and to the lack of strong interactions between the organic phase and the -P=N- side substituents.

A remarkable exception to this general trend is provided by Landry and Ferrar [13, 16], who have succeeded in blending polyethyleneoxide-substituted POPs with polyvinyl phenol in the whole range of composition of these two substrates, due to the formation of intermolecular hydrogen bonding that significantly decreases mixing enthalpy and favors blend formation.

A second consideration that has emerged from these studies is that the poly(organophosphazenes) selected for the above-described blending processes were preferentially virgin materials, not previously subjected to modification or functionalization reactions. Again, there is an exception to this case, i.e. the insertion of maleimide functionalities in poly[bis(phenoxy)(4-aminophenoxy)phosphazene] copolymers to improve blending processes [20].

Recently, it has been proposed [21-27] that the modification of phosphazene substrates by introducing suitable groups into these materials may lead to the preparation of the so-called "compatible agents", i.e. substrates that are able to reduce the surface tension existing between two different polymeric phases [28], therefore favoring the formation of polyphosphazene blends.

Thus, a cyclophosphazene substituted with Nylon 6 and polystyrene units could be used to improve the compatibilization process between poly(2,6-dimethylphenyleneoxide) and Nylon 6 macromolecules [26].

Furthermore, small but controlled amounts of maleic anhydride [21-25, 27] or maleate [29] units were introduced into aryloxy-substituted phosphazene substrates containing different alkyl residues in the para position of the phenoxy substituents, using both thermal [21-25, 29] and photochemical [27] techniques. The new macromolecules obtained containing grafted anhydride residues are important because of their high reactivity toward $-NH_2$ or -OH end-capped organic polymers [30-32], while those with inserted succinate groups are potentially able to undergo transesterification or alcoholysis reactions with -OH terminated polyesters or polycarbonates [33, 34]. Both these processes would eventually lead to the preparation of phosphazene-based compatibilizing agents able to sustain the formation of blends between POPs and commercial organic macromolecules.

Expanding upon this research, we herewith report the light-induced grafting reaction of methyl-, ethyl-, and butyl-maleates, and of ethyl fumarate onto four different poly(organophosphazenes), i.e.

poly[bis(4-methylphenoxy)phosphazene], PMPP, $[NP(OC_6H_4CH_3)_2]_n$;
poly[bis(4-ethylphenoxy)phosphazene], PEPP, $[NP(OC_6H_4CH_2CH_3)_2]_n$;
poly[bis(4-isopropylphenoxy)phosphazene], PiPP,
$NP[(OC_6H_4CH(CH_3)_2]_n$, and
poly[bis(4-secbutylphenoxy)phosphazene], PsBPP,
$NP[(OC_6H_4CH(CH_3)(C_2H_5]_n$,

which leads to the preparation of polyphosphazene substrates containing grafted succinate groups.

This relatively low quantity of succinate residues could be enhanced by carrying out the grafting experiments of maleate species onto polyphosphazene matrices in the presence of selected unsaturated organic monomers (e.g. 1-vinyl-2-pyrrolidone). It is known, in fact, that in the presence of these species an alternate copolymerization process takes place between the electron-rich 1-vinyl-2-pyrrolidone and the electron-deficient maleates and fumarates [35, 36], leading to the growth of pyrrolidone/succinate copolymer chains from the main polyphosphazene substrate. These latter materials are very interesting products, not only for their possible exploitation in blending processes, but also because of their considerably improved hydrophilicity and wettability properties.

EXPERIMENTAL

All the polyphosphazene preparations used in this work were obtained using anhydrous solvents, dried according to standard procedures [37], and operating under inert (nitrogen) atmosphere. The solvent used, i.e. *n*-hexane, *n*-heptane, toluene, xylene, tetrahydrofuran (THF), dioxane, ethanol, methanol, were C. Erba analytical grade products.

Hexachlorocyclophosphazene, $(NPCl_2)_3$, was a white crystalline product purchased from Shinn Nisso Kako, purified by repeated vacuum sublimations and precipitations from hexane, until a constant melting point of 113°C was reached [38]. The heating of this product for several hours at 250°C in sealed, evacuated (10^{-2} torr) ampoules induced the opening of the phosphazene cyclic structure to form the linear polydichlorophosphazene, $(NPCl_2)_n$ [39-41], from which the preparation of the poly(organophosphazenes) used in this work was achieved. Thus, xylene solutions of 4-methylphenol, 4-ethylphenol, 4-isopropylphenol and 4-secbutylphenol (Aldrich products), dried by azeotropic distillation of the solvent, were first treated with the stoichiometric amount of NaH 60% oil dispersion (Aldrich) to produce the corresponding phenoxide ions, and successively with a dioxane solution of polydichlorophosphazene to prepare the corresponding poly[bis(4-methylphenoxy)phosphazene], PMPP [24], poly[bis(4-ethylphen-oxy)-phosphazene], PEPP [23], poly[bis(4-isopropylphenoxy)phosphazene] PiPP [42], poly[bis(4-secbutylphenoxy)phosphazene], PsBPP [21]. The macromolecules were purified by repeated precipitation in ethanol, water, ethanol (twice) and *n*-heptane in this order, and vacuum dried for two days.

TABLE 1. Characterization Data for the Aryloxy-Substituted Phosphazene Polymers. Elemental Analysis Calculated Data in Parentheses

Polymer	%C	%H	%N	^{31}P NMR ppm	Intrinsic Viscosity (ml/gr)
PMPP	64.44 (64.86)	5,42 (5.40)	5,37 (5.40)	-19.68	240
PEPP	67.24 (66.90)	6.06 (6.27)	4.69 (4.87)	-19.07	260
PiPP	67.65 (68.57)	6.96 (6.98)	4.45 (4.44)	-18.91	110
PsBPP	69.08 (69.97)	7.74 (7.58)	4.13 (4.08)	-18.74	160

The polymers obtained showed the elemental analyses and the characterization data reported in Table I.

The content of residual, unreacted chlorine was always < 0.3%.

The procedure for grafting dimethylmaleate (DMM), diethylmaleate (DEM), dibutylmaleate (DBM) or diethyl fumarate (DEF) (all of them Aldrich products) onto the above described polyphosphazenes was as follows: 50 mg of the selected polyphosphazene were dissolved in 1 ml of aerated toluene together with variable amounts of the selected maleate and the suitable photoinitiator (usually benzoin ethyl ether, BEE, from Aldrich), in 10 ml pyrex ampoules (10 mm thick). They were then irradiated at 20°C for times ranging between 20 and 240 minutes, using a 150 W HBO high pressure mercury lamp at a distance of 30 cm from the sample. Cut-off filters were also used to allow the selective excitation of the photoinitiator at $\lambda > 350$ nm. From time to time, oxygen was excluded from the reactor by repeated freeze-pump-thaw cycles (10^{-2} torr). When necessary, the light-induced grafting reaction of maleate or fumarate moieties onto POPs was carried out in the presence of equimolecular amounts of 1-vinyl-2-pyrrolidone (Aldrich), in order to allow the formation of phosphazene copolymers containing grafted side arms formed by alternating succinate/vinylpyrrolidone chains.

The functionalized phosphazene polymers were recovered by precipitating the reaction mixture in chilled methanol, according to the procedure already described in previous publications [29].

The quantitative determination of the absolute amount of dimethyl succinate (DMS), diethyl succinate (DES) or dibutyl succinate (DBS) residues grafted onto the polyphosphazene substrate was obtained by IR spectroscopy, according to the previously reported procedure [29] using the following equation:

$$G_g(\%) = \text{weight percentage of grafted succinates} = (A_{1740}/A_{1610}) \times 1/S$$

TABLE 2. Slope of the Calibration Plots of Different Polyphosphazenes with Different Maleates.

Poly(organophosphazenes)	Slope of the Calibration Plot
PMPP	0.293(DMS); 0.286(DES); 0.217(DBS).
PEPP	0.216(DMS); 0.211(DES); 0.16(DBS).
PiPP	0.185(DMS); 0.180(DES); 0.137(DBS).
PsBPP	0.225(DMS); 0,220(DES); 0.167(DBS).

The slope concerning the calibration plot of diethyl fumarate was assumed to be equal to that of the diethyl maleate.

where A_{1740} and A_{1610} are the absorbance at 1740 (ν of the ester carbonyl group) and 1610 (ν C=C of the aromatic ring taken as a reference band) cm^{-1}, respectively, of the functionalized films, and "S" are the slopes of the calibration plot measured for each couple of POP/succinate derivatives, reported in Table 2.

The equilibrium swelling yields, $G_{se}(\%)$ of POP films (30 x 12 x 0.08 mm) immersed in methanol at 20°C ware determined gravimetrically according to the equation:

$$G_{se}(\%) = \frac{W_{se} - W_0}{W_0} \cdot 100$$

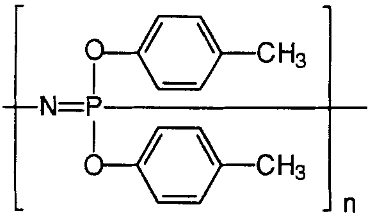
where:

W_{se} is the weight of the phosphazene film swollen in methanol, and W_0 is the initial weight of the phosphazene film.

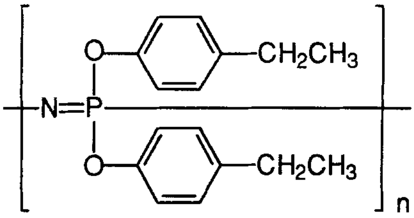
The IR characterization data for the succinate-containing phosphazene copolymers were obtained using Perkin-Elmer spectrophotometers model 399. NMR char-acterization was performed by a Bruker 200 AC spectrometer. The intrinsic viscosity [η] measurements for the polyphosphazenes utilized in this work were obtained using a Desreux-Bischoff, suspended level, viscosimeter at 20°C in THF solvent.

RESULTS AND DISCUSSION

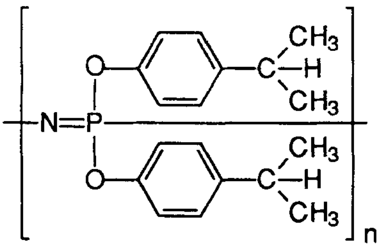
The poly(organophosphazenes) exploited for the light-induced functionalization processes with maleates belong to the class of aryloxy-substituted phosphazene macromolecules and have the following chemical structure:



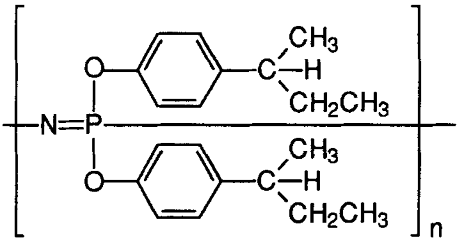
PMPP



PEPP



PiPP



PsBPP

in which phenoxide substituents, containing different alkyl residues in para position of the aromatic ring, are attached to the inorganic -P=N- skeleton.

The light-induced grafting reaction of dimethyl maleate (DMM), diethyl maleate (DEM), dibutyl maleate (DBM) and diethyl fumarate (DEF) onto the above described phosphazene polymers was carried out by dissolving the phosphazene polymers and the maleates or fumarate species in toluene, in the presence of suitable amounts of benzoin ethyl ether (BEE) as a photoinitiator, and by the selective irradiation (λ_{exc} > 350 nm) of this last species at room temperature for a few hours, both in the presence and in the absence of molecular oxygen.

The functionalized polymers recovered after this reaction showed a new peak in the Infrared spectrum located at 1740 cm^{-1}, which was assigned to the carbonyl stretching of the succinate ester groups grafted onto the polyphosphazene substrates. This fact is reported in Figure 1 for the light-induced grafting reaction of DMM onto PMPP.

Moreover, it must be stressed that the intensity of this peak is clearly related to the experimental conditions adopted for the grafting process, in the sense that it increases, for instance, with the increase in irradiation time, to indicate that higher amounts of succinate groups could be grafted onto the polyphosphazene matrices for longer periods of light exposure.

Similarly to previous findings on the photochemically-induced grafting reaction of maleic anhydride (MA) onto POPs induced [27], the final amount of succinate groups grafted onto POP systems ranged between 0.1 and 1.8% w/w, to

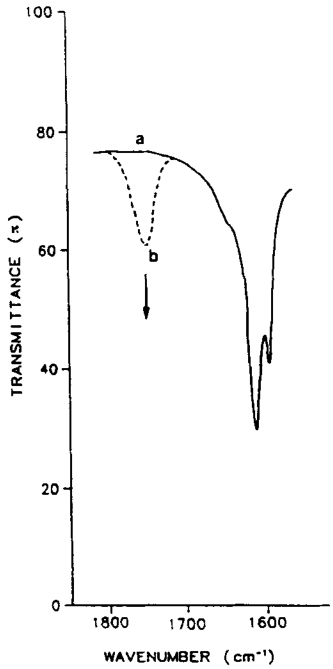


Figure 1. IR transmittance variations in PMPP following the light-induced grafting reaction with DMM.

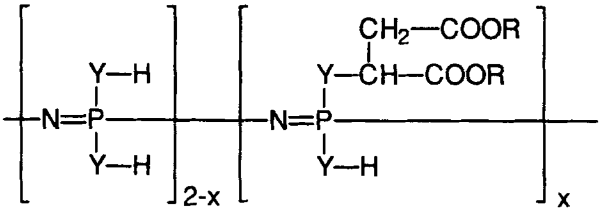
(a) original polymer.

(b) polymer after the functionalization reaction.

confirm that, also in the case of maleate substrates, the efficiency of the photochemically-induced grafting process is considerable lower (two or three times) than that of the corresponding reaction carried out thermally.

This fact has the important consequence that it is not possible to effect an NMR analysis of the functionalized POPs to complete the characterization data of the grafted phosphazene copolymers because of the very low amounts of succinate residues inserted into the polymeric substrates, amounts which are well below the sensitivity threshold of the NMR technique.

However, on the basis of the above reported considerations on the IR characteristics of the new, succinate-containing polyphosphazenes, also taking into account the previously reported results on the thermally-induced grafting of maleates onto POPs [29], we may tentatively assign the following chemical structure for the POP-g-Succinate grafted copolymers:



where Y stands for: -O-C_6H_4-CH_2 for PMPP, -O-C_6H_4-$CHCH_3$
for PEPP, -O-$C_6H_4C(CH_3)_2$
for PiPP and -O-C_6H_4-$C(CH_3)(C_2H_5)$ for PsBPP;
while R stands for: CH_3 for DMS, C_2H_5 for DES, and C_4H_9 for DBS.

As far as the grafting reaction mechanism is concerned, it may be hypothesized that the selective irradiation of the BEE photoinitiator leads to the fragmentation of this molecule to form benzoyl and alkyl/aryl radicals [43] able to abstract hydrogen atoms from the polyphosphazene substrate. The phosphazene macroradicals thus formed, react with the unsaturated molecules (maleates or fumarates), opening their double bond and eventually leading to the preparation of succinate group-containing phosphazene grafted copolymers.

Similarly to the previously reported findings for the thermal grafting of MA [21-25] or DEM [29], the light-induced grafting process of different maleates or fumarates onto poly(organophosphazenes) was found to be dependent on several experimental factors; these were studied in detail in order to gain complete control of this functionalization reaction.

The systematic investigation into the influence of the reaction conditions, i.e. irradiation time, molecular oxygen, type and concentration of the exploited phosphazene polymers and maleates, and BEE concentration, on the final percentage of grafted succinates, is described below.

Effect of the Reaction Time and of Molecular Oxygen

The effect of the reaction time and of molecular oxygen on the weight percentage of DES grafted onto PEPP was investigated by dissolving this polymer in toluene, together with DEM and the BEE photoinitiator, and irradiating this last species at room temperature for 120 minutes in the presence or in the absence of molecular oxygen. The corresponding results are reported in Figure 2A.

As can be seen from this Figure, the weight percentage of grafted DES increases with the increase in irradiation time, the enhancement being more elevated when the grafting process is carried out in the absence of molecular oxygen.

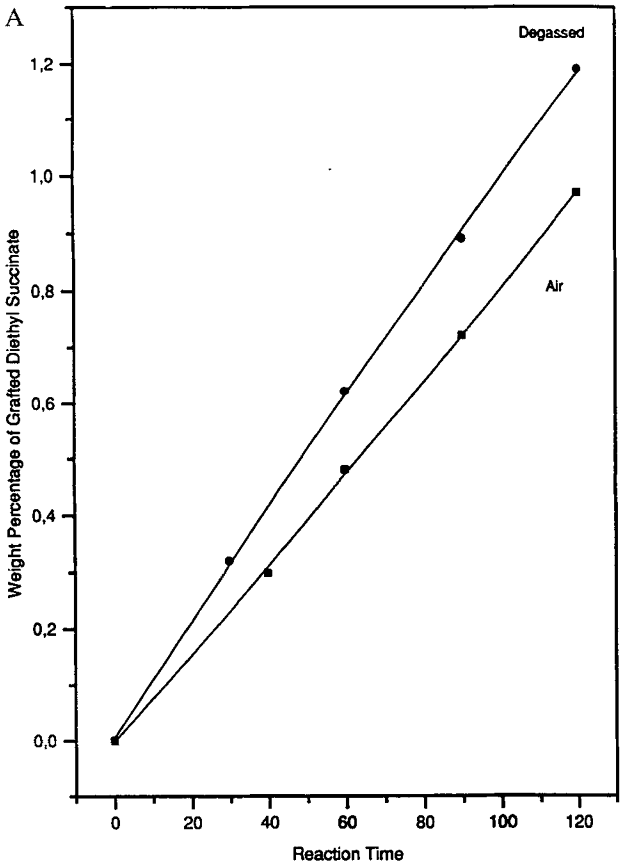


Figure 2. Part A: Influence of reaction time on the light-induced grafting reaction of DEM onto PEPP (1 ml toluene, 1.7 x 10^{-4} mol PEPP m.u., 7.6 x 10^{-4} mol DEM, 7.1 x 10^{-5} mol BEE);

Part B: Influence of reaction time on the light-induced grafting reaction of DMM onto PiPP (1 ml toluene, 1.59 x 10^{-4} mol PiPP m.u., 7.6 x 10^{-4} mol DMM, 7.1 x 10^{-5} mol BEE);

Part C: Influence of reaction time on the light-induced grafting reaction of DEM onto PsBPP (1 ml toluene, 1.46 x 10^{-4} mol PsBPP m.u., 1.7 x 10^{-4} mol DEM, 7.1 x 10^{-5} mol BEE).

in the presence or in the absence of molecular oxygen.

Similar findings were obtained when the same series of experiments was carried out on the PiPP/DMM (Figure 2B) and PsBPP/DEM (Figure 2C) systems. In this last case, a lower DEM concentration (29 mg = 1.7x10^{-4} mol) was used.

These results can be interpreted on the basis of the radical nature of the

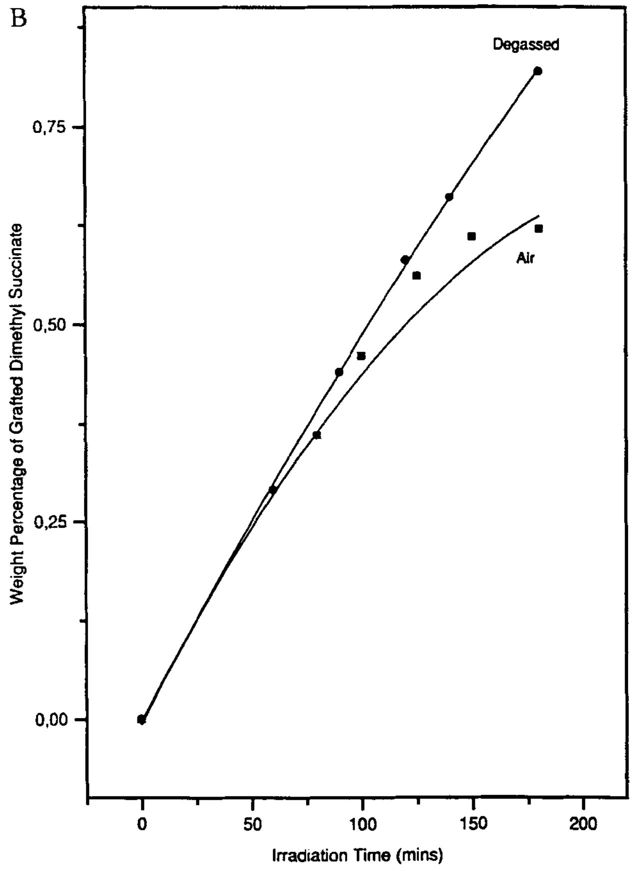


Figure 2. Continued

(continued)

grafting reaction and on the capacity of molecular oxygen to scavenge the radical species produced during photolysis, reducing the relative concentration in solution of species able to contribute towards the grafting process, and eventually depressing the overall efficiency of the maleate grafting onto POPs.

Furthermore, if we consider Figures 2A-2C, can be seen that the three polyphosphazenes exploited in these experiments, treated under comparable experimental conditions, show rather different values for the weight percentage of grafted succinate groups. This suggests that the type of phenoxy side substituent attached to the polyphosphazene backbone may play a certain role in determining the overall grafting yield of the succinate groups onto POPs. This fact prompted us to investigate this particular aspect of the polyphosphazene functionalization process.

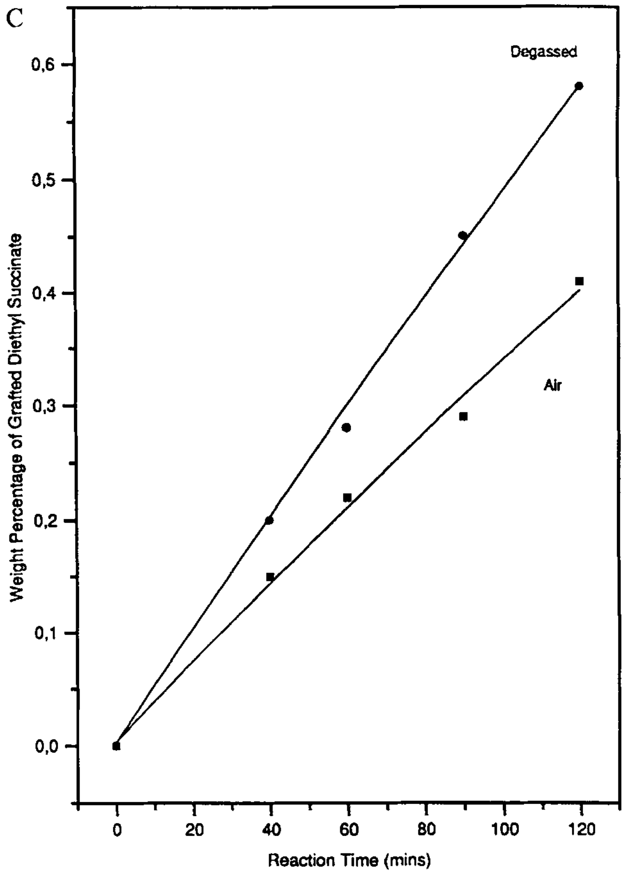


Figure 2. Continued

Effect of Polyphosphazene Substituents

The effect of the substituent groups, attached to the inorganic skeleton of the phosphazene polymers, on the grafting efficiency of DEM was studied by dissolving PMPP, PEPP, PiPP and PsBPP polymers in toluene together with the BEE photoinitiator and by irradiating this substrate at room temperature, for 120 minutes.

The corresponding grafting yields of DES are reported in Figure 3, where the weight percentage of grafted diethyl succinate is plotted vs. irradiation time for the four above mentioned polyphosphazenes.

This Figure shows that the reactivity order of these materials follows this trend:

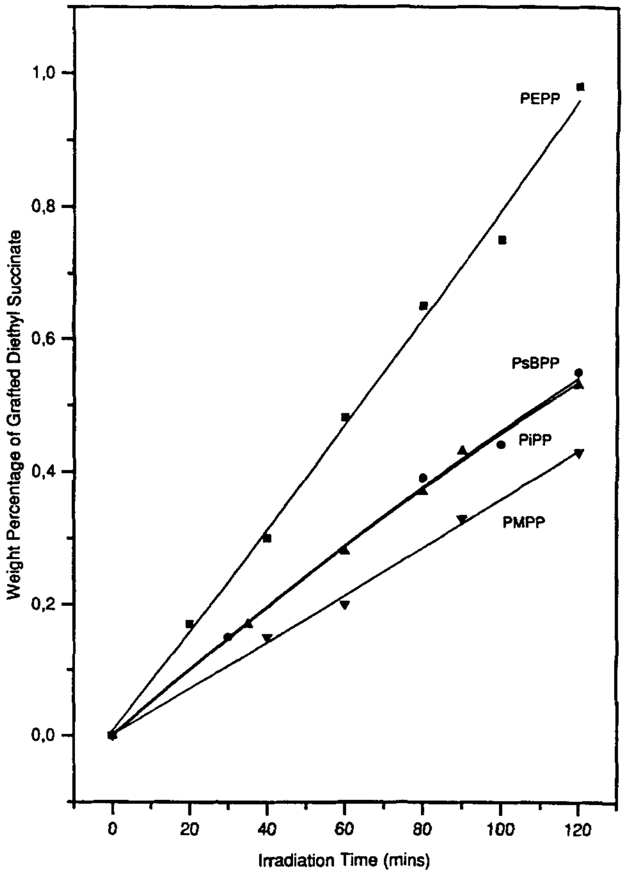


Figure 3. Influence of the type of polyphosphazene substrate on the light-induced grafting reaction of DEM onto POPs (1 ml toluene, 50 mg POPs, 7.6 x 10^{-4} mol DEM, 7.1 x 10^{-5} mol BEE).

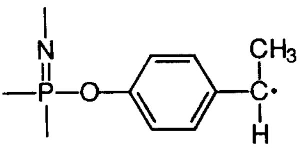
PEPP > PsBPP≈PiPP > PMPP

Similar to the previous findings concerning the thermal grafting reaction of MA onto a series of aryloxy-substituted polyphosphazene polymers [25], this sequence may be interpreted in terms of both thermodynamic parameters and steric factors.

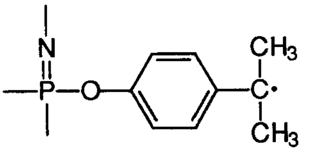
In fact, it is known that the energy necessary to abstract the primary hydrogen atom in PMPP is higher than that needed for splitting the secondary hydrogen of PEPP, which, in turn, is more elevated than that required to cleave the tertiary C-H bonds in PiPP and PsBPP [44]. For this reason, it may be expected that the phosphazene macroradicals necessary for the grafting reaction will be produced less efficiently for PMPP (primary C-H bonds, only), while the process yield should increase for PEPP (the abstraction of the hydrogen atoms in this polymer is known to take place on the methylene groups of the 4-ethylphenoxy units [23,45, 46]), to reach the highest efficiency in the case of PiPP and PsBPP, where tertiary C-H bonds are present in the 4-isopropyl and 4-sec-butyl residues, respectively). As a consequence, the yield for the formation of POP-g-Succinate phosphazene copolymers should be higher for PiPP and PsBPP, than that for PEPP, which in turn is more elevated than that of PMPP.

As shown before, this reactivity order is followed by PMPP only, which proved to have the lowest reactivity, but the predictions are not respected for PEPP, which showed the highest reactivity among the four aryloxy-substituted polyphosphazenes used.

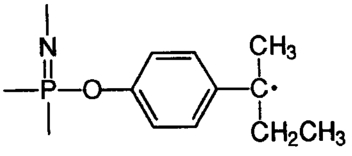
This last fact can be explained by observing the chemical structure of the phosphazene macroradicals of PEPP, PiPP and PsBPP that are active during the grafting processes of maleic anhydride [21-25, 27] and maleates [29] reported below.



PEPP•



PiPP•



PsBPP•

In fact, is we consider these species, it can be seen that the macroradical sites in PEPP are considerably less sterically hindered than those of PiPP and PsBPP. This fact seems to provide great accessibility to the incoming molecules of maleates for the ethylphenoxy-substituted phosphazene polymer, and highly facilitates the grafting reaction that takes place onto this substrate with respect to that occurring onto PiPP and PsBPP polymers.

In this way, the high reactivity of PEPP with maleates is reasonably explained and the above-reported experimental reactivity sequence for the four phosphazene polymers used satisfactorily accounted for.

These findings are in agreement with analogous results reported by Ciardelli on the thermally-induced grafting reaction of DEM onto polyolefins [47].

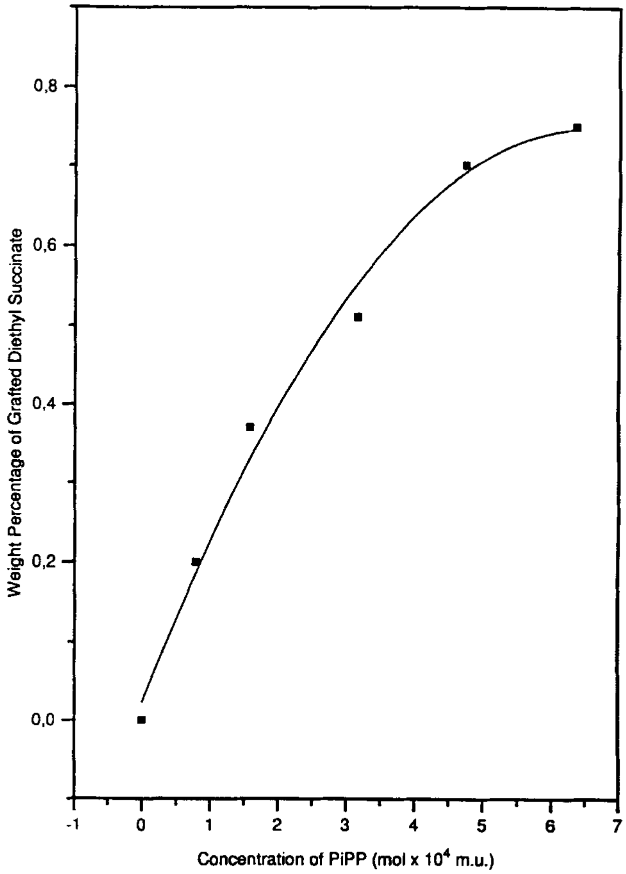


Figure 4. Influence of the PiPP concentration on the light-induced grafting reaction of DEM onto this polyphosphazene (1 ml toluene, 7.6 x 10^{-4} mol DEM, 7.1 x 10^{-5} mol BEE, irradiation time 80 minutes).

Effect of the Poly(Organophosphazene) Concentration

The effect of the polyphosphazene concentration on the grafting yield of DEM onto POPs is reported in Figure 4.

This is the case of a reaction mixture made up of variable amounts of PiPP, DEM and BEE, by selective irradiation of the photoinitiator for 80 minutes at room temperature, at $\lambda_{exc} > 350$ nm. The PiPP polymer was selected for this experiment because of its relatively low intrinsic viscosity (and molecular weight) (see Table 1), which allowed the solution concentration of this material to be in-creased up to 6.4 x 10^{-4} mol (based on the molecular weight of the monomeric units).

This Figure shows that the concentration of the polyphosphazene substrate is able to influence the overall grafting yield of DEM, which increases with the increase of the phosphazene concentration in the reaction mixture, up to 0.7% w/w of grafted DES for the highest concentration reached for the polymer in solution.

Effect of the Type of Unsaturated Substrate to be Grafted Onto the POPS

The influence of the type of unsaturated substrate to be grafted onto poly(organophosphazenes) was investigated considering the reaction mixture formed by PEPP as a suitable polymeric substrate (since this polymer has proved to be the most reactive POP used in this work), DMM, DEM, DBM and DEF as double bond-containing compounds, and BEE as a photoinitiating species. The solution was irradiated for variable periods of time (up to 120 minutes), at a wavelength longer than 350 nm, to allow the benzoin ethyl ether to produce reactive radicals and the grafting reaction of succinate residues to take place.

The grafting percentage of the corresponding succinates is reported in Figure 5 in which the maleic anhydride (MA) grafting plot (vs. the weight percentage of grafted succinic anhydride) is also reported as a comparison.

As can be seen from this Figure, the amount of grafted succinates is almost identical for DMM, DEM and DBM, and is considerably lower than that found for MA groups; this is not unexpected because maleic anhydride is known to be a substrate which is considerably more reactive than the maleates themselves [29].

Quite surprisingly, however, it was observed that diethyl fumarate (DEF), i.e. the trans isomer of DEM, was also able to react with PEPP under the above-described experimental conditions to form PEPP-g-DES grafted copolymers, showing a grafting efficiency that was intermediate between that of MA and those of the exploited maleates. This indicates that unsaturated species are active in the grafting processes onto polyphosphazene substrates regardless of their cis or trans configuration.

At present, no reasonable explanations can be presented to account for these findings.

Effect of the Maleate Concentration

The influence of the maleate concentration on the succinate grafting yield onto poly(organophosphazene) substrates was studied considering a reaction

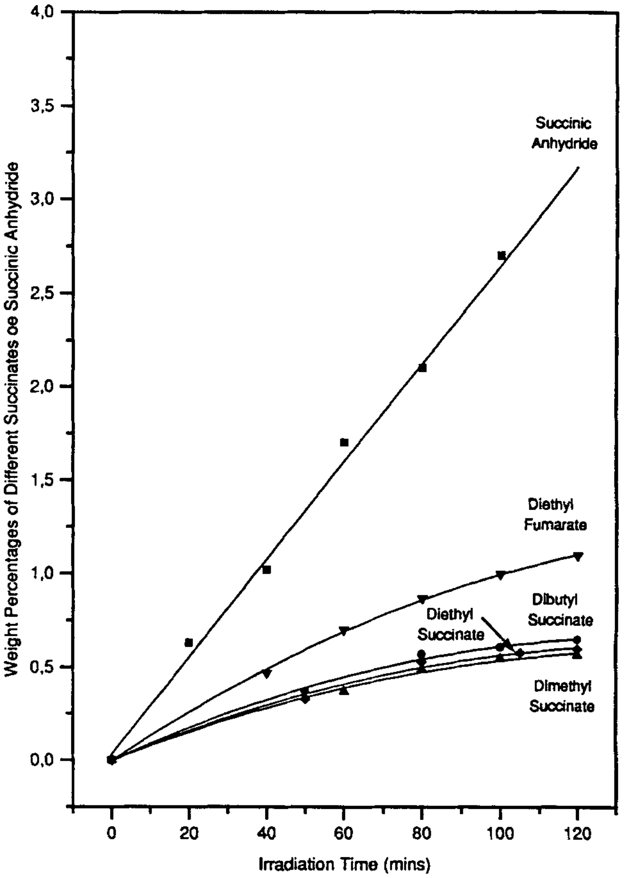


Figure 5. Influence of the type of unsaturated molecules on the light-induced grafting reaction of these substrates onto PEPP (1 ml toluene, 1.7 x 10^{-4} mol PEPP m.u., 7.6 x 10^{-4} mol DMM, DEM, DBM, DEF, 7.1 x 10^{-5} mol BEE).

system formed by PEPP dissolved in toluene, BEE and variable quantities of DEM, and irradiating the reaction mixture at room temperature for 120 minutes.

The findings obtained are shown in Figure 6.

In this Figure, the grafting of DES residues onto PEPP shows a sigmoidal trend, as the amount of grafted succinate groups is very small at low maleate concentrations in the reaction mixture, but it sharply increases as soon as the percentage of the unsaturated substrate in the system increases until a plateau is reached. After this point, no further enhancement of the grafting yield is observed, even for considerably high quantities of DEM introduced into the reaction system.

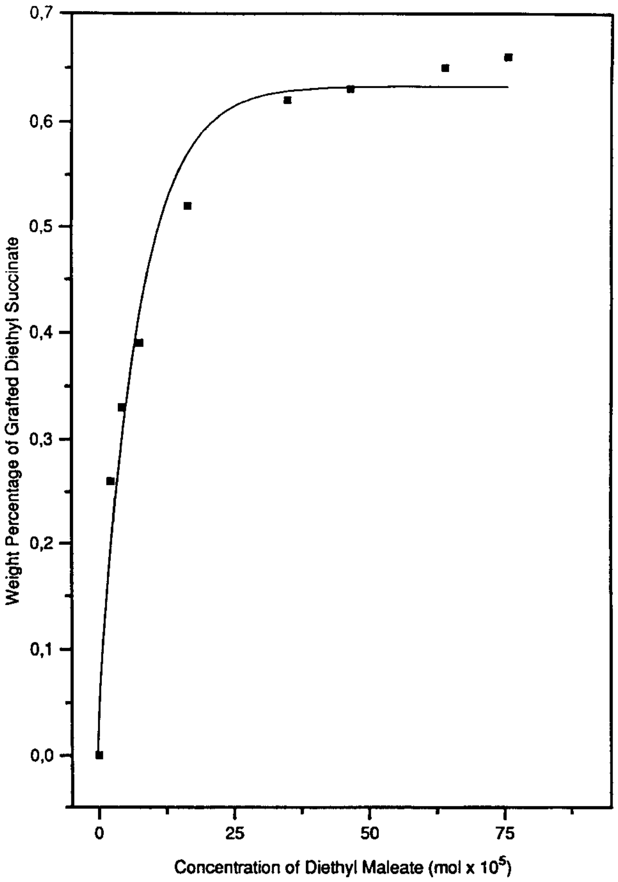


Figure 6. Influence of the concentration of DEM on the light-induced grafting reaction of this substrate onto PEPP (1 ml toluene, 1.7 x 10^{-4} mol PEPP m.u., 7.6 x 10^{-4} mol DEM, 7.1 x 10^{-5} mol BEE, irradiation time 80 minutes).

Effect of the BEE Photoinitiator Concentration

The last parameter we investigated in this work, that was seen to play a role in determining the overall grafting efficiency of DEM onto polyphosphazene substrates, was the concentration of the benzoin ethyl ether photoinitiator.

The reaction conditions exploited implied the irradiation of a reaction mixture formed by PEPP dissolved in toluene, DEM and variable amounts of BEE, at room temperature for 80 minutes .

The grafting yields obtained are reported in Figure 7.

As can be seen from this plot, the weight percentage of grafted DES residues onto PEPP increases almost linearly with the increase of BEE

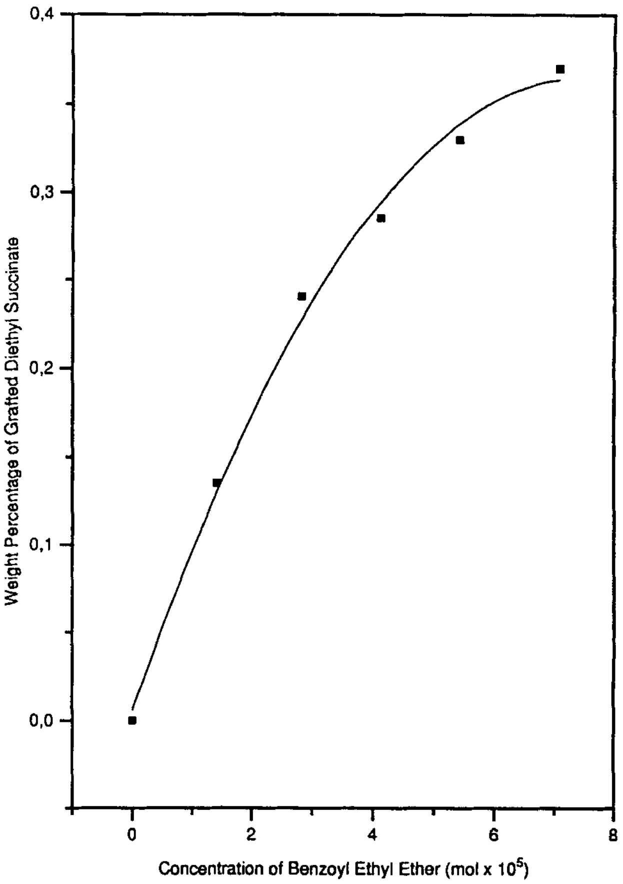


Figure 7. Influence of the concentration of BEE photoinitiator on the light-induced grafting reaction of DEM onto PEPP (1 ml toluene, 1.7 x 10^{-4} mol PEPP m.u., 7.6 x 10^{-4} mol DEM, irradiation time 80 minutes).

concentrations in the reaction system, reaching the value of 0.37% w/w when the BEE concentration is about 7 x 10^{-5} mol in solution.

Grafting Experiments of Diethylmaleate Onto PIPP (or PSBPP) in the Presence of Unsaturated Monomers

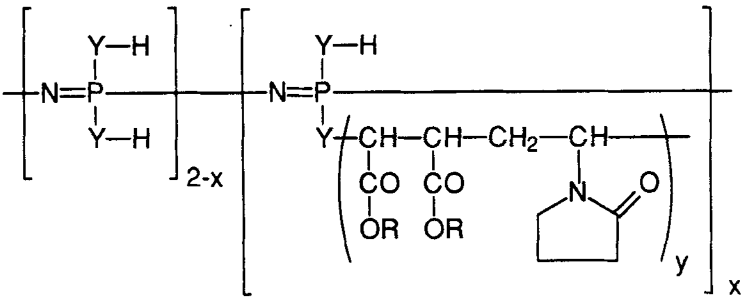
The above-described grafting procedure of DEM onto POPs and the related modification of the experimental parameters that influence the overall grafting yield allowed us to control the reaction efficiency and to obtain the final amounts of succinate groups introduced into the polyphosphazene matrices.

In general, this quantity ranged around 0.7-0.8% (w/w) after 2 hours irradiation, and was considerably lower than that previously reached performing the same series of grafting reactions using peroxide thermal initiators [29]. This is not unexpected, as similar findings were observed in the case of the thermal-[21-25] and the photochemical-[27] grafting of maleic anhydride groups onto aryloxy-substituted phosphazene copolymers.

Therefore, to enhance the final yield of succinate groups photochemically grafted onto selected POPs we decided to carry out the grafting process of DEM onto POPs in the presence of equimolecular amounts of unsaturated vinyl monomers, such as 1-vinyl-2-pyrrolidone.

This last species, in fact, is an interesting monomer, able to polymerize with a radical mechanism, showing remarkable electron-donating characteristics and a noticeable aptitude to copolymerize in the presence of the dialkyl esters of the maleic and fumaric acids, giving rise to linear alternating copolymers [35, 36]. It may be expected, therefore, that new phosphazene grafted materials can be obtained, containing grafted side branches formed by succinate/pyrrolidone alternate copolymers, when the light-induced grafting reactions onto POPs are carried out in the presence of equimolecular amounts of these species.

As matter of fact, when treating PiPP (or PsBPP) dissolved in toluene with equimolecular amounts of DEM and 1-vinyl-2-pyrrolidone in the presence of BEE, and irradiating the resulting mixture for 2 hours at room temperature, with wavelength light longer than 350 nm, a grafting process takes place that leads to the formation of phosphazene copolymers showing the following chemical structure:



in which alternating succinate/pyrrolidone copolymers are grafted onto the polyphosphazene substrates.

These facts could be inferred both on the basis of data found in literature on the reactivity of maleate groups [35, 36] as well as on the analysis of the IR spectra of the final polyphosphazene grafted copolymers reported in Figure 8.

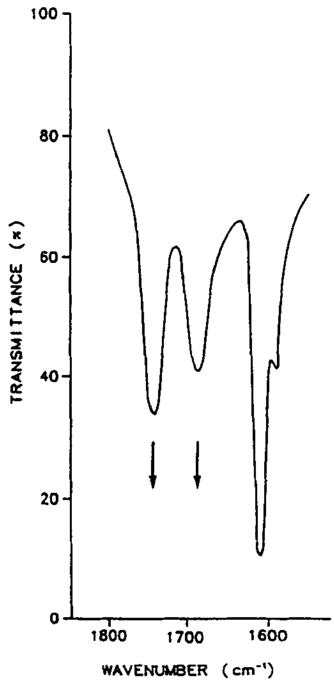


Figure 8. IR transmittance spectrum of functionalized PiPP following the light-induced grafting reaction with DEM in the presence of 1-vinyl-2-pyrrolidone (1 ml toluene, 1.59 x 10^{-4} mol PiPP m.u., 3.4 x 10^{-4} mol of DEM and 1-vinyl-2-pyrrolidone, 7.1 x 10^{-5} mol BEE).

As can be seen from this Figure, besides the typical absorptions related to the polyphosphazene material [48], and the band at 1740 cm^{-1} assigned to the stretching of the grafted succinate groups, a new band is present at 1680 cm^{-1}, and this is attributed to the vibration of the pyrrolidone carbonyl groups [49].

In this way, up to 1.8% of the maleate groups could be inserted into the polyphosphazene matrices by the light-induced grafting process, thus considerably increasing the final amount of esteric groups grafted with this procedure.

This fact is of remarkable importance, not only because it represents the first example of linear alternate copolymers grafted onto selected poly(organophosphazenes), but also because the new phosphazene materials, prepared in this way and containing higher amounts of grafted succinate residues, may offer better performance in the reacting blending processes with -OH end-capped polyesters or polycarbonates.

TABLE 3. Equilibrium Swelling Yields in Methanol for PiPP and PsBPP Containing Grafted Succinate Residues and Succinate/Vinylpyrrolidone Alternate Copolymers.

Polymer	% of grafted DES	% of DES grafted in the presence of 1-vinyl-2-pyrrolidone	G_{se}(%)
PiPP	0		18
	0.35		62
	0.55		85
		0.8	170
PsBPP	0		6.4
	0.22		8.6
	0.58		12.9
		0.44	23.5

It should be emphasized, moreover, that the presence of pyrrolidone units in the grafted alternate copolymers is able to remarkably improve the hydrophilicity of the functionalized phosphazene substrates, as can be proved by the swelling experiments in methanol reported in Table 3.

In fact, this Table shows that PiPP and PsBPP films are swollen considerably more efficiently in methanol when these polymers are treated with DEM in the presence of 1-vinyl-2-pyrrolidone, than when the same substrates are grafted with succinate groups only, indicating the important role played by the pyrrolidone residues in influencing the swelling capacity of the grafted phosphazene copolymers.

Intrinsic Viscosity Measurements

Our previous investigation on the grafting of maleic anhydride [21-25] and of maleates [29] onto selected POPs proved that this process took place quite efficiently when the grafting reaction was thermally initiated using suitable peroxide species. The main drawback of the thermal process, however, concerned the very high degradation phenomena that always occurred simultaneously with the grafting reaction which deeply degraded the polyphosphazene substrate. We were able to overcome this problem in the case of maleic anhydride when we started to investigate the light-induced grafting of this molecule onto POPs [27], as we realized that in this case no degradation phenomena for the exploited POPs could be observed.

To ascertain whether these facts are generally valid and whether they can also be applied to the light-induced grafting processes of maleate groups onto POPs described in this work, we measured the intrinsic viscosity [η] of the four POPs involved (see Table 1) and we also carried out the same series of viscosity characterizations for the POP-g-Succinate grafted copolymers produced photochemically under the above described different experimental conditions.

From these experiments, can be seen that no intrinsic viscosity variations could be observed for the photochemically produced phosphazene substrates, indicating that no degradative phenomena of the polymers actually took place during the above-described grafting experiments.

CONCLUSIONS

In this paper we have investigated the light-induced grafting reactions of dimethyl maleate, diethyl maleate, dibutyl maleate and diethyl fumarate, onto selected phosphazene macromolecules. The polymers most suitable for this goal were found to be aryloxy-substituted polyphosphazenes containing a methyl (PMPP), an ethyl (PEPP), an isopropyl (PiPP) and a secbutyl (PsBPP) radical attached to the para position of the side phenoxy substituents, since these substrates can undergo the easy abstraction of a hydrogen atom to form phosphazene macroradicals that are able to graft the succinate groups.

As in the previously investigated grafting reaction of maleic anhydride [21-25, 27], the light-induced grafting of maleate substrates onto POPs was found to be a rather complicated reaction, radical in nature, that can be influenced by several experimental factors: the type and concentration of the phosphazene substrate and of the maleate molecules, the concentration of the photoinitiating species, the presence or the absence of molecular oxygen, etc. It is therefore necessary to have a detailed knowledge of these parameters in order to prepare phosphazene grafted copolymers containing predictable amounts of succinate groups.

It is particularly important to stress that the experiments for the photochemical preparation of POP-g-Succinate grafted copolymers were carried out at room temperature, in such a way that the impinging light could not be directly absorbed by the polyphosphazene substrate. Under these conditions, no variations in the intrinsic viscosity of the polymers could be observed, indicating that the molecular weight of the POP did not undergo degradative phenomena. This fact allows the mechanical properties of POPs to be preserved for longer service periods.

A second, very important, observation concerning the above-described grafting processes of maleate and fumarate groups onto selected phosphazene macromolecules is that the final yield of grafted succinate groups is considerably lower (two or three times) than that obtained by means of the peroxide-initiated thermal process. This is not detrimental for the successive utilization of the functionalized phosphazene copolymers in reactive blending processes, since the degree of functionalization required by the macromolecules for this application is, in principle, very low. However, it can be completely overcome by carrying out the grafting experiments in the presence of equimolecular mixtures of 1-vinyl-2-pyrrolidone and maleate or fumarate compounds. Under these conditions, in fact, an alternating copolymerization process takes place between the maleate (or fumarate) species and the organic monomers, allowing the growth of mixed 1:1 copolymers from the main polyphosphazene substrate. In this way the swelling capability of the obtained grafted copolymers, with respect to that of the pristine POP, is remarkably increased.

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