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Functionalization of Poly(organophosphazenes). 4.[1] Radical-Induced Grafting of Anhydride Groups onto Poly[bis(4-ethylphenoxy)phosphazene]

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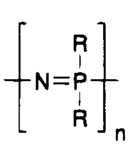
ABSTRACT: In this paper we describe the free-radical-promoted grafting of maleic anhydride onto poly[bis(4-ethylphenoxy)phosphazene] carried out in solution under variable experimental conditions. It was found that this reaction depends on several different experimental parameters, i.e. the percentage of maleic anhydride in the system, the type and the thermal stability of the exploited peroxide initiators, the solvents used to run the grafting experiments, the amount of molecular oxygen present in the reaction medium, the heating time, and the reaction temperature. The grafting of maleic anhydride onto poly[bis(4-ethylphenoxy)phosphazene] induces profound modifications both in the physical (viscosity and glass transition temperature) and in the chemical (reactivity) properties of the phosphazene polymer and opens up unexpected perspectives to further functionalization reactions and compatibilization processes for the phosphazene polymer.

Introduction

Nowadays the fulfillment of the acute needs of the modern plastic industry seems to be more conveniently achieved by means of the unconventional utilization to already established types of macromolecules instead of the development of new polymers. In this perspective, one of the most promising approaches to the preparation of new materials appears to be the formation of polymeric blends,[2] as obtained by bringing different types of macromolecules into strong contact, e.g. using casting or extrusion techniques.

Polymer blending, in fact, is not only a suitable method of grading existing types of macromolecules normally used as *commodities* but can also be considered as a way of developing new materials with original property profiles to be regarded as *specialties*, this because interactive phenomena and synergistic effects leading to novel characteristics or enhanced properties are rather common in multicomponent systems.

In the field of poly(organophosphazenes), POPs,



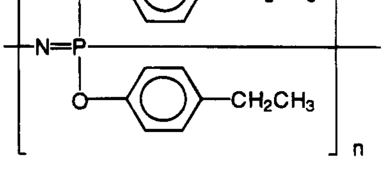
$$\left[-N{=}\overset{R}{\underset{R}{P}}-\right]_n$$

a class of polymers disclosed scientifically by Allcock in 1965[3−5] and brought recently to an industrial level in the U.S.A., Europe, and Japan by Ethyl Corp.,[6−11] Atochem,[12−14] and Shin Nisso Kako,[15,16] respectively, the preparation of new materials through the formation of blends seems to be a really difficult task. These polymers, in fact, show a reduced tendency to give mixtures both with other polyphosphazenes (i.e. polymers of the same series but bearing different substituent groups on the phosphorus)[17−19] and with conventional, carbon-backboned macromolecules (polystyrene or polyolefins, for instance).[20−22]

However, the compatibilization of phosphazene macromolecules with other plastics could be, in principle, obtained by exploiting the so-called "coupling agents" or "compatibilizers,[23,24] i.e. low molecular weight molecules or functionalized macromolecules capable of specific interactions and/or chemical reactions with the blend components. In this way the interfacial energy between the basic constituents of the blend will be greatly reduced and the new materials formed.[23]

We faced the problem of synthesizing compatibilizing agents for POP blends both by exploring the light-induced grafting reactions of conventional organic polymers onto suitable polyphosphazenes[25−35] and by using the free-radical grafting of maleic anhydride onto selected polyphosphazenes.[29,30,34] The functionalized copolymers obtained show completely different chemical and physical properties as compared to the characteristics of the pristine materials and lend themselves nicely for exploring the formation of blends with POPs.

On the basis of these considerations, we herewith present results on the chemical functionalization of poly[bis(4-ethylphenoxy)phosphazene], PEPP,



by grafting anhydride groups onto this polymer using thermally-induced free-radical reactions, as a preliminary step for the utilization of these functionalized polymers for the preparation of blends based on polyphosphazene materials.

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The choice of poly[bis(4-ethylphenoxy)phosphazene] as a valuable polymer for this kind of modification was suggested by the fact that the secondary, highly reactive hydrogens present in the side phenoxy substituents of this polymer impart to the material high reactivity under mild experimental conditions,[30,34,36] and also by the consideration that phosphazene copolymers bearing high amounts of 4-ethylphenoxy substituents (about 50%) have been developed industrially due to their outstanding properties as heat and flame resistant macromolecules.[12] The results presented here, therefore, will allow for the facile chemical functionalization of materials already industrially available without the need for modifying production plants and/or synthetic procedures.

Experimental Section

Hexachlorocyclophosphazene was purchased from Shin Nisso Kako and purified by precipitations in *n*-hexane and repeated vacuum sublimations until a constant melting point (113−114 °C) was reached.[37] Poly(dichlorophosphazene) was prepared by bulk thermal polymerization at 250 °C in vacuum for several hours[3−5] and freed from the residual unreacted trimer by vacuum sublimation at 65−70 °C.[38] 4-Ethylphenol (Aldrich) was dried by means of azeotropic distillation from xylene,[39] treated with NaH 60% oil dispersion (Aldrich) and reacted eventually with the poly(dichlorophosphazene) for 3 days[40] in the presence of phase transfer catalysts.[38] The resulting poly[bis(4-ethylphenoxy)phosphazene], PEPP, is a white, fibrous, film-forming solid showing characterization data similar to those previously reported.[40,41] The intrinsic viscosity of the polymer, as measured at 20 °C using tetrahydrofuran (THF) solvent freshly distilled over NaOH, was found to be 264 mL/g. The glass transition temperature of PEPP was −12.9 °C (literature[41] $T_g = -19$ °C).

Maleic anhydride (MA), succinic anhydride (SA), benzoyl peroxide (BP), lauroyl peroxide (LP), dicumyl peroxide (DCP) and *tert*-butylperoxy benzoate (tBPB), Aldrich products, were used as received. The solvents used for the grafting experiments, i.e. mesitylene, xylene isomer mixture (32% *m*-xylene, 59% *p*-xylene, and 9% *o*-xylene by gas chromatography/mass spectrometry, hereafter referred to as "xylene i.m."), *o*-xylene, *m*-xylene, *p*-xylene, ethylbenzene, toluene, benzene, dichloromethane, and *o*-dichlorobenzene were analytical grade Carlo Erba or Aldrich solvents.

The functionalization of PEPP was achieved according to literature[29] by dissolving the polymer (50 mg) in sealed Pyrex ampules containing different solvents (1 mL), in the presence of variable amounts of molecular oxygen, maleic anhydride, and peroxide initiator, and heating the system at temperatures ranging between 60 and 200 °C for times varying between 5 and 40 min. When necessary, the solutions were degassed (0.01 Torr) by several freeze−pump−thaw cycles or saturated with pure oxygen (1 atm) with a vacuum line. The PEPP-*g*-SA grafted copolymers were recovered by precipitation in methanol, quickly dried with filter paper, and characterized.

The quantitative determination of the amount of succinic anhydride grafted onto PEPP was obtained by IR spectroscopy.[29] In fact, considering PEPP films that contain weighted quantities of succinic anhydride, the absorbances of these films were measured at 1785 and 1605 cm^{-1}, and the values obtained were plotted vs the percentage of succinic anhydride. The actual amount of grafted SA was obtained directly by the following equation:

$$\%\text{ of grafted SA} = A_{1785}/A_{1605} \times 1/0.452$$

where A_{1785} and A_{1605} are the absorbances at 1785 and 1605 cm^{-1}, respectively, and 0.452 is the slope measured for the calibration plot.

The determinations of the charge-transfer complexes between maleic anhydride and the aromatic solvents used for the grafting processes were obtained spectrophotometrically by measuring the optical densities of MA ($C = 3.37 \times 10^{-3}$ mol) dissolved in CH_2Cl_2/aromatic solvent 10/90 v/v mixtures.

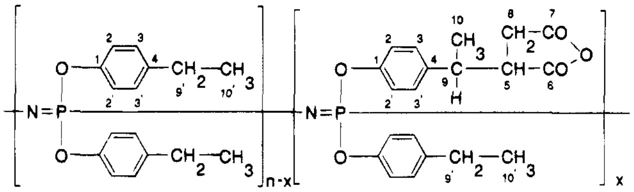
The IR spectra of PEPP-*g*-SA grafted copolymers were carried out with a Perkin-Elmer IR spectrophotometer model 399. The UV determinations were run using a Perkin-Elmer UV−visible spectrophotometer, model 320, using quartz cells 0.1 cm thick. NMR spectra were obtained with a Varian FT 80 (^{31}P NMR) and a Bruker 200 AC (^{1}H and ^{13}C NMR). Viscosity measurements were performed with a Desreux-Bischoff-type suspended level viscosimeter. Gas chromatography/mass spectrometry (GC/MS) 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). The measurements of the glass transition temperatures for the PEPP homopolymer and the PEPP-*g*-SA grafted copolymers were carried out with a DSC 30 Mettler differential scanning calorimeter.

Results and Discussion

The reaction between poly[bis(4-ethylphenoxy)phosphazene], PEPP, dissolved in xylene i.m and maleic anhydride, MA, in the presence of different peroxides as thermal initiators, leads to the formation of poly[bis(4-ethylphenoxy)phosphazene]-*g*-succinic anhydride, PEPP-*g*-SA, grafted copolymers, in which variable amounts of SA residues are attached into the polyphosphazene substrate.

The mechanism of this reaction, already discussed in previous publications,[29,30,34] implies first the thermal cleavage of the peroxide molecules to form free radicals in the system; these species are successively able to abstract hydrogens from the phosphazene polymer, forming POP macroradicals from which the grafting of the maleic anhydride can start by opening the ethylene double bond of this product. The very low capability of MA to homopolymerize[24,42−45] stops the grafting reaction at the monomolecular level.

The final PEPP-*g*-SA grafted copolymers obtained in this way show the following chemical structure:



in which succinic anhydride residues are randomly attached into the 4-ethylphenoxy units. In this formula we have indicated the secondary hydrogens of the ethyl groups of the phenoxyphosphazene substituents as a grafting site for the SA moieties onto PEPP on the basis of both the energy requirements for the cleavage of the primary C−H bond ($-CH_3$) and of the secondary C−H bond ($-CH_2-$) of the 4-ethylphenoxy substituents of the POP[46] and on the basis of the results of grafting experiments of maleic anhydride onto ethylbenzene reported in the literature, in which the SA residues are found to react with the secondary hydrogens of the ethyl radical of this substrate.[36] The possibility of grafting the maleic anhydride groups onto the methyl groups of the ethylphenoxy moiety, too, cannot, of course, be ruled out completely.

The above discussed data are supported by IR and NMR spectroscopy. In fact, the IR spectrum of PEPP shows bands at 3040 cm^{-1} (ν_{CH} aromatic), 2970−2870 cm^{-1} (ν_{CH} aliphatic), 1605 and 1510 cm^{-1} (ν_{C-C} of the phenoxy ring), 1250−1200 cm^{-1} (ν of the −P=N− skeletal units), and 945 cm^{-1} (ν of the P−O−Ph moi-

Table 1. NMR Characterization Data

^{1}H NMR	^{13}C NMR	^{31}P NMR
	A. PEPP	
CH_2(9′): 2.34 (q)	C(1): 149.68	−19.07 (s)
CH_3(10′): 1.01 (t)	CH(2,2′) and CH(3,3′): 127.79 and 121.14	
Ph: 6.76 and 6.72; 6.57 and 6.53 (AA′BB′)	CH_2(9′): 28.05 (t)	
	CH_3(10′): 15.49 (q)	
	B. PEPP-*g*-SA	
Ph: 6.93−6.54 (m)	CH(5): 46.90 (d)	−19.22 (s)
CH(5): 2.79	CO(6): 169.64	
CH_2(8): 3.06	CO(7): 172.28	
CH(9): 2.01	CH_2(8): 32.23 (t)	
CH_2(9′): 2.35 (q)	CH(9): 35.16 (d)	
CH_3(10): 1.09	CH_2(9′): 27.99 (t)	
CH_3(10′): 1.02 (t)	CH_3(10): masked	
	CH_3(10′): 15.50 (q)	

eties). All these bands can also be found in the spectrum of the PEPP-*g*-SA grafted copolymers, where two additional absorptions at 1870 and 1785 cm^{-1}, attributed to the stretching of the succinic anhydride groups, are also present.

On the same line we can find the results of the NMR data reported in Table 1. In fact, the singlet in the ^{31}P NMR of neat PEPP is only slightly broadened in the ^{31}P NMR spectrum of PEPP-*g*-SA, and its position is almost unchanged by the grafting process. This is not unexpected, given the great distance between the skeletal phosphorus and the grafting site on the polyphosphazene substituents that considerably attenuates the effects of the insertion of SA groups on the PEPP. The same behavior has previously been observed in the case of other poly(organophosphazenes).[29] In the ^{1}H NMR spectra, the signals at 2.34 ($-CH_2-$) and 1.01 ($-CH_3$) ppm of the original PEPP are also present in the spectrum of PEPP-*g*-SA, accompanied, however, by new signals at 2.79 ($-CH-$) and 3.06 ($-CH_2-$) ppm assigned to the anhydride functions and by peaks at 1.09 ($-CH_3$) and 2.01 ($-CH-$) ppm due to the modified ethylphenoxy units.[47] The same holds true in the case of ^{13}C NMR spectra of PEPP-*g*-SA grafted copolymers that also show, besides the signals of the pristine PEPP units, well-detected additional peaks at 169.64 and 172.28 ppm attributed to the carbonyl functions of the anhydride groups.

All these data indicate that the grafting reaction of maleic anhydride onto PEPP was successful. This process, however, was found to be dependent on several different experimental parameters, such as the percentage of MA in the system, the nature and the type of peroxide initiators, the solvents exploited for the reaction, the temperature, the reaction time, and the presence or the absence of molecular oxygen. It was found, moreover, that the initial molecular weight of the PEPP and the T_g of the polymer are influenced by the grafting process. We decided, therefore, to investigate the functionalization reaction of PEPP with MA in detail with the aim of completely rationalizing the overall process.

Influence of the Percentage of Maleic Anhydride on the Grafting of MA onto PEPP. The reaction of 50 mg of PEPP dissolved in 1 mL of xylene i.m. with variable amounts of maleic anhydride, carried out at 139 °C in the presence of 10% w/w of benzoyl peroxide as a thermal initiator, leads to the grafting of SA groups onto the polyphosphazene substrate. The results of these experiments are reported in Figure 1. From this picture it is evident that, when low quantities of MA are present in the system, a low percentage of SA groups is actually grafted onto PEPP. However, the increase of maleic anhydride concentration in the reaction medium results in an enhanced efficiency of the grafting process, until 6% w/w of SA residues are grafted onto the polyphosphazene matrix. At this value, the percentage of SA grafted onto the phosphazene polymer reaches a plateau and does not increase any further by successive additions of MA in the reaction mixture.

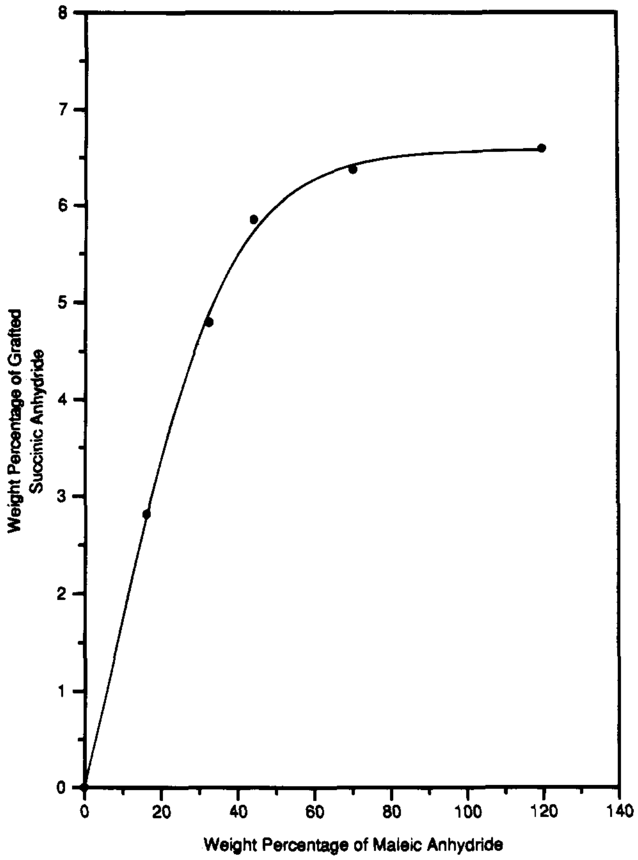


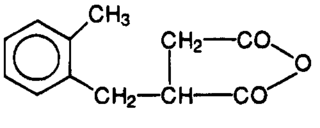
Figure 1. Influence of the weight percentage of maleic anhydride in the reaction mixture on the weight percentage of succinic anhydride grafted onto PEPP.

These results are very similar to those previously obtained in the case of grafting maleic anhydride onto poly[bis(4-*sec*-butylphenoxy)phosphazene].[29]

Solvent Influence on the Grafting of MA onto PEPP. In this work we also explored the grafting of maleic anhydride onto PEPP dissolved in several different solvents and heated for variable periods of time at 125 °C, with the aim of investigating the role played by the solvents on the efficiency of the overall grafting process. These experiments were accompanied by a series of UV−visible spectroscopic characterizations and by GC/MS measurements.

The rationale of this research stands on the fact that the radicals produced by the thermal cleavage of the peroxide initiators used to promote the grafting process are known to interact with solvent molecules through chain-transfer reactions to form solvent radicals that can also participate in the reaction with the maleic anhydride groups.[44] Moreover, strong evidence exists in the literature that maleic anhydride is able to form charge-transfer complexes with the aromatic solvents used for the grafting processes that are supposed to play a fundamental role in the overall grafting reaction of MA onto PEPP.

The actual interaction between maleic anhydride and the solvents used for the grafting process was proved by heating *o*-xylene and maleic anhydride in the presence of benzoyl peroxide and analyzing the resulting products by means of the gas chromatography/mass spectrometry technique. The gas chromatogram of the reaction mixture shows a peak at the retention time of 21.15 min, for which the following structure is suggested on the basis of its fragmentation pattern.



In fact, the mass spectrum of the peak presents the molecular ion $[CH_3C_6H_4CH_2\overline{CHCOOCOCH_2}]^{\bullet +}$ at *m/z* 204, which loses both CO_2 and CO residues to give the ions $[C_{10}H_{12}]^{\bullet +}$ at *m/z* 132. A subsequent loss of $CH_3^{\bullet}$ leads to the ions $[C_9H_9]^+$ at *m/z* 117. The base peak of the spectrum corresponds to ions $[CH_3C_6H_4CH_2]^{\bullet +}$ at *m/z* 105, likely formed by a retrosynthetic process.

The above reported chemical structure of this intermediate is of remarkable importance because it gives direct evidence of the interactions that take place between the solvent radicals and the anhydride molecules, thus subtracting species active in the formation of PEPP macroradicals and depressing the final production of PEPP-*g*-SA grafted copolymers.

As for the formation of charge-transfer complexes betwen the solvents used for the grafting process and MA molecules, it has already been reported in early UV spectroscopic studies[48-56] that maleic anhydride dissolved in aromatic solvents is able to form charge-transfer complexes by acting as an electron acceptor, while the organic solvents behave as electron donors. We confirmed these experiments, using mesitylene, *p*-xylene, toluene, ethylbenzene, and *o*-dichlorobenzene as solvents in combination with MA, and the corresponding absorption spectra are reported in Figure 2. As can be seen from this picture, the maximum of the absorption bands of MA solutions in selected aromatic solvents, is shifted toward high wavelengths with the decrease of the ionization potentials (IP)[57-59] of the solvents, indicating that the spectroscopic transitions involved are charge-transfer in nature. Moreover, the more intense spectrum was found for mesitylene, i.e. for the solvent showing the lowest IP (8.39 eV), while the less intense one is due to *o*-dichlorobenzene that has an IP considerably more elevated (9.07 eV). These facts can easily be accounted for by considering the +I effect of the methyl groups in the mesitylene that inject electrons into the aromatic ring, thus facilitating the formation of the CT complex with MA, and also by evaluating the strong electron-withdrawing ability of the chlorines in the *o*-dichlorobenzene that deactivated the aromatic ring, thus preventing this solvent from generating strong CT interactions with the anhydride groups.

These CT species are expected to deeply influence the efficiency of the grafting of MA onto PEPP. In fact, the unsaturated double bond present in the MA structure is strongly deactivated by the two carbonyl groups of the anhydride function and, therefore, it is prevented from undergoing radical reactions easily. In the presence of aromatic solvents, however, electrons are injected into the anhydride substrate in an amount that depends on the nature of the aromatic groups, thus facilitating the opening of the unsaturated double bond. These facts would lead to an enhancement of the reactivity of the dissolved MA molecule, originally relatively inert, toward, for instance, homopolymerization reactions.[24,42-45]

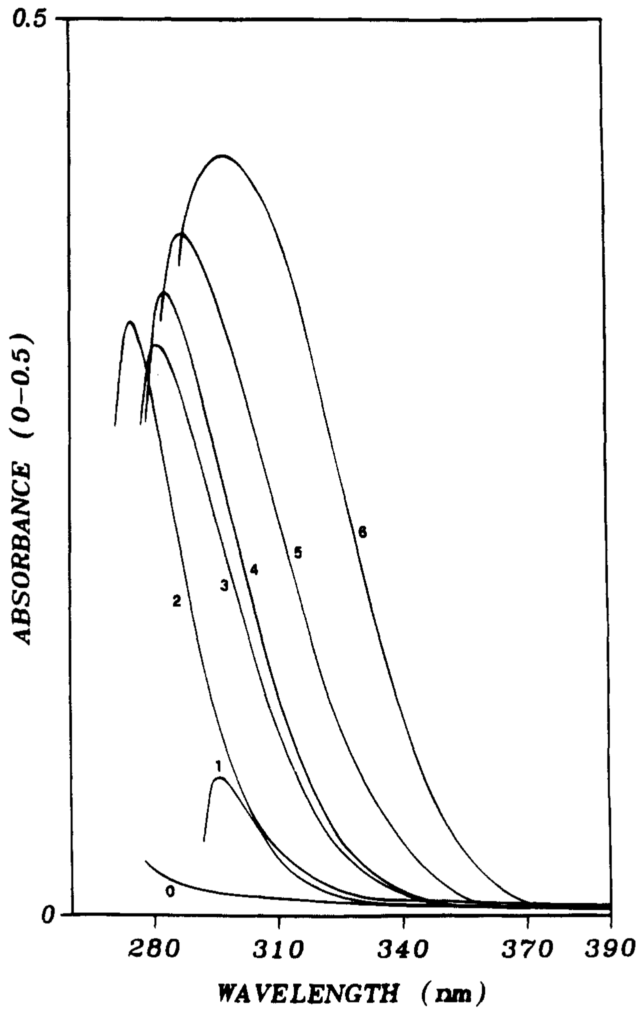


Figure 2. Charge-transfer complexes formed by maleic anhydride dissolved in (0) dichloromethane, (1) dichloromethane 10%–*o*-dichlorobenzene 90%, (2) dichloromethane 10%–benzene 90%, (3) dichloromethane 10%–ethylbenzene 90%, (4) dichloromethane 10%–toluene 90%, (5) dichloromethane 10%–*p*–xylene 90%, and (6) dichloromethane 10%–mesitylene 90%.

As a matter of fact, when 50 mg of PEPP is dissolved in 1 mL of xylene i.m., *p*-xylene, *m*-xylene, *o*-xylene, or *o*-dichlorobenzene, in the presence of (70% w/w) maleic anhydride and benzoyl peroxide (10% w/w) initiator, and the mixture is heated at 125 °C for variable periods of time, the results shown in Figure 3 are obtained.

From this picture it appears that the reactivity of MA toward PEPP increases following the order:

p-xylene ≫ xylene i.m. > *m*-xylene > *o*-xylene = *o*-dichlorobenzene

p-xylene being the most effective solvent of this series to induce the grafting of MA onto PEPP. Although no direct relationship is evident between the efficiency of the grafting reaction and the strength of the charge-transfer complexes formed by MA and the aromatic solvents, the above reported facts confirm the great influence of these species in determining the grafting yield of MA onto PEPP.

Time and Oxygen Influence on the Grafting Reaction of MA onto PEPP. When 50 mg of PEPP dissolved in 1 mL of xylene i.m. is heated in the presence

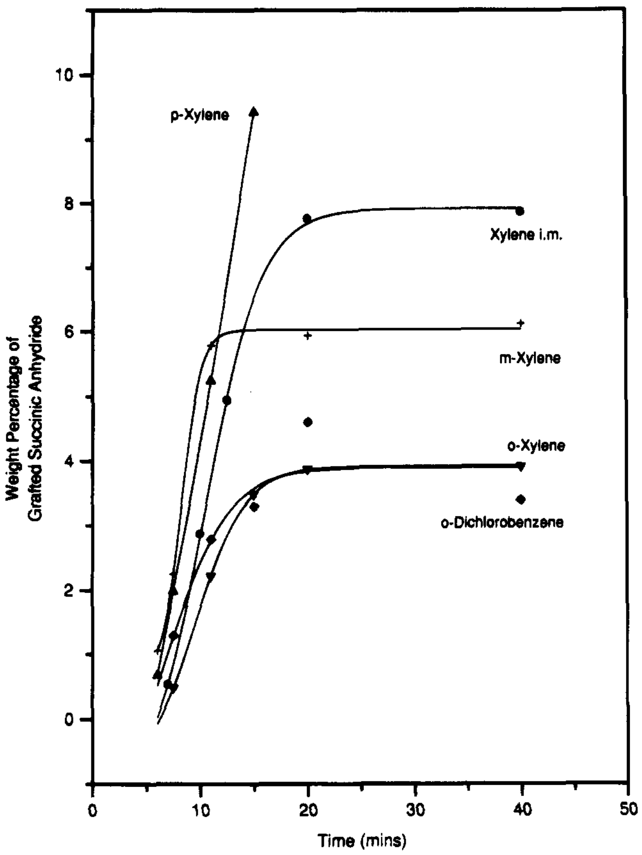


Figure 3. Influence of different reaction solvents on the percentage of SA grafted onto PEPP, at variable reaction times.

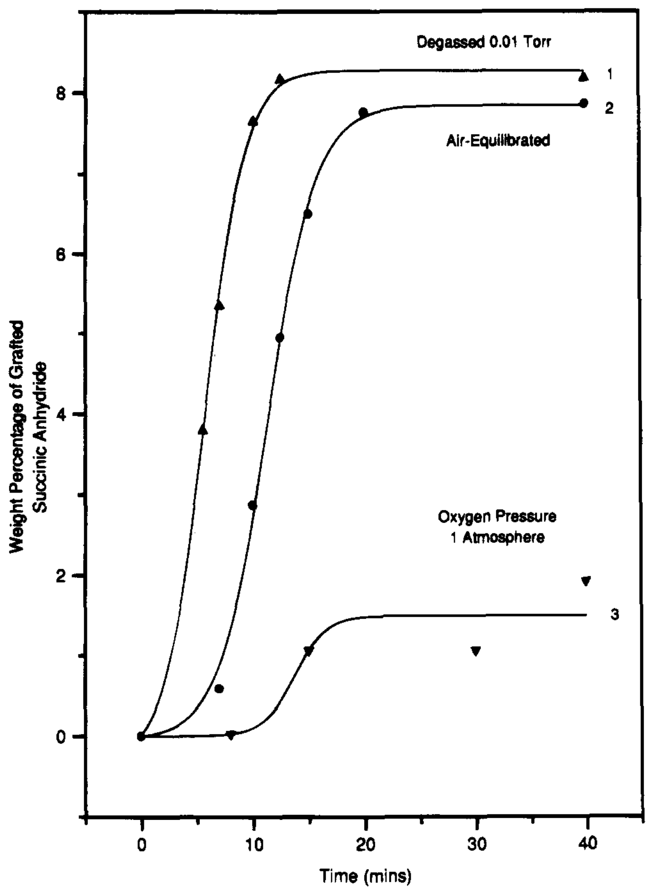


Figure 4. Influence of molecular oxygen on the percentage of SA grafted onto PEPP, at different reaction times.

of maleic anhydride (70% w/w) and benzoyl peroxide (10% w/w) at 125 °C for variable periods of time and in different environmental conditions (oxygen-free solutions, air-equilibrated media, and reaction mixtures containing 1 atm of oxygen pressure), the grafting of SA groups onto the phosphazene polymer takes place according to the data reported in Figure 4.

As can be seeen from this picture, the degree of functionalization of the phosphazene matrix clearly depends on two experimental parameters: the amount of time the grafting mixtures are heated and the concentration of the molecular oxygen present in the system.

The influence of the heating time on the overall grafting process results from the observation that, in all three experiments carried out in different oxygenation conditions reported in Figure 4, the percentage of SA grafted onto PEPP is very low for short periods of heating and increases as the reaction time increases until a plateau is reached. After this point, additional heating of the system does not induce further enhancements of the percentage of the SA grafted onto the polyphosphazene matrix.

As for the importance of molecular oxygen, it is evident from Figure 4 that the absence of oxygen in the reaction mixture (curve 1) results in an enhancement of the grafting efficiency of MA onto PEPP with respect to the yield found in the case of air-equilibrated solutions (curve 2), while the saturation of the grafting mixture with 1 atm pressure of O_2 strongly depresses the reaction efficiency.

According to Figure 4, moreover, it may be pointed out that the induction period necessary to observe the onset of the grafting reaction with short heating times is almost imperceptible when the grafting experiments are carried out in an oxygen-free atmosphere but becomes more pronounced in air-equilibrated media and increases up to 10 min heating when the oxygen pressure in the system reaches 1 atm.

A reasonable explanation is that the radicals formed from the reaction of peroxide initiator with solvent, maleic anhydride, and PEPP in principle interact with molecular oxygen, forming hydroperoxides. In this way, the highly reactive radical intermediates that play a fundamental role in the formation of PEPP-*g*-SA grafted copolymers, are removed from the reaction mixture and transformed into species that do not contribute to the grafting reaction; therefore the presence of molecular oxygen in the reaction medium during the free-radical-induced functionalization of PEPP with MA results in a decrease of grafting efficiency due to the presence of undesired, side reactions.

It must be noted, moreover, that the IR spectra of PEPP-*g*-SA grafted films prepared in an atmosphere of pure oxygen do not show any appreciable absorption in the spectral range 3000–3500 cm^{-1}, where polyphosphazene hydroperoxides usually absorb,[28] indicating that no oxygen uptake occurs in the phosphazene macroradicals under the above illustrated experimental conditions. It may be concluded, therefore, that molecular oxygen preferentially scavenges solvent and/or maleic anhydride radicals instead of phosphazene macroradicals during the grafting reaction.

Influence of the Type and Quantity of the Peroxide Initiator on the Grafting of MA onto PEPP. These experiments were run by dissolving 50 mg of PEPP in 1 mL of xylene i.m. in the presence of maleic anhydride (70% w/w), heating the system at 125

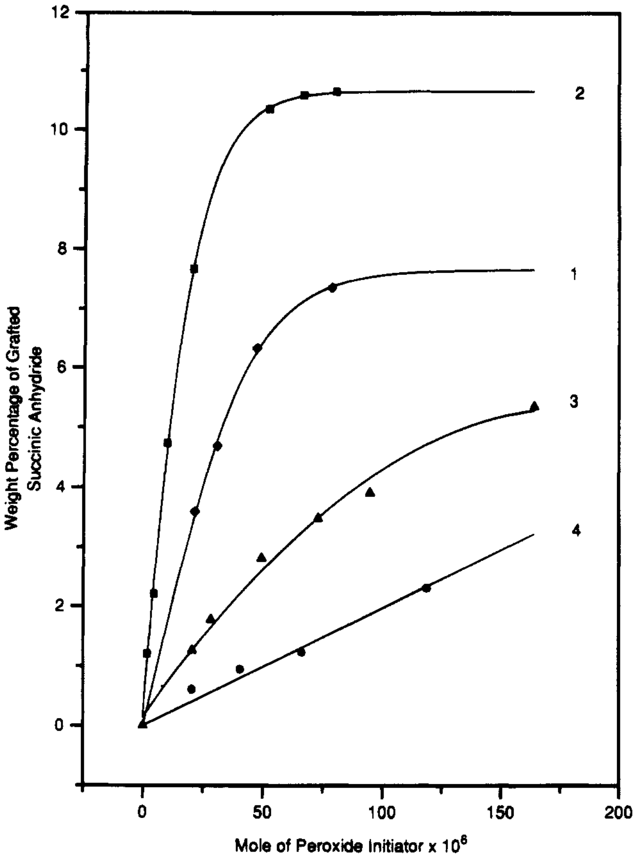


Figure 5. Influence of the peroxide initiators on the percentage of SA grafted onto PEPP: (1) lauroyl peroxide; (2) benzoyl peroxide; (3) *tert*-butylperoxy benzoate; (4) dicumyl peroxide.

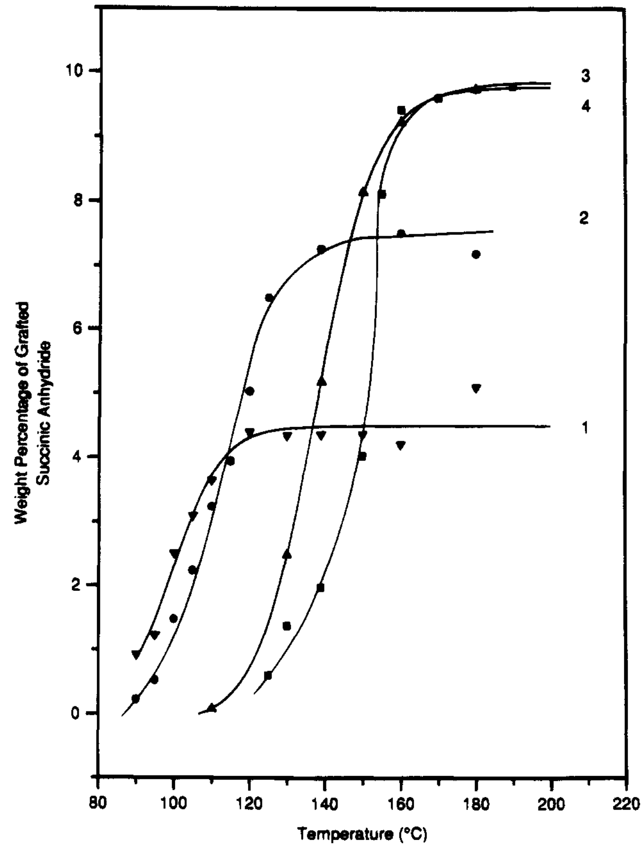


Figure 6. Influence of the peroxide initiators on the percentage of SA grafted onto PEPP, at different reaction temperatures: (1) lauroyl peroxide; (2) benzoyl peroxide; (3) *tert*-butylperoxy benzoate; (4) dicumyl peroxide.

°C for 15 min and using different peroxides as initiators of the grafting processes.

For these reactions we took into consideration four different peroxides, i.e. lauroyl peroxide (LP), benzoyl peroxide (BP) *tert*-butylperoxy benzoate (tBPOB) and dicumyl peroxide (DCP). All these species are characterized by the possibility of cleaving their peroxide bonds upon heating, giving rise to very reactive radical species; this process, however, can take place with an efficiency that depends on ${}^{10}t_{1/2}$ of the exploited peroxides, i.e. the temperature at which the amount of peroxide is decreased by half in 10 h of heating. This parameter can be considered as an indication of the thermal stability of the peroxide molecules.

According to the literature,[60,61] lauroyl peroxide decomposes to half the original concentration after 10 h at 65 °C, while dicumyl peroxide takes 10 h at 115 °C to do the same. Intermediate values, i.e. 73 and 105 °C, are found for benzoyl peroxide and for *tert*-butylperoxy benzoate, respectively. It may be expected, therefore, that, at the fixed temperature of 125 °C, i.e. a temperature above the ${}^{10}t_{1/2}$ of all the selected peroxides, the efficiency of the grafting reaction of MA onto PEPP in the presence of LP, BP, tBPOB, and DCP should follow the order reported below: lauroyl peroxide > benzoyl peroxide > *tert*-butylperoxy benzoate > dicumyl peroxide according to the scale of thermal stability.

These facts are partially confirmed by the data reported in Figure 5, where the weight percentage of grafted SA is reported vs the molar content of peroxide initiators in the reaction mixture.

As can be seen from the figure, the percentage of SA residues grafted onto PEPP increases with the increase of the mole content of the peroxides in the system for all the selected initiators. However, for a defined quantity of peroxide present in the grafting mixture, e.g. 5×10^{-5} mol, dicumyl peroxide is able to induce the grafting of about 1% of SA (curve 4); this amount rises to 3% when *tert*-butylperoxy benzoate is used (curve 3) and increases eventually to over 10% w/w in the case of benzoyl peroxide (curve 2). This reactivity order is in agreement with the scale of thermal stability of the peroxide initiators reported above. The only exception to this trend is found in the case of lauroyl peroxide (curve 1), whose reactivity is at least 25–30% lower than that expected on the basis of the reported ${}^{10}t_{1/2}$ value. A possible explanation to account for this fact is that, at relatively low temperatures, the highly reactive peroxide fragments coming from the cleavage of the peroxide, react predominantly with solvent or MA molecules instead of abstracting hydrogens from PEPP, giving rise to species that do not eventually form PEPP-*g*-SA grafted copolymers.

Effect of the Reaction Temperature on the Grafting of MA onto PEPP. A series of experiments were run to graft MA onto PEPP using the following experimental conditions: 50 mg of PEPP dissolved in 1 mL of xylene i.m., in the presence of maleic anhydride (70% w/w) and peroxides (10% w/w), heating the system for 15 min at variable temperatures. The corresponding curves obtained for the lauroyl (curve 1), benzoyl (curve 2), and dicumyl peroxides (curve 4) and for the *tert*-butylperoxy benzoate (curve 3) thermal initiators are reported in Figure 6.

This picture shows that, for temperatures below 139 °C, i.e. the boiling point of the xylene i.m., the efficiency of the grafting reaction of MA onto PEPP rigorously

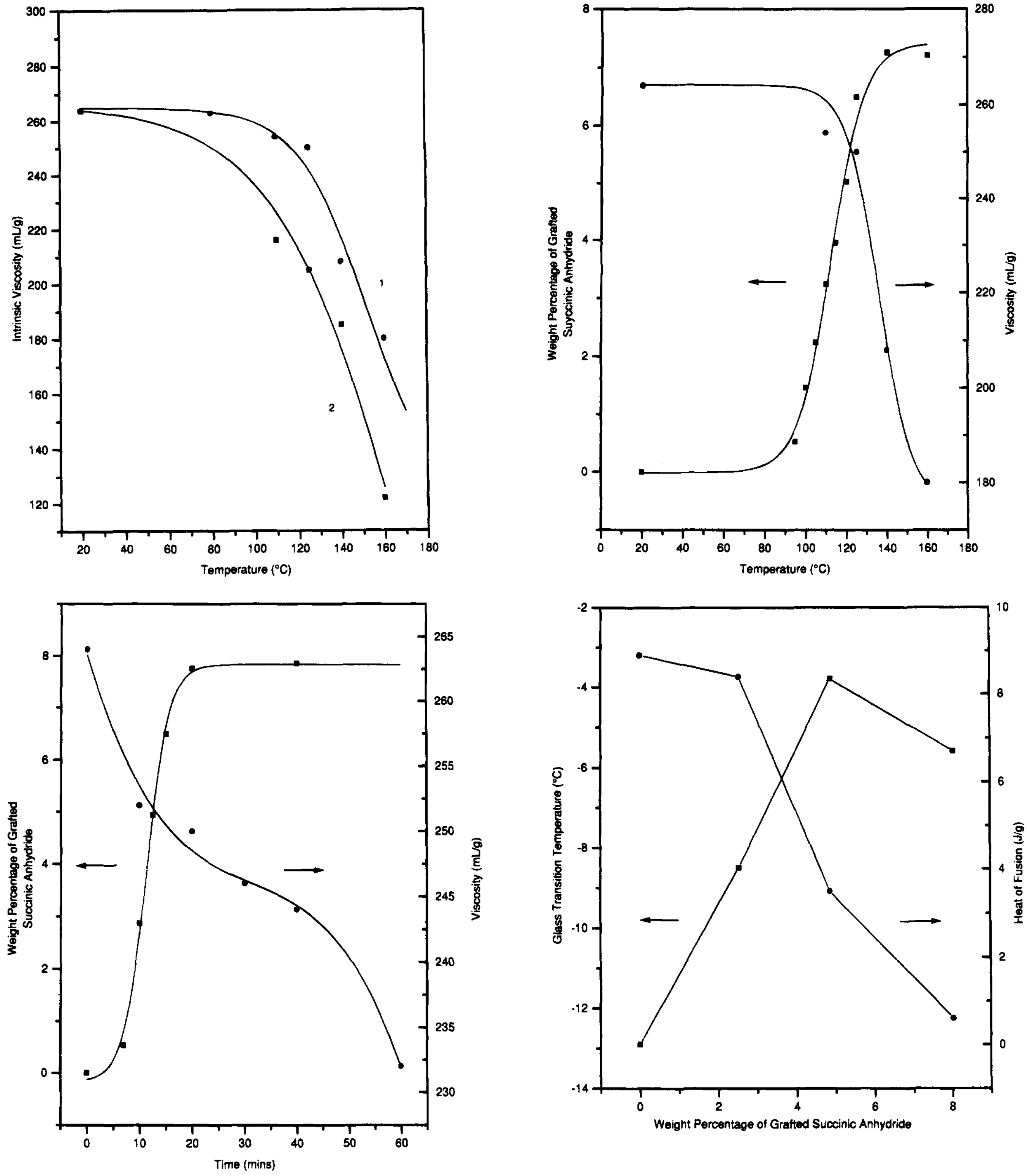


Figure 7. (A, top left) Influence of the molecular oxygen on the intrinsic viscosity of a xylene i.m. solution of PEPP at different temperatures: (1) air-equilibrated solutions; (2) de-aerated solutions (0.01 Torr). (B, top right) Influence of the reaction temperature on the weight percentage of grafted SA and on the intrinsic viscosity of a xylene i.m. solution of PEPP. (C, bottom left) Influence of the reaction time on the weight percentage of grafted SA at 125 °C and on the intrinsic viscosity of a xylene i.m. solution of PEPP. (D, bottom right) Influence of the weight percentage of grafted SA on the glass transition temperature and on the heat of fusion of PEPP.

follows the stability trend of the peroxide molecules mentioned above. In fact, benzoyl peroxide (grafted % of SA above 7% w/w, see surve 2) is a more efficient thermal initiator than *tert*-butylperoxy benzoate (grafted % of SA below 7% w/w, see curve 3), which, in turn, is more effective than dicumyl peroxide (grafted % of SA is about 2% w/w, see curve 4). Carrying out the same series of experiments at temperatures above 139 °C, the grafting on MA onto PEPP still takes place, but with an efficiency that increases for all the peroxides used until a plateau is reached. Moreover, the reactivity order expected on the basis of the initiator thermal stability scale is not followed any further, possibly due to the enhanced reactivity of the initiator radicals toward both solvent and MA molecules at high temperatures.[44] These reactions, that produce inert intermediates, compete with the formation of phosphazene macroradicals, thus decreasing the grafting efficiency of the MA molecules onto PEPP.

We must remark upon the anomalous behavior of the lauroyl peroxide in the promotion of the grafting reaction of MA onto PEPP (see Figure 6, curve 1) that once again proved to be the poorest thermal initiator with respect to the other peroxides, probably for the same reasons reported above (*vide supra*).

Influence of the Grafting Reaction of MA onto PEPP on Some PEPP Physical Properties. The grafting reaction of MA onto PEPP, carried out according to the above reported procedure, was found to introduce deep modifications in the physical properties of POPs.

In previous papers we already reported that the adhesion properties of poly[bis(4-*sec*-butylphenoxy)phosphazene] containing variable amounts of succinic anhydride grafted onto the side 4-*sec*-butylphenoxy groups[29,34] are strongly increased with respect to those of the pristine material.

In this paper we investigate the influence of the grafting process of MA onto PEPP on the intrinsic viscosity of xylene i.m. solutions of PEPP, as a parameter strictly related to the molecular weight of the polymer. The corresponding results are reported in Figure 7A–D.

Figure 7A reports the behavior of the intrinsic viscosity $[\eta]_{\text{intr}}$ of PEPP dissolved in xylene i.m. during the grafting process carried out at different reaction temperatures, in the presence (curve 1) or in the absence (curve 2) of molecular oxygen. In both cases, the increase in the grafting temperature is accompanied by a strong decrease in the solution viscosity of PEPP, the phenomenon being more evident when the grafting process is carried out in de-areated solutions.

In Figure 7B,C we also report the variations of the weight percentage of SA grafted onto PEPP and of the intrinsic viscosity of xylene i.m. solutions of this polymer vs the reaction temperature and the heating time, respectively, for the grafting of MA onto PEPP. In both these figures it appears that the percentage of the grafted SA increases with the increase of the reaction temperature and time until a plateau is reached; after this value the percentage of grafted SA does not increase any further, even using high reaction temperatures and long heating periods.

Simultaneously to this trend, however, the drastic decrease in the intrinsic viscosity is observed to indicate the collapse of the molecular weight of the phosphazene polymer, whose value reaches the minimum when the highest quantity of SA is grafted onto the phosphazene matrix.

Concurrently with these phenomena, the glass transition temperature, T_g, of PEPP and the crystallinity content of this polymer, as determined by DSC measurements, undergo remarkable modifications, induced by the grafting of the anhydride groups onto the polymeric phosphazene substrate.

These facts are reported in Figure 7D, where the T_g and the heat of fusion of the crystalline part of PEPP and PEPP-*g*-SA grafted copolymers are reported vs the weight percentage of grafted SA residues.

This figure shows that the PEPP T_g is increased by increasing the grafting percentage of SA, suggesting an enhanced rigidity of the polyphosphazene skeleton due to the insertion of the bulky SA groups in the phosphazene matrix. These groups are also responsible for the decrease in crystallinity observed in the PEPP-*g*-SA grafted copolymers with respect to that of the pristine PEPP, as the heat necessary to melt the crystalline phase of PEPP is progressively decreased with the increase in the percentage of the grafted SA residues, evidencing an enhanced difficulty of the phosphazene chains to pack in regular structures when increasingly high amounts of SA groups are grafted onto PEPP.

Conclusions

In this paper we describe the grafting reaction of maleic anhydride onto poly[bis(4-ethylphenoxy)phosphazene] carried out in solution. This reaction is investigated by taking into consideration the possible parameters that may play some role in determining the overall efficiency of the process.

The chemical reactivity of maleic anhydride toward PEPP seems to depend on the reaction temperature, heating time, type of solvent, amount of maleic anhydride, peroxides initiator, and molecular oxygen. The reaction seems to be reasonably controllable, and the quantity of succinic anhydride groups inserted into PEPP can be varied from fractions of percent up to 14% depending on the experimental conditions selected for the process.

After the reaction, the recovered PEPP-*g*-SA grafted copolymers show completely new reactivities due to the presence of the anhydride groups in the structure and deep modifications in their physical properties. The investigation of the chemical reactivity of the PEPP-*g*-SA grafted copolymers and the study on the possible further chemical functionalizations of these materials are beyond the purpose of this paper and will be reported elsewhere.[62] However, an investigation into the physical characteristics of the PEPP-*g*-SA grafted copolymers, as compared with those of the original PEPP, shows that the intrinsic viscosity of xylene i.m. solutions of PEPP is greatly decreased during the grafting process, indicating that the molecular weight of the phosphazene macromolecule is diminished. This is observed for high grafting temperatures, for long heating times, and in the presence or absence of molecular oxygen in the solution. A common feature of these reactions seems to be that, regardless of the experimental conditions used, the higher the percentage of grafted SA inserted in the PEPP, the more enhanced the degradation of the phosphazene polymeric backbone and the decrease in the molecular weight of PEPP.

Further investigations into the grafting of maleic anhydride onto phosphazene substrates that bear different alkoxy and/or aryloxy substituents are under way and will be reported in a forthcoming paper.[62]

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