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Functionalization of Poly(organophosphazenes). 8. Thermally-Induced Grafting Reactions of Maleates onto Poly[bis(4-ethylphenoxy)phosphazene]

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ABSTRACT: In this paper the radical-induced solution grafting of diethyl maleate onto poly[bis(4-ethylphenoxy)phosphazene] is reported, together with the possible parameters that can influence this reaction, i.e., the maleate, molecular oxygen, and dicumylperoxide concentration in the reaction mixture, the solvent, time, and temperature of the process. A possible mechanism of this process is inferred on the basis of literature data concerning analogous grafting processes carried out onto polyolefins. The importance of the decrease of the intrinsic viscosity of the reaction mixture that takes place during the grafting reaction is also discussed in terms of chain scission and molecular weight degradation of the phosphazene macromolecule. The possible implication of the final phosphazene copolymers containing variable quantities of grafted diethyl succinate groups, poly[bis(4-ethylphenoxy)phosphazene]-*g*-diethyl succinate, in blending processes with commercial, carbon-backboned macromolecules (polyesters and polycarbonates) is stressed.

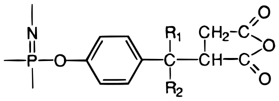
Introduction

A few years ago, we initiated a long-range research program mainly devoted to the modification of poly(organophosphazenes), POPs, by exploiting grafting[1−10] and functionalization[3,11−14] reactions of these macromolecules.

In the case of functionalization processes, the general strategy followed was the introduction of anhydride moieties into the polyphosphazene substrates under relatively mild experimental conditions, using unsaturated organic monomers able to undergo the opening of the double bond in the presence of peroxide initiators to bring about the grafting of a single molecule onto the POP substrates, without starting undesired radical chain polymerization reactions.[15]

For this research we selected maleic anhydride as a functionalizing group because of the strong importance of this substrate in the modification of polyolefins[16] and its very low capability of undergoing homopolymerization reactions,[17−21] and we chose the (aryloxy)-substituted phosphazene substrates containing different aliphatic residues in the para position of the phenoxy side groups as suitable POPs for these experiments. In particular, poly[bis(4-methylphenoxy)phosphazene], PMPP,[13,14] poly[bis(4-ethylphenoxy)phosphazene], PEPP,[12,14] poly[bis(4-isopropylphenoxy)phosphazene], PiPP,[14] poly[bis(4-*sec*-butylphenoxy)phosphazene], PsBPP,[11,14] and poly[bis(4-benzylphenoxy)phosphazene], PBPP,[14] were considered.

The final functionalized poly(organophosphazenes) had the following structure:



where $R_1 = R_2 = H$ for PMPP; $R_1 = H$ and $R_2 = CH_3$ for PEPP; $R_1 = R_2 = CH_3$ for PiPP; $R_1 = CH_3$ and $R_2 = C_2H_5$ for PsBPP; and $R_1 = H$ and $R_2 = C_6H_5$ for PBPP and where a variable amount of succinic anhydride groups was randomly inserted along the polyphosphazene chain.

The resulting phosphazene copolymers containing anhydride moieties proved to be macromolecular substrates very reactive toward $-OH$ and $-NH_2$ terminated organic molecules and macromolecules, with a particular concern about the possibility of using these functionalized POPs for the preparation of "compatibilizing agents", i.e., substances able to reduce the surface tension between two different polymeric materials and to facilitate the formation of polymeric blends.[22]

Expanding upon this research, we recently started to investigate a new series of unsaturated products able to modify the chemical structure of POPs by grafting reactions, i.e., dimethyl, DMM, diethyl, DEM, and dibutyl, DBM, maleates.[23] These molecules, in fact, although considerably less reactive, volatile, and toxic than the previously exploited maleic anhydride (this could be a very important point for their possible industrial application in the chemical modification of POPs, for instance, in reactive blending processes[24,25]), are still able to react with phosphazene macromolecules to form inorganic copolymers containing variable amounts of randomly grafted succinate groups.

In this paper we present the results obtained for the radical-induced grafting process of DMM, DEM, or DBM onto poly[bis(4-ethylphenoxy)phosphazene], the polymers that resulted in being the most reactive macro-

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molecules among those previously explored in the grafting process of maleic anhydride (MA) onto POPs.[12] The experimental findings on the formation of phosphazene blends using these copolymers by transesterification or alcoholysis reactions with polycarbonates[26,27] will be reported elsewhere.[28]

Experimental Section

Hexachlorocyclophosphazene (Shin Nissho Kako) was purified by repeated precipitation in *n*-hexane, followed by vacuum sublimations until a constant melting point of 113 °C was obtained.[29] The product was successively polymerized at 250 °C in evacuated sealed ampoules according to literature,[30−32] and the corresponding polydichlorophosphazene, $(NPCl_2)_n$ thus obtained was freed of the residual unreacted trimer either by precipitation in *n*-hexane[33] or by vacuum sublimation[34] and treated with an excess of 4-ethylphenate[12] (by reaction of dry 4-ethylphenol with the stoichiometric amount of NaH 60% oil dispersion). The resulting PEPP has the following elemental analysis data (calculated values in parentheses): C, 67.24 (66.90); H, 6.06 (6.27); N, 4.69 (4.87); Cl, <0.3% (0).

4-Ethylphenol, an Aldrich product, was anhydrified by azeotropic distillation from xylene. NaH 60% oil dispersion, dimethyl, diethyl, and dibutyl maleates, dimethyl, diethyl, and dibutyl succinates, *p*-xylene, *o*-xylene, *m*-xylene, and *o*-dichlorobenzene were Aldrich products, used as received.

Dioxane, xylene isomer mixture (hereafter referred as "xylene i.m."), tetrahydrofuran, etc. were Carlo Erba analytical grade solvents, purified or anhydrified according to literature.[35]

The grafting procedure for the maleates onto poly[bis(4-ethylphenoxy)phosphazene] was as follows: in a 10 mL pyrex flask, 50 mg (1.74×10^{-4} mol, as calculated on the basis of the molecular weight of the repetitive units) of PEFF were dissolved in 1 mL of xylene i.m., treated with variable amounts of diethyl maleate (DEM) and dicumylperoxide (DCP), in the presence or in the absence of molecular oxygen, for variable periods of times and at different temperatures. The resulting polymer, now containing variable percentages of diethyl succinate (DES) randomly grafted along the inorganic −P═N− skeleton, was recovered by precipitation in chilled methanol, dried with blotting paper, redissolved in methylene chloride (1 mL), deposited as thin film on a KBr disk, and eventually analyzed by infrared spectroscopy.

The final amount of diethyl succinate moieties grafted onto PEPP was determined by infrared spectroscopy by comparing the ratio of the intensities of two bands located at 1740 cm^{-1} (stretching of the carbonyl groups of the ester moieties) and 1610 cm^{-1} (stretching of the C−C bond of the aromatic phosphazene substituents) for the functionalized polymer, with the same ratio obtained by introducing known quantities of diethyl succinate into unmodified polyphosphazene films.

The final equation used was the following: weight percentage of grafted diethyl succinate $= A_{1740}/A_{1610} \times 1/0.211$ where 0.211 is the slope of the calibration plot experimentally measured for PEPP.

This was possible because the band at 1610 cm^{-1} does not modify its own intensity and position during the radical-induced grafting process of DEM onto PEPP.

Both the original PEPP and the phosphazene copolymers modified according to the above-described grafting procedure were characterized using different spectroscopic techniques, i.e., infrared spectroscopy using a Perkin-Elmer spectrophotometer Model 399, NMR spectroscopy using a Bruker 200 AC for ^{1}H and ^{13}C measurements, a Varian FT 80 for ^{31}P {^{1}H} NMR spectra, and by UV spectroscopy by utilizing a Perkin-Elmer UV−visible spectrophotometer Model 320. The viscosity of the polymer was determined with a Desreux−Bischoff-type suspended level viscosimeter. The gas chromatographic/mass spectrometric data were obtained by means of a Carlo Erba spectrometer Model QMD 1000 using a PS 264 capillary column of 30 m length (temperature from 100 to 250 °C; 10 °C/min, He 1 mL/min). Glass transition temperatures of both PEPP and PEPP-*g*-DES grafted copolymers were measured with a DSC 30 differential scanning calorimetry. For the grafting experiments, an oven CEAST Model 1175 was used, which was able to maintain the selected temperature with ±0.5 °C precision.

Table 1. IR Characterization Data of PEPP-*g*-DES Grafted Copolymers

3040 cm^{-1}	ν CH aromatic
2970−2870 cm^{-1}	ν CH aliphatic
1740 cm^{-1}	ν C═O ester groups
1610−1510 cm^{-1}	ν C−C phenoxy groups
1250−1200 cm^{-1}	asymmetric ν skeletal −P═N−
945 cm^{-1}	ν P−O−Ph

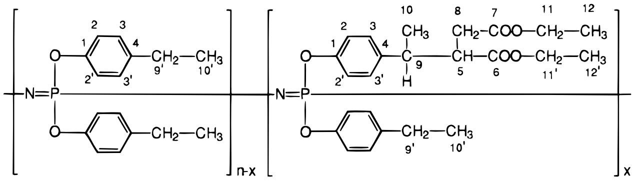
Table 2. NMR Characterization Data of PEPP-*g*-DES Grafted Copolymers

^{1}H	^{13}C	^{31}P
Ph 6.77−6.59(m, br)	C(1) 150.35	−19.22
CH(5) 2.9(m, br)	C(2,2′ and 3,3′) 128.54 and 121.82	
CH_2(8) 2.7(d, br)	C(4) 139.24	
CH(9) 2,1(s, br)	C(5) 49.13	
CH_2(9′) 2.39(q)	C(6) 173.83	
CH_3(10) 1.2(d, br)	C(7) 170.55	
CH_3(10′) 1.06 (t, $^3J_{HH} = 6.6$)	C(8) 35.33	
CH_2(11) 4.01(m, br)	C(9) 42.40	
CH_3(12) 1.23(m, br)	C(9′) 28.70	
	C(10) 14.72	
	C(10′) 16.18	
	C(11) 61.05	
	C(12) 14.72	

Results and Discussion

The reaction of poly[bis(4-ethylphenoxy)phosphazene], (PEPP), with dimethyl (DMM), diethyl (DEM), or dibutyl (DBM) maleate, in the presence of dicumyl peroxide (DCP) leads to the opening of the maleate double bond and to the grafting of the corresponding succinate (DMS, DES, or DBS) onto the polyphosphazene substrate.

In the case of the grafting reaction of diethyl maleate onto PEPP, the corresponding phosphazene copolymers, PEPP-*g*-DES, have the following structure:



in which highly polar ester functions are randomly grafted along the polymer backbone.

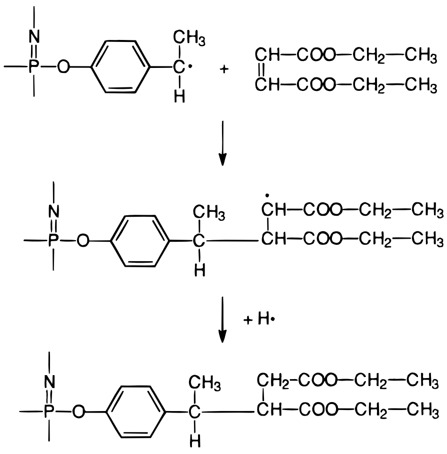
The IR and NMR (^{1}H, ^{13}C, and ^{31}P) spectroscopic characterization data for the native PEPP have been reported in a previous publication.[12] The corresponding IR and NMR results for the modified PEPP-*g*-succinate grafted copolymers are reported in Tables 1 and 2.

The analysis of the IR data quite clearly indicates[36] the presence in the functionalized copolymers of the phosphazene structure (1250−1200 cm^{-1}, asymmetric stretching of the −P═N− moieties, 945 cm^{-1}, stretching of the P−O−Ph groups, and 1610 and 1510 cm^{-1}, assigned to the breathing vibration of the C−C bond of the phenoxy substituents) and of ester residues (1740 cm^{-1}, attributed to the stretching of the ester carbonyls), while the vibration of the original double bond of the pristine DEM disappeared (no bands at 1645 cm^{-1}, assigned the stretching of the C═C double bond, are present).

NMR spectroscopic measurements, carried out on the same batch of PEPP-*g*-DES grafted copolymers are in agreement with the above reported IR data.

In the ^{1}H NMR spectrum of PEPP-*g*-DES, in fact, beside the signals at 2.39 (CH_2, 9′) and 1.06 (CH_3, 10′)

Scheme 1



ppm, assigned to the ethyl unit of the original PEPP, new signals at 2.90 (CH, 5), 2.70 (CH_2, 8), 2.10 (CH, 9), and 1.2 (CH_3, 10) are also present, which are attributed to the introduced succinate residues and to the modified ethylphenoxy units, respectively.

The same holds true in the case of ^{13}C NMR spectra, as the spectroscopic determinations carried out on PEPP-*g*-DES show both the peaks attributed to the pristine PEPP and two additional feeble peaks at 170.55 and 173.83 ppm that are due to the resonance of the freshly introduced succinate carbonyl functions.

In the ^{31}P {^1H} NMR spectra, finally, the original, very sharp, peak at −19.07 ppm belonging to the neat PEPP maintains its chemical shift and intensity unaffected, even if it remarkably broadens due to the partial modification of the phosphorus environment induced by the introduction of a low percentage of ethyl succinate groups in the (4-ethylphenoxy)phosphazene substituents.

It should be stressed that the NMR signals of the PEPP-*g*-DES phosphazene grafted copolymers are very weak due to the extremely low (less than 3−4% w/w) amount of DES moieties grafted onto PEPP using the solution-grafting technique described in this work. Nevertheless the peak assignment for these substrates could be possible with the help of previously published literature data concerning both organic[37,38] and phosphazene[13] macromolecules containing grafted diethyl succinate or succinic anhydride units, respectively.

The mechanism of the grafting reaction, inferred on the basis of literature data on the grafting reaction of DEM onto high-density polyethylene, is reported in Scheme 1.

Following previous investigations by Ciardelli,[39] Aglietto,[38,39] and Maglio and Musto,[40−42] in fact, the initial step of the grafting reaction is proposed to be the homolytic cleavage of the dicumyl peroxide initiator to form cumyl radicals that are able to abstract an hydrogen atom from the ethylphenoxy side phosphazene substituents giving rise to phosphazene macroradicals. According to literature[12,43,44] the abstracting site of the hydrogen is preferentially the methylene group in the ethylphenoxy units. The produced phosphazene macroradicals are so reactive to induce the opening of the maleate double bonds and allow the grafting of the succinate residues onto the polyphosphazene substrate to occur. As reported in Scheme 1, the radical species present in the grafted succinate units may abstract hydrogens from the solvent, from impurities, or from other phosphazene units in the polymer,[38,39] thus stabilizing the functionalized phosphazene macromolecule.

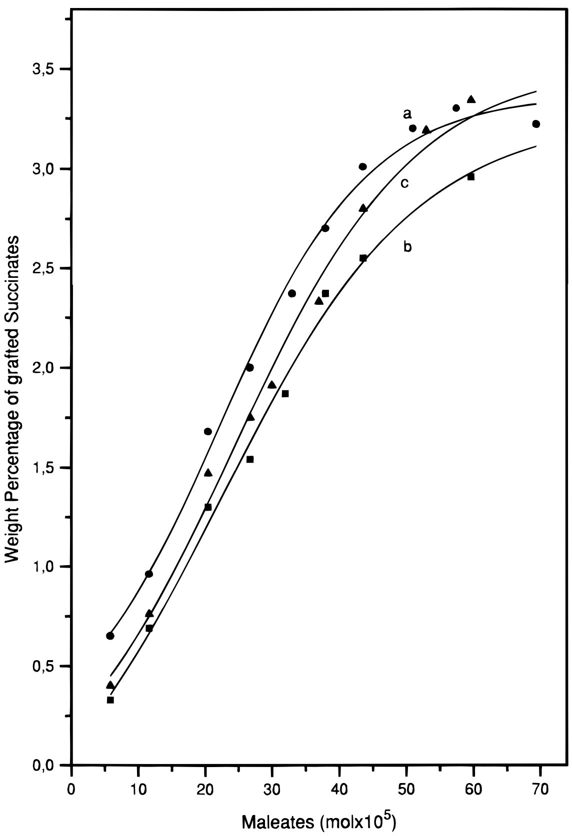


Figure 1. Influence of the molar content of (a) dimethylmaleate, (b) diethyl maleate, and (c) dibutylmaleate present in the reaction mixture on the weight percentage of the corresponding grafted succinates. (1.74×10^{-4} mol of PEPP; 5×10^{-5} mol of DCP; 1 mL of xylene i.m.; $T = 160$ °C; $t = 60$ min.)

The above described functionalization appears to be a quite controllable, reproducible, and smooth reaction. The final grafted phosphazene copolymers, PEPP-*g*-DES, furthermore, were found to be soluble in the most typical organic solvents and able to form transparent films. In spite of this apparent simplicity, however, the grafting efficiency of the succinate residues onto PEPP was found to depend on several different experimental parameters, as it could be expected by considering the radical nature of the process.[45] Starting from these considerations, therefore, we initiated the investigation of the grafting reaction of DEM onto PEPP in more details, with the aim of shedding additional light on the intimate characteristics of this process.

Influence of the Molar Concentration of DMM, DEM, and DBM on the Grafting Reactions of these Substrates onto PEPP. The influence of the molar content of DMM, DEM, and DBM on the grafting reaction of these molecules onto PEPP was investigated by dissolving this polymer and DCP in xylene i.m. and heating the reaction mixture in the presence of increasingly high amounts of the three different maleates.

The resulting copolymers, analyzed by IR spectroscopy, give the grafting percentages reported in Figure 1.

As can be seen in this Figure, the three maleates investigated (DMM, curve a; DEM, curve b, and DBM, curve c) show comparable behaviors both from a qualitative and a quantitative point of view, in the sense that a very low percentage of succinate groups is grafted onto PEPP when low amounts of DMM, DEM, and DBM are present in the reaction mixture, but these amounts increase steeply by increasing the maleate concentrations in the system, until a plateau is reached. After

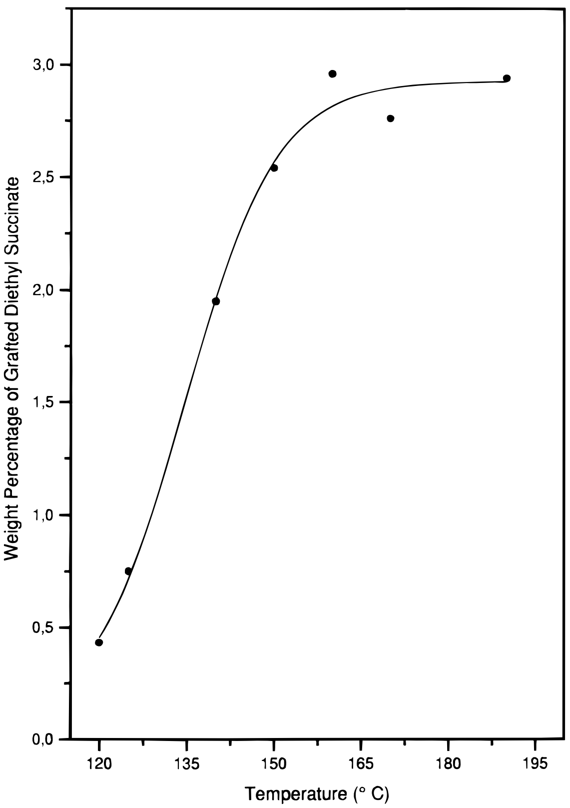


Figure 2. Influence of the reaction temperature on the weight percentage of DES grafted onto PEPP. (1.74×10^{-4} mol of PEPP; 5×10^{-5} mol of DCP; 5.8×10^{-4} mol of DEM; 1 mL of xylene i.m.; $t = 60$ min.)

this point, no further enhancement of the grafting yields is detected even for higher quantities of maleates in the system.

It may be observed, moreover, that the measured grafting yields of succinate groups onto PEPP are roughly the same for all the three exploited maleates, to suggest that no influence of steric factors, associated to the incoming maleate molecules, on the final grafting yields is operative. Thus, we decided to carry out the successive grafting experiments of maleates onto PEPP, considering the reaction of DEM only.

Influence of the Reaction Temperature and Heating Time on the Grafting Reaction of DEM onto PEPP. The importance of reaction temperature and heating time in determining the overall grafting yields of DEM onto PEPP was investigated by dissolving PEPP in xylene i.m., in the presence of DCP and DEM, and heating the reaction mixture at variable temperatures for fixed times, or at a stated temperature for variable time periods. The corresponding results are reported in Figures 2 and 3, respectively.

In both cases, the observed trend is similar to that previously observed, changing the percentage of DEM in the reaction mixture (see Figure 1), i.e., the grafting yields are considerably low at low temperatures or at short heating times and increase very rapidly with the increase of these parameters until a plateau is reached, after which no further enhancement of the grafting yields is detected even at very high temperatures or for very long reaction times.

Influence of the Peroxide Concentration on the Grafting Yield of DEM onto PEPP. As reported above for the previously described parameters (i.e., concentration of DEM, reaction time, and reaction temperature), the influence of the DCP concentration on the grafting yield of DES onto PEPP was investigated by dissolving this polymer in xylene i.m. in the presence of DEM and heating the reaction mixture in the presence of variable amounts of DCP in the system.

The obtained grafting yields are reported in Figure 4 where it can be seen that the percentage of grafted DES

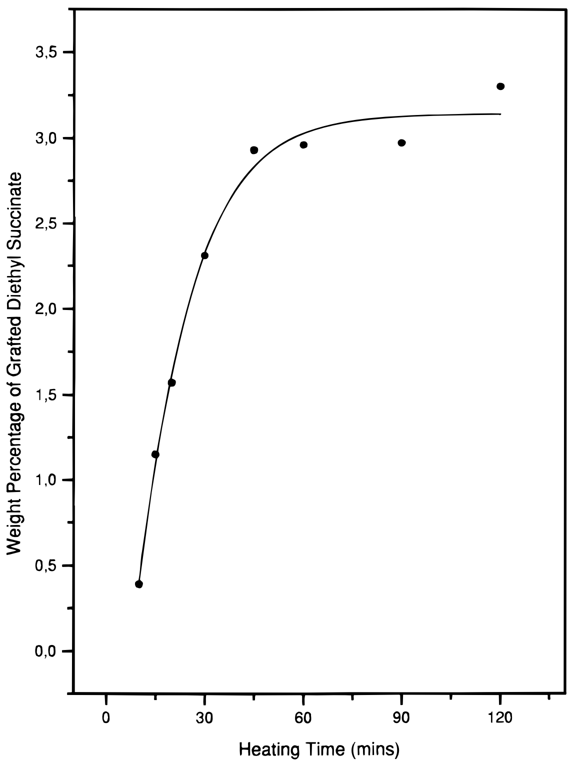


Figure 3. Influence of the heating time on the weight percentage of DES grafted onto PEPP. (1.74×10^{-4} mol of PEPP; 5×10^{-5} mol of DCP; 5.8×10^{-4} mol of DEM; 1 mL of xylene i.m.; $T = 160$ °C.)

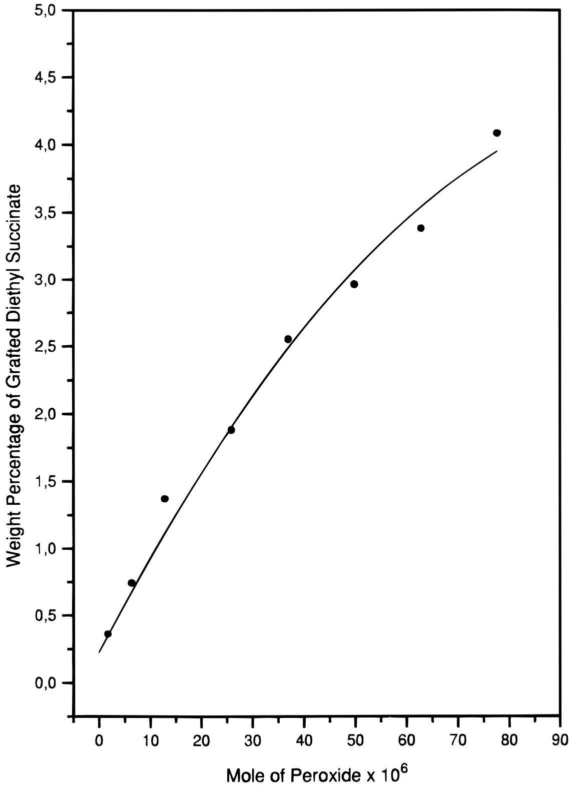


Figure 4. Influence of the DCP concentration on the weight percentage of DES grafted onto PEPP. (1.74×10^{-4} mol of PEPP; 5.8×10^{-4} mol of DEM; 1 mL of xylene i.m.; $T = 160$ °C; $t = 60$ min.)

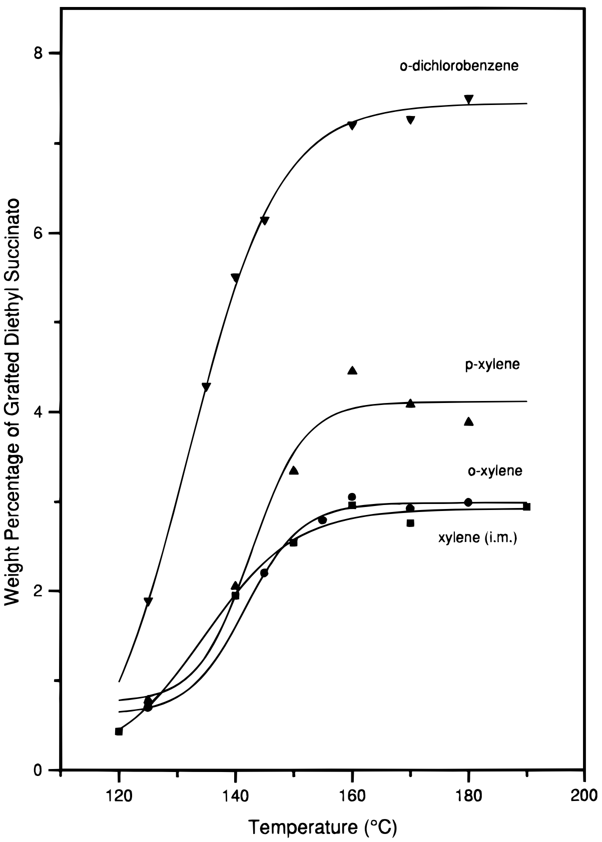


Figure 5. Influence of the different reaction solvents on the weight percentage of DES grafted onto PEPP at different termperatures. (1.74×10^{-4} mol of PEPP; 5×10^{-5} mol of DCP; 5.8×10^{-4} mol of DEM; 1 mL of xylene i.m.; $t = 60$ min.)

increases steadily with the increase of the peroxide concentration in the system. Different to the previous cases, no plateau is observed in the experimental curve of Figure 4.

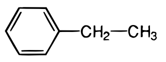
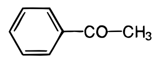
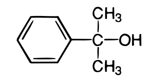
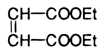
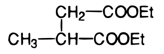
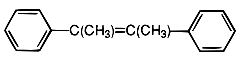
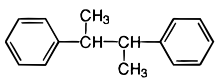
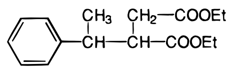
Influence of the Reaction Solvents on the Grafting Yield of DEM onto PEPP. The experiments on the grafting reaction of DEM onto PEPP were carried out in several different solvents (*o*-dichlorobenzene, *p*-xylene, *o*-xylene, and xylene i.m.) in order to check the influence of this parameter on the overall grafting yield of DES onto this polymer.

The results obtained by plotting the grafting yield of DES vs reaction temperature, for experiments carried out in these solvents, are reported in Figure 5.

This figure shows that *o*-dichlorobenzene is by far the most active solvent in favoring high-grafting yields, followed by *p*-xylene, while *o*-xylene and xylene i.m. show the lowest reactivity of the series.

The role played by the solvent used for carrying out the grafting experiments was already investigated in the case of the grafting of maleic anhydride (MA) onto PEPP.[12] In that case the experimental reactivity of the anhydride onto the poly(organophosphazenes) measured for the exploited solvents was interpreted in terms of the contrasting influence of two factors, i.e., the presence of charge-transfer (CT) complexes formed between the aromatic solvents (electron donor) and the maleic anhydride (electron acceptor)[12,16,46−53] that inject electrons into the ethylenic double bond of MA, thus enhancing its grafting reactivity; the role of side, undesired reactions that take place between the radicals formed in solution following the primary cleavage of the thermal initiator and the exploited solvents that subtract species active in the grafting process from the reaction mixture, thus depressing the final grafting yield.[20]

Table 3. Structure of the Reaction Products Formed by Reaction of DEM in Ethylbenzene in the Presence of DCP

Products	Structure	Molecular Weight	Retention Time (mins)
Ethylbenzene		106	6.5
Acetophenone		120	12.4
Cumyl Alcohol		136	12.8
Diethyl Maleate	 $\begin{array}{l}\mathrm{CH{-}COOEt}\\ \|\\ \mathrm{CH{-}COOEt}\end{array}$	172	15.0
α-Methyl-Diethyl Succinate	 $\begin{array}{l}\quad\mathrm{CH_2{-}COOEt}\\ \quad\;|\\ \mathrm{CH_3{-}CH{-}COOEt}\end{array}$	188	16.1
cis,trans-2,3-Diphenylbutene		208	29.0
2,3-Diphenylbutane		210	29.5
4-Phenyl-3-Carboethoxypentanoic Acid Ethyl Ester		278	35.2

On the basis of these previous findings on the grafting process of MA onto PEPP,[12] and with the aim of shedding additional light in the grafting process of DEM onto PEPP using different reaction solvents, we undertook a series of spectrophotometric investigations on the capability of DEM of forming CT complexes with the aromatic solvents, and we successively investigated the thermal reaction of DEM dissolved in ethylbenzene when heated at 160 °C for 60 min in the absence of the phosphazene polymer, using a gas chromatograph coupled with mass spectrometer to analyze the reaction products.

UV−visible spectrophotometric investigations on the DEM/aromatic solvent system showed that very feeble, if any, CT complexes are formed between DEM and mesitylene (a solvent that possesses a very low ionization potential[54−56]), while no evidence was found of the existence of these species in different types of xylenes or in an ethylbenzene solvent. These facts imply that no activation of the DEM double bond is possible by the solvents used for the grafting process, and that, therefore, DEM behaves as a substrate considerably more inert than MA toward the radical-induced grafting reaction onto PEPP. This is also confirmed by the comparison of the grafting data relative to maleic anhydride[12] and diethyl maleate reported for PEPP which demonstrated that the amount of grafted succinic anhydride units are considerably more elevated than that of diethyl succinate under comparable experimental conditions.

Quite interesting results, furthermore, came from gas chromatographic/mass spectrometric measurements carried out on the reaction mixture formed by DEM dissolved in ethylbenzene and heated in the presence of dicumyl peroxide, at 160 °C, for 2 h, in the absence of PEPP. The results obtained showed that eight different products are formed during the process, to indicate the extremely high reactivity of the maleate substrate in these experimental conditions. The structure of these species, as identified on the basis of the MS fragmentation patterns, is reported in Table 3.

It is interesting to observe that, besides ethylbenzene solvent and DEM (substrates already present in the

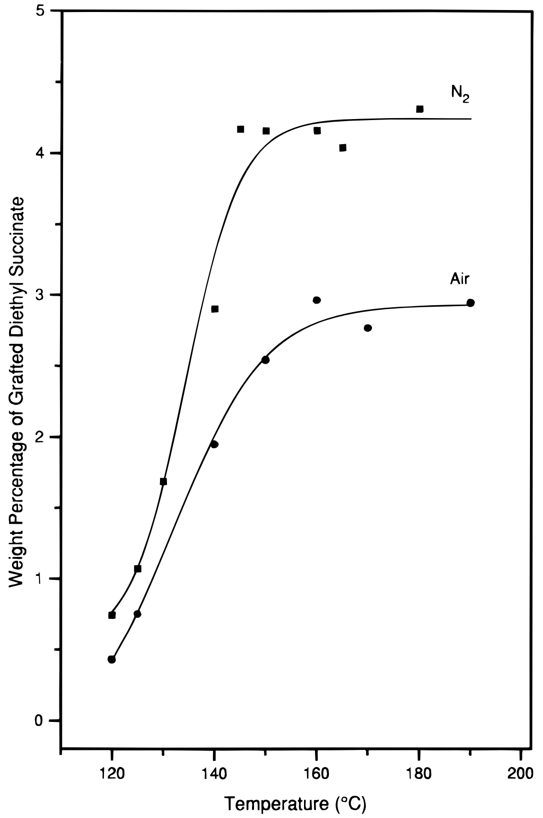


Figure 6. Influence of molecular oxygen on the weight percentage of DES grafted onto PEPP, at different temperatures, in the presence of DCP. (1.74×10^{-4} mol of PEPP; 5×10^{-5} mol of DCP; 5.8×10^{-4} mol of DEM; 1 mL of xylene i.m.; $t = 60$ min.)

starting reaction mixture), cumyl alcohol, (from the homolytic cleavage of the DCP and hydrogen uptake), 2,3-diphenylbutane (from the coupling of solvent radicals), acetophenone (from both the oxidation of ethylbenzene and the dicumylperoxy radicals by β-scission processes), and 2,3-diphenylbutene (from the coupling reaction of solvent radicals and DCP fragments), two additional products are formed in this reaction, i.e., diethyl α-methylsuccinate and 4-phenyl-3-carboethoxypentanoic acid ethyl ester, that are products probably derived from the reaction of DEM with methyl- and ethylbenzene radicals, respectively.

These facts clearly demonstrated that when DEM is dissolved in aromatic solvents that contain reactive alkyl radicals in the rings (xylenes, ethylbenzenes, etc.), chain-transfer processes between the initiating DCP fragments and the solvents themselves easily take place, leading to the formation of the species already mentioned in Table 3.

In this way substrates that are active in the grafting process of DEM onto PEPP are subtracted from the reaction system, thus strongly reducing the final grafting yield. This fact, together with the lack of CT complex formation between the maleate and the exploited xylenes that should activate the ethylene double bond of the maleate group by injecting electrons in the unsaturated system, reasonably accounts for the very low yields observed during the grafting reaction of maleates onto PEPP dissolved in xylenes. The opposite holds true using *o*-dichlorobenzene as a solvent, where relatively high yields are found for the grafting of DEM onto PEPP, as no chain-transfer reactions are possible in this medium due to the lack of easily abstractable hydrogen atoms in the chemical structure of this compound.

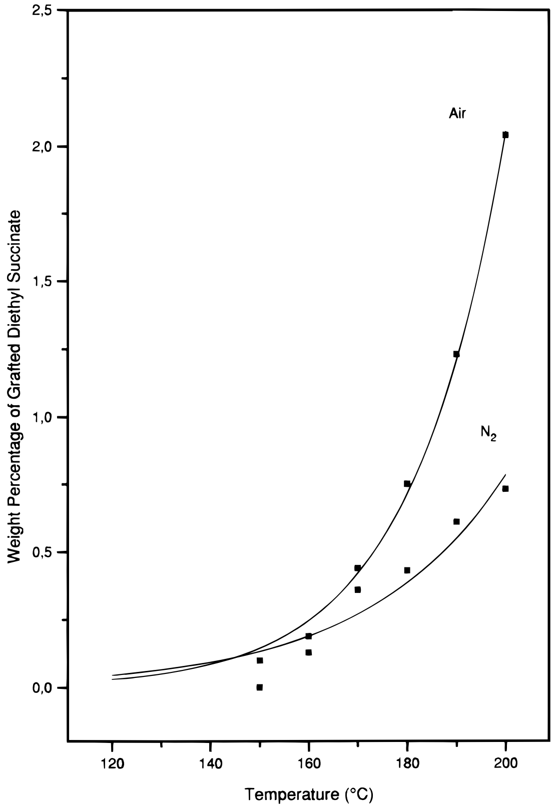


Figure 7. Influence of molecular oxygen on the weight percentage of DES grafted onto PEPP, at different temperatures, in the absence of DCP. (1.74×10^{-4} mol of PEPP; 5.8×10^{-4} mol of DEM; 1 mL of xylene i.m.; $t = 60$ min.)

Influence of the Molecular Oxygen on the Grafting Reaction of DEM onto PEPP. The effect of the molecular oxygen on the grafting yield of DEM onto PEPP was investigated by carrying out two different sequences of experiments, exploiting in one case air-equilibrated solutions and in the second one deaerated solutions obtained by bubbling nitrogen in the system for 15 min. In both cases the reaction mixture was prepared by dissolving PEPP in xylene i.m., in the presence of DCP and of DEM, heating the reaction at temperatures that ranged between 120 and 200 °C. The corresponding results are reported in Figure 6.

This plot demonstrates that the percentage of grafted DES is considerably higher for the experiments carried out in nitrogen atmosphere than for those performed in air, to indicate that molecular oxygen plays quite an important role in the determination of the overall grafting yield of DES onto PEPP. This may be reasonably attributed to the diradicalic nature of the molecular oxygen that makes this species very susceptible to reacting with the radicals formed in the reaction mixture and subtracting reactive intermediates from the process, eventually depressing the overall grafting yield.

Quite interestingly, the IR analysis of the grafted copolymers PEPP-*g*-DES formed showed no bands in the spectral region of 3600−3200 cm^{-1}, to indicate that the above-mentioned oxygen reactivity does not involve the polyphosphazene substrate.

It is worth mentioning, moreover, that, when the sequence of experiments reported above, in the presence or in the absence of molecular oxygen, is performed without the DCP thermal initiator, the reaction sequence found is exactly the opposite with respect to that reported in Figure 6 (see Figure 7) in the sense that (1) the grafting yield no longer displays a sigmoidal trend, as in previous figures; (2) the reaction that is not very

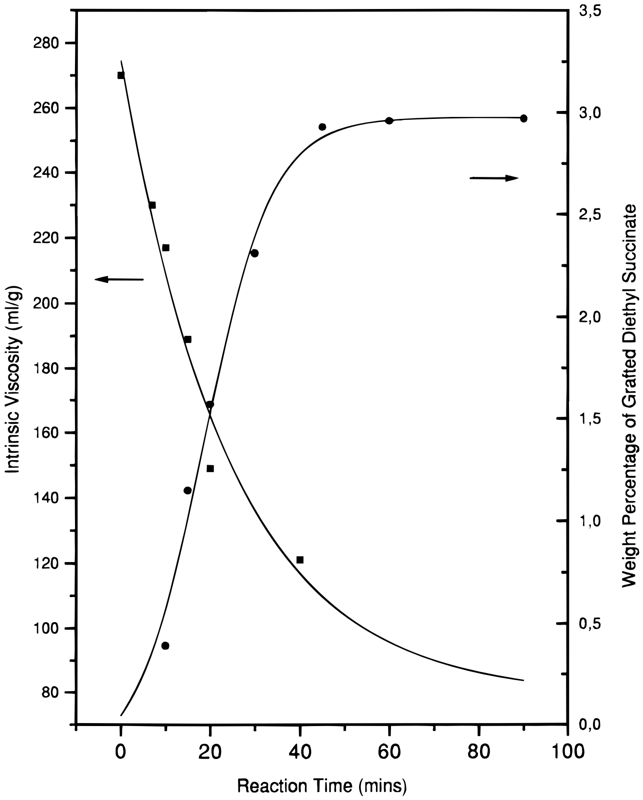


Figure 8. Influence of the reaction time on the weight percentage of DES grafted onto PEPP at 160 °C (right) and on the intrinsic viscosity of a xylene i.m. solution of PEPP-*g*-DES (left).

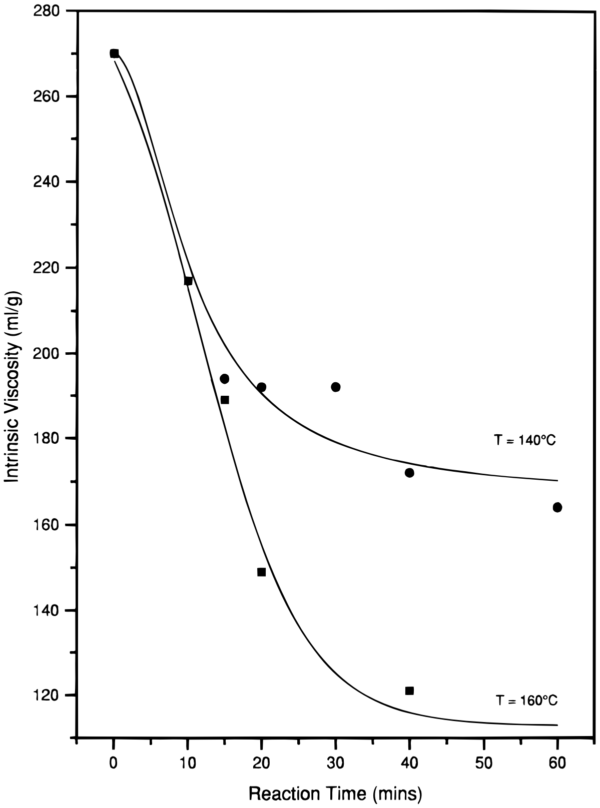


Figure 9. Influence of the reaction time on the intrinsic viscosity xylene i.m. solutions of PEPP-*g*-DES grafted copolymers, at different temperatures.

efficient at temperatures until 160 °C starts to be appreciable in the temperature range between 160 and 200 °C; (3) the processes carried out in air-equilibrated solutions are more effective than those performed in an inert atmosphere.

Although no indications are available on the possible reaction mechanism of the grafting reactions at high temperature and in the absence of the peroxide initiator, the experimental findings seem to indicate that the presence of molecular oxygen favors the grafting of DEM onto PEPP, possibly by a radical formation mechanism that implies, as an initial step, the oxidation reaction of the polyphosphazene substrate.

Modification of the Physical Properties of PEPP Following the Solution Grafting of DEM. Our previous experience on the grafting reaction of MA onto PEPP evidenced that the grafting process of unsaturated monomers onto poly(organophosphazenes) is accompanied by the simultaneous cleavage of the polymer skeleton and decrease in molecular weight.

For this reason we carried out a series of grafting experiments coupled with parallel measurements on the solution viscosity of the modified PEPP-*g*-DES grafted copolymers, also in the case of the thermally-induced grafting of DEM onto PEPP, and we report the corresponding results in Figure 8 where both viscosity changes and the weight percentage of grafted DES are plotted vs reaction times.

As can be seen from this figure, the increase of the grafting yield of DEM onto PEPP increases with reaction time, while the solution viscosity concurrently collapses to very low values. As it is well-known that the solution viscosity is a parameter intimately related to the molecular weight of the polymer, we have to conclude that the experimentally observed reductions of intrinsic viscosity for PEPP are indicative of the strong degradation undergone by this polymer during the grafting reaction of DEM onto PEPP.

It is interesting to note, moreover, that the viscosity of the phosphazene solution reaches the lowest value when the grafting yield reached the plateau, to clearly indicate that the chain cleavage processes for PEPP and chain degradation phenomena are more efficient when the percentage of grafted DES reaches the highest value. These observations are in strong agreement with the experimental findings previously reported for the grafting experiments of MA onto PEPP.[12]

Furthermore, we report in Figure 9 two sequences of grafting reactions carried out according to the previously reported procedure, but at different temperatures (140 and 160 °C). In both cases the degradation of the phosphazene polymer appears to be the prevailing process in these experimental conditions, but the entity of this phenomenon seems to be intimately related to the temperature of the process, in the sense that the decrease of the solution viscosity is much more accentuated when the grafting experiments are performed at 160 °C than when the reaction takes place at 140 °C.

Conclusions

In this work we reported the thermally-induced grafting reaction of diethyl maleate onto poly[bis(4-ethylphenoxy)phosphazene] in solution of aromatic solvents, and we investigated the importance of numerous experimental parameters that influenced this reaction. In particular the role played by the concentration of DEM, DCP, and molecular oxygen was studied, and the importance of the reaction solvents, temperature, and time was examined.

These investigations demonstrated that the grafting reaction of DEM onto PEPP is a rather controllable and reproducible process that allows the introduction of a predictable amount of ester functionalities into the polyphosphazene substrate. Moreover, preliminary experiments[23,28] indicated that this process is equally effective for other phosphazene macromolecules substituted with different types of aryloxy derivatives.

However, the introduction of these ester groups into variably substituted POPs is a process always accompanied by concurrent degradation phenomena that decrease the solution viscosity and the molecular weight of the polymers, ultimately leading to the loss of the mechanical properties of the final, functionalized materials.

The accurate control of the experimental conditions during the process is, therefore, necessary to minimize the entity of the damages introduced during the grafting reactions.

It has to be stressed that the introduction of highly polar ester groups into POPs may dramatically change not only the physical properties of the polyphosphazene substrates (e.g., solution viscosity), as above reported, but also the chemical ones, in the sense that transesterification or alcoholysis reactions between succinate-containing polyphosphazenes and polyesters or polycarbonates in principle become accessible for these materials by means of reactive blending processes,[24,25] thus favoring the formation of blends between POPs and organic macromolecules.

This aspect of the polyphosphazene functionalization is still under investigation and will be reported elsewhere.

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