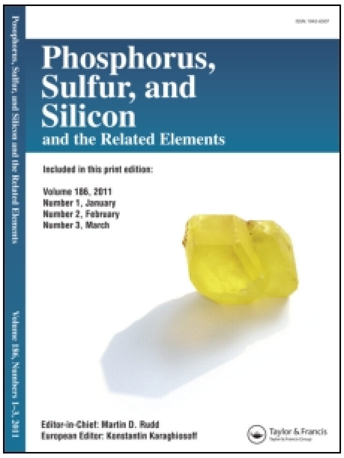

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Reactive Cyclophosphazenes Containing Oxazoline Groups: the Case of Hexakis(4-Oxazolinophenoxy)Cyclophosphazene

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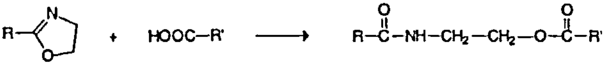
Hexakis(4-oxazolinophenoxy)cyclophosphazene, a multifunctional cyclophosphazene derivatives containing six pending oxazoline groups, was prepared by reacting hexachlorocyclophosphazene with 2-(4-hydroxyphenyl)-2-oxazoline. The resulting trimer was successively treated with carboxylic group-containing molecules (4-benzoyl-benzoic acid) and macromolecules (polyethylene terephthalate) to produce a novel photoinitiator and a polymer having higher molecular weight and improved mechanical properties, respectively.

Keywords: cyclophosphazenes; oxazolines; photoinitiators; poly(ethylene terephthalate); chain extenders

INTRODUCTION

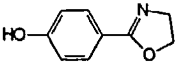
2-Oxazolines are important organic derivatives[1] not only because of their aptitude to act as monomer species for polymerization reactions[1,2], or as a core for dendrimer preparation[3], etc., but also because of their chemical reactivity with carboxylic group-containing organic substrates, as shown in the Reaction Scheme 1:



Scheme 1

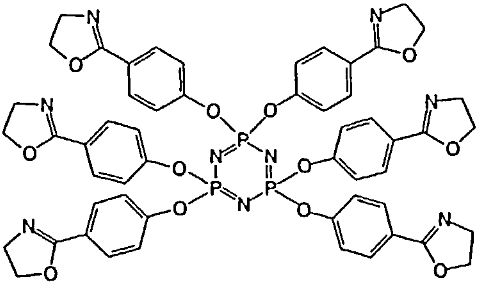
The most important feature of this process is that the residual groups "R" and "R' " in the Scheme are eventually linked together through an amido-ester group, regardless they are low molecular weigh substrates or high molecular weight macromolecules.

The combination between oxazoline functionalities and phosphazene derivatives was first considered by Chang[4], who polymerized 2-methyloxazoline using hexakis(4-bromomethylenephenoxy)cyclophosphazene as an ionic initiator to obtain the preparation of cyclophosphazene-based star polymers. This topic was successively developed in our Institute by thermally-grafting maleates containing oxazoline derivatives onto suitable aryloxy-substituted phosphazene polymers[5], or by preparing both cyclo- and poly- phosphazenes substituted with 2-(4-hydroxyphenyl)-2-oxazoline[6]



The obtained phosphazenes were successively used to favor blending processes between organic macromolecules functionalized with –COOH groups (e.g. polyacrylic or polymethacrylic acids), or for successive functionalization processes.

In this paper we would like to report on the synthesis of hexakis(4-oxazolinophenoxy)cyclophosphazene, C6OXA,



and on its capability of undergoing further functionalization processes with both low- and high- molecular weight organic substrates containing accessible carboxylic functions.

EXPERIMENTAL

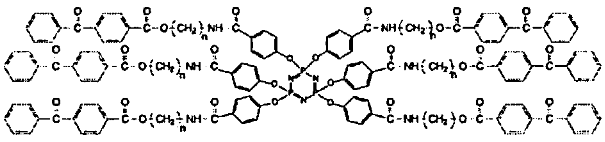
2-(4-Hydroxyphenyl)-2-oxazoline was prepared according to the procedure settled by Saegusa[7]. Hexakis(4-oxazolinophenoxy) cyclophosphazene was synthesized by treating 2-(4-hydroxyphenyl)-2-oxazoline with hexachlorocyclophosphazene in anhydrous THF[6]. 2,2'-(1,4-phenylene)bis(2-oxazoline) (Φ2OXA) were obtained according to literature[8]. 4-Benzoylbenzoic acid (Aldrich), and poly(ethylene terephthalate) (Montefibre, inherent viscosity 0.64 dl/g, M_w=33.500, polydispersity ratio 1.73) were used as received. Characterization data were obtained using: Perkin Elmer Spectrophotometer 2000 Explorer (IR), Perkin Elmer spectrophotometer model 320 (UV-visible), Bruker AC 200 Spectrometer (^{1}H, ^{13}C and ^{31}P NMR); Finnigan LCQ mass spectrometer (C6OXA molecular weight determination); RMS-800 Rheometric Scientific (rheological properties); Mettler DSC 30 calorimeter (thermal analysis); PL-DMTA MkII Instrument Polymer Laboratories (mechanical properties). PET thermal modification was obtained by using a Rheomix 60 Haake mixer.

RESULTS AND DISCUSSION

The reaction between methyl-4-hydroxybenzoate with an excess of 2-aminoethanol leads to N-2-hydroxyethyl-4-hydroxybenzamide, whose cyclization process by the action of thionyl chloride eventually produces 2-(4-hydroxyphenyl)-2-oxazoline[7]. This product was successively reacted with hexachlorocyclophosphazene in anhydrous THF and in the presence of NaH, to eventually form C6OXA.

Once prepared, C6OXA was exploited in a variety of chemical processes due to the strong reactivity of the oxazoline residues towards carboxylic group-containing organic substrates.

Thus the reaction of C6OXA with 4-benzoylbenzoic acid produces a cyclophosphazene containing six, highly photosensitive benzophenone groups



which could be used as a novel and very efficient photoinitiator to induce, for instance, the photopolymerization of acrylamide monomer to polyacrylamide, or the controlled photocrosslinking of poly(ethylene oxide), that could be a relevant process in the preparation of light batteries.

Furthermore, high molecular weigh polyesters (*e.g.* PET) were reacted with the oxazoline-containing cyclophosphazene under suitable experimental conditions and the resulting samples were analyzed and characterized using different techniques. Thus, the reaction between PET and C6OXA in an internal mixer, a 270°C in melt state produces PET samples having higher molecular weight, and improved rheological, thermal and mechanical properties with respect to those of the pristine material. For comparison purposes PET alone, and PET treated with Φ2OXA were also analyzed and characterized.

The torque diagrams throughout the processing for all the samples are reported in Figure 1.

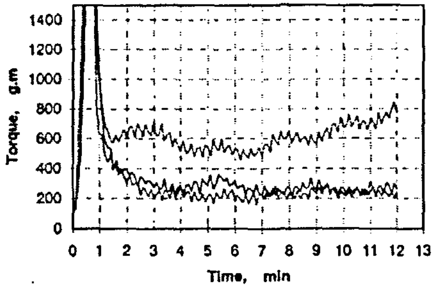


Figure 1

Both PET and PET+Φ2OXA (lower curves) have a torque moment of about 300 g·m, while for PET+C6OXA (upper curve) an increase in this parameter up to 600 g·m is observed. At the same time, complex viscosity of PET is markedly enhanced from the rather low value of 15 Pa·s for PET to 10^2 Pa·s for PET+Φ2OXA, to reach 10^4 Pa·s when PET is treated with C6OXA. Finally, observing the viscoelastic response (Figure 2), it turns out that the elastic component of C6OXA-modified PET is quite pronounced with respect to that of unmodified resin and the crossover between loss and storage moduli occurs at a relatively low frequency.

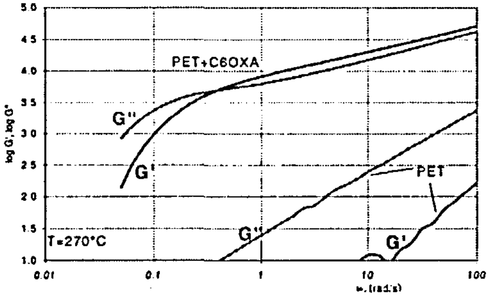


Figure 2

This behavior can be easily related to the coupling reactions that take place between the cyclophosphazene-supported oxazoline groups and the terminal carboxylic functions of the polyester skeleton (see Reaction Scheme 1) that resulted in a series of branching reactions and possible crosslinking phenomena at the end of the mixing process.

Moreover, results concerning the thermal (DSC) characterization of PET samples in the different experimental conditions reported in Table 1

	T_g I (°C)	T_c I (°C)	ΔH_c I (J/g)	T_m I (°C)	ΔH_m I (J/g)		T_g II (°C)	T_c II (°C)	ΔH_c II (J/g)	T_m II (°C)	ΔH_m II (J/g)
PET	64	127	33	253	52		76	132	19	252	50
PET+ C6OXA	75	127	28	247	39		79	144	34	245	38
PET+ Φ2OXA	63	117	31	251	48		76	135	21	251	49

where: T_g stands for Glass Transition Temperature, T_c and ΔH_c crystallization temperature and enthalpy and T_m and ΔH_m melting temperature and enthalpy

indicated that T_g of PET+C6OXA is slightly higher with respect of T_gs of the other samples, while the presence of C6OXA in PET induced lower cristallizzability and melting temperatures.

Finally, mechanical properties of PET under the above *described experimental conditions summarized in Table 2*

	Modulus (Mpa)	Yield Stress (Mpa)	Yield Strain (Mpa)	Stress at Break (Mpa)	Strain at Break (Mpa)	Tenacity (Mpa)
PET	1822 ±146	44.2 ±5.6	4.25 ±0.04	19.0 ±8.5	137 ±34	46 ±13
PET+ C6OXA	1782 ±160	44.4 ±9.2	4.25 ±0.73	40.2 ±3.5	415 ±190	153 ±74
PET+ Φ2OXA	1895 ±93	47.0 ±5.0	4.18 ±0.29	39.8 ±5.5	541 ±140	203 ±56

suggested that a large increase is obtained in both stress and strain at break, together with an improved tenacity, for PET treated with F2OXA or C6OXA, with respect to those of the neat PET. The large standard deviation of both strain at break and tenacity of the samples does not allow a clear distinction between the true influence of Φ2OXA and C6OXA on the mechanical properties of PET.

CONCLUSIONS

In this paper we described the role played by hexakis(4-oxazolinophenoxy)cyclophosphazene (C6OXA), in the preparation of a new type of phosphazene-based, multiple photoinitiator, together with the photoactivity of the formed compound in inducing the polymerization of organic monomers (acrylamide, for instance) and the reticulation of poly(ethylene oxide). We analyzed successively the influence of the same cyclophosphazene on the rheological, thermal and mechanical properties of poly(ethylene terephthalate) (PET) once blended with this polymer at high temperature (270°C); we also discussed the possible influence of this reaction in recycling processes of degraded organic polymers. These two phenomena, moreover, appear to be absolutely general, in the sense that other low molecular weight substrates (*e.g.* lactic acid) or high molecular weight macromolecules (*e.g.* Nylon 6) are found to have the same behavior described in this paper for 4-benzoylbenzoic acid and PET, respectively,

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