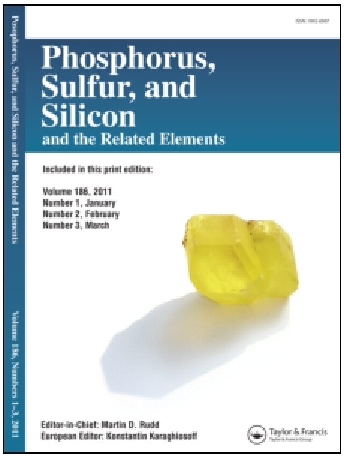

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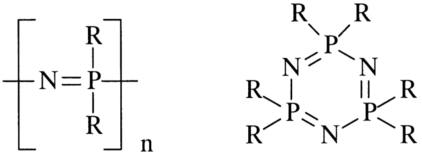
In this article we present the synthesis of new cyclophosphazenes and their use as chain extenders, polymers compatibilizers, and monomers.

Keywords: Chain extenders; compatibilizers; cyclophosphazenes; monomers; self-assembly; supramolecular chemistry

During the past 30 years the scientific scenery in the phosphazene field was mostly dominated by two classes of compounds: poly(organophosphazenes) (POPs) and cyclophosphazenes (CPs).



The scientific and technologic importance of POPs is now well established.[1] Cyclophosphazenes, on the contrary, have been considered up to now mostly as model compounds for the corresponding POPs.[2] In the last two decades, however, it emerged clearly that cyclophosphazenes are important compounds themselves able to cover a wide range of practical applications.[1]

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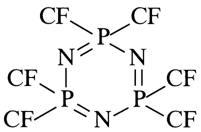
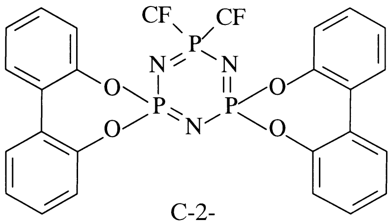
In this article we present results on new types of cyclophosphazene utilization, as chain extenders and blend compatibilizers for commercial organic macromolecules and as new unconventional monomers for the synthesis of polymeric materials.

DISCUSSION

The cyclophosphazenes exploited in this research have the following general structure:



C-6-

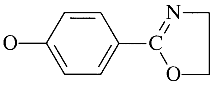


C-2-

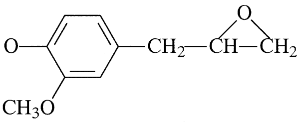
where CF stands for "chemical functions," and whose name is defined as C-6-CF or C-2-CF to indicate that these molecules are based on a cyclophosphazene substrate containing six or two chemical functions, respectively, and on different chemical functions attached to it, i.e. chlorine atoms (Cl), 2-oxazoline groups (OXA), epoxide units (EPOX), and pyridine substituents (Py).

Cl

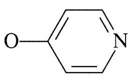
Cl



OXA



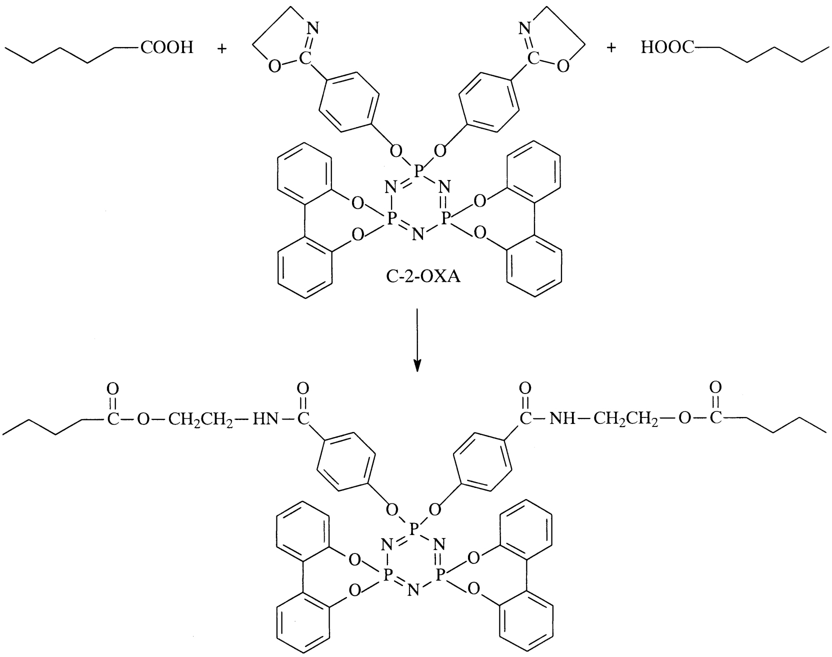
EPOX



Py

The utilization of CPs as chain extenders implies the preparation of C-2-OXA,[3] C-6-OXA,[4] and C-2-EPOX,[5] and their reaction with two (or more[4]) functionalized polymer backbones to form new macromolecules in which polymer chains are linked together through the cyclophosphazene ring. A typical example of this strategy deals with the reaction between C-2-OXA and poly(ethylene terephthalate) (PET),[3] reported below:

The resulting materials show an increase in T_g and storage modulus, accompanied by a corresponding decrease in percent deformation, crystallinity content and melt entalphy.[3]



The utilization of C-6-OXA as compatibilizing agent between polycarbonate (PC) and polyamide-6 (PA-6) has been also reported.[6] Although the reaction mechanism between this trimer and the exploited plastic materials is not fully understood, it could be proved that the cyclophosphazene plays an important role in determining the nature of the dispersing phase in the polymer blend and in improving the mechanical properties of the final materials obtained as compared with those of the physical mixture PA-6/PC.

Finally, the utilization of CPs as new types of monomers for the preparation of polymeric materials could be obtained in two ways, i.e., by polymerizing cyclophosphazenes containing six reactive functions in the cycle (e.g., C-6-OXA[3]) to form totally insoluble cyclomatrix polymers, and by using CPs containing two reactive chemical functions (e.g., C-2-OXA,[3] C-2-Cl,[7] and C-2-Py[8]) as bifunctional monomers to be reacted with similar bifunctional co-monomers to form linear polymers. Thus the reaction of C-2-Cl with PEG-400, PEG-1000 or equimolecular mixtures of these two compounds leads to the formation of linear polymers formed by short poly(ethylene oxide) segments linked together by means of cyclophosphazene rings[7] that are susceptible to show ionic conductivity. Similarly, treating C-2-OXA with adipic acid at 180°C produced a linear oligomer, formed by cyclophosphazene/diacid units.

A rather interesting result could be obtained eventually treating 1,4-diiodo-2,3,5,6-tetrafluorobenzene with C-2-Py to form a solid compound in which cyclophosphazene and diiodobenzene self-assembled in a linear infinitive structure by halogen bonding, thus producing, a new type of supramolecular array for these two compounds.[8]

CONCLUSIONS

In this article, we presented the synthesis and the characterization of variably functionalized cyclophosphazenes for new practical applications as chain extenders for conventional organic macromolecules, as compatibilizing agents to favor the formation of blends between incompatible polymers, and as new monomers for the preparation of cyclomatrix resins or of cyclolinear macromolecules.

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