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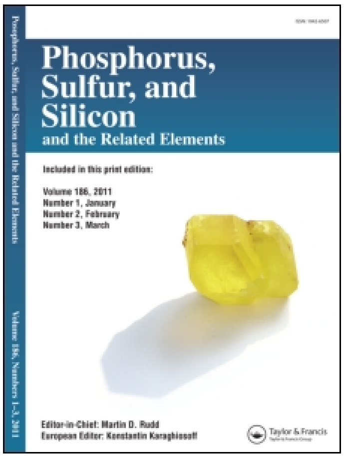

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Poly(Organophosphazenes) Containing Oxazoline Groups

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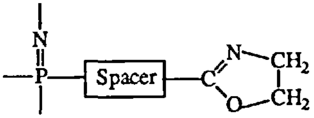
The synthesis, the characterization and the utilization of cyclo- and poly-phosphazenes functionalized with oxazoline residues are discussed.

Keywords: Cyclophosphazenes; Polyphosphazenes; Oxazoline; Blends; Photoinitiators

INTRODUCTION

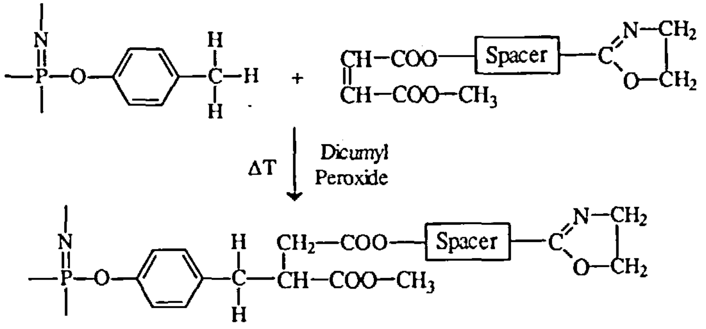
Our research on the functionalization of phosphazenes[1-3] recently led us to introduce free oxazoline residues in both cyclic and polymeric phosphazene derivatives through a spacer group[4]. The structure of these compounds is as follows:



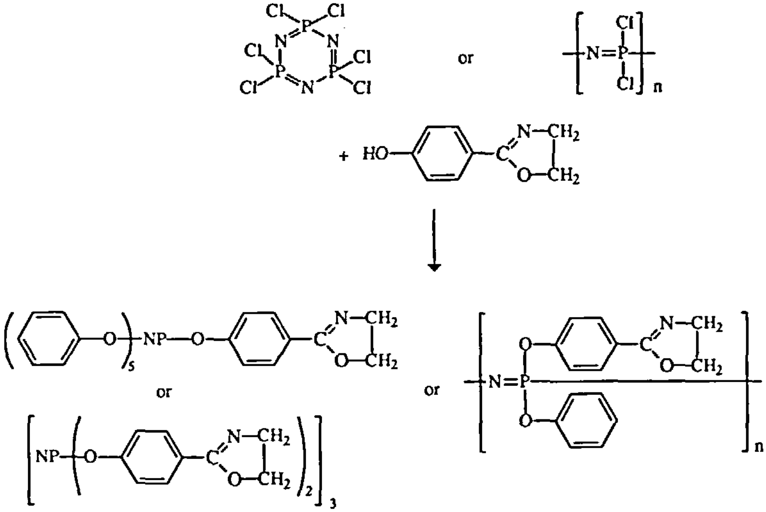
RESULTS AND DISCUSSION

The preparation of these substrates was achieved according to the two following strategies:

1)by thermally-induced grafting reaction of a maleate product containing free-pending oxazoline groups[4], according to the following reaction scheme:



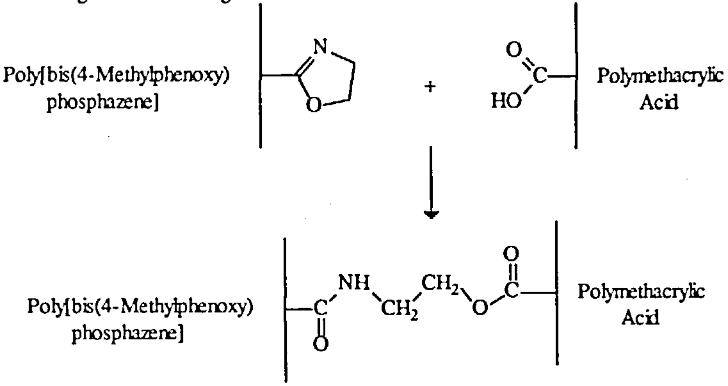
2)the direct reaction of hexachlorocyclophosphazene and polydichlorophosphazene with 4-hydroxyphenyloxazoline[5] giving rise to penta(phenoxy)mono(4-oxazolinephenoxy)cyclophosphazene, hexakis(4-oxazolinephenoxy)cyclophosphazene and to a phosphazene phenoxy copolymers containing about 5-10% of 4-phenoxyoxazoline groups, respectively. The reaction scheme is as follows:



The importance of these types of functionalizations of the phosphazene substrates stands on the extraordinary versatility of the oxazoline groups to react under a variety of conditions[6] leading to the formation of polymers, free carboxylic units, amidoesters, etc. The resulting phosphazene copolymers are very interesting substrates susceptible of a large series of practical applications.

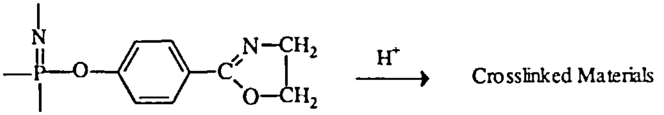
In fact:

A)high molecular weight phosphazene copolymers containing variable percentages of free oxazoline groups can be used to promote the formations of blends between phosphazene copolymers and free carboxylic group-containing organic macromolecules, according to the following reaction:



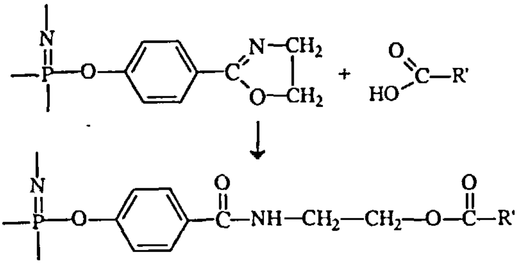
in which genuine chemical bonds are formed between poly[bis(4-methylphenoxy)phosphazene]-g-oxazoline succinate and polymethacrylic acid, that are actually incompatible polymers.

B)the acid-catalyzed opening process of the oxazoline cycle in both functionalized cyclo- and poly-phosphazenes leads to the generation of crosslinked insoluble materials, possibly formed by tridimensional cyclomatrix polymers or by crosslinked linear macromolecules, respectively, according to reaction Scheme reported below:



whose nature is not very well identified so far.

C)the solution reaction of oxazoline-functionalized cyclophosphazenes with organic compounds containing free carboxylic functionalities induces the opening of the heterocyclic ring and the formation of phosphazene substrates functionalized with amidoesters residues. The reaction sequence is reported below:



The reaction between hexakis(4-oxazolinephenoxy)cyclophosphazene and benzoic acid (i.e. R' = C_6H_5) has been taken as the prototype process for investigating the opening of the oxazoline ring; the "R' " group, however may be of very different nature, such as, for instance, -C_6H_4-CO-C_6H_5 thus allowing the preparation of phosphazene substrates that support benzophenone photoinitiating species able to promote the radical polymerization process of vinyl monomers.

CONCLUSIONS

The introduction of oxazoline functions into phosphazenes is an intriguing way to modify these materials and to enlarge the possibility of their practical utilization, for instance in blending processes or in the preparation of new, highly photosensitive, additives.

ACKNOWLEDGEMENTS

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