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PHOSPHAZENE HIGH POLYMERS; MOLECULAR DESIGN AND THE ROLE OF PHOSPHORUS IN MODERN POLYMER CHEMISTRY

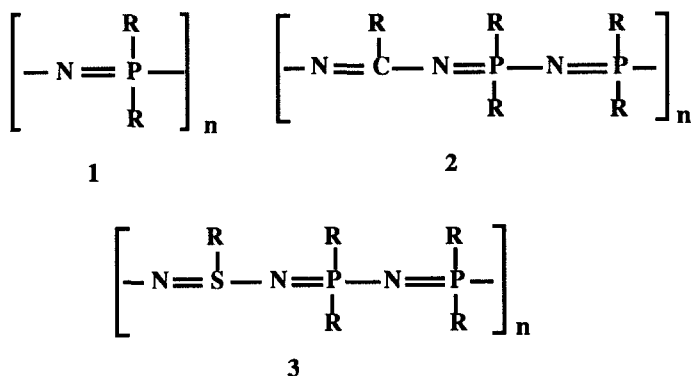
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Abstract Molecular design and synthesis in phosphazene high polymers is discussed, with an emphasis on structure-property relationships

INTRODUCTION

Nearly all synthetic polymers are organic macromolecules derived from petroleum. The two major exceptions are the poly(organosiloxanes) and the poly(organophosphazenes) (1).

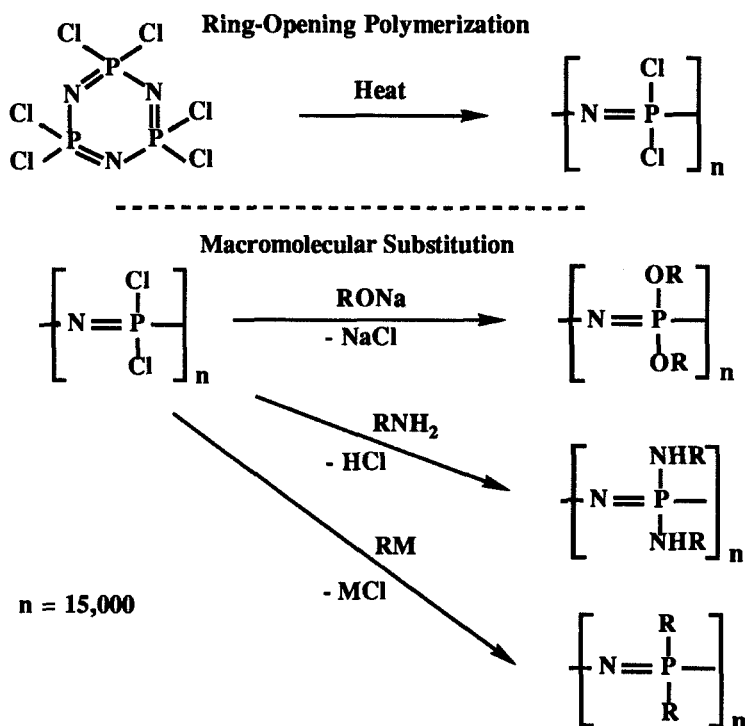


More than 300 different polymers of type 1 have been synthesized, with numerous side groups, R, and different combinations of side groups attached to the macromolecular skeleton.¹⁻¹² This broad molecular diversity, which rivals that found in classical organic polymers, is mainly a consequence of the macromolecular substitution reactions which provide the principal means of access to these structures. The overall synthesis pathway developed in our program begins with the ring-opening polymerization of cyclic chloro-, fluoro-, or halogeno-organo-phosphazenes, followed by nucleophilic substitutions of the types shown in Scheme I. These efficient macromolecular substitutions are made possible by the high reactivity of P-Cl or P-F bonds and by the inherent strength and stability of the backbone.

Several properties and concepts underly the chemistry of polyphosphazenes. First, the phosphorus-nitrogen backbone is highly flexible, a consequence of the low torsional barrier in P-N bonds. Second, the backbone has a high stability to oxidation and

reduction, even though it contains formal unsaturation. However, the properties of polyphosphazenes are a consequence of both the backbone structure and the types of side groups linked to that skeleton. This side group influence, and the means for introducing different side units are the main topics to be discussed, together with the recent discovery in our program of new skeletal structures such as those found in poly(carbophosphazenes) (2) and poly(thiophosphazenes) (3).

Scheme I



SIDE GROUP - PROPERTY CORRELATIONS

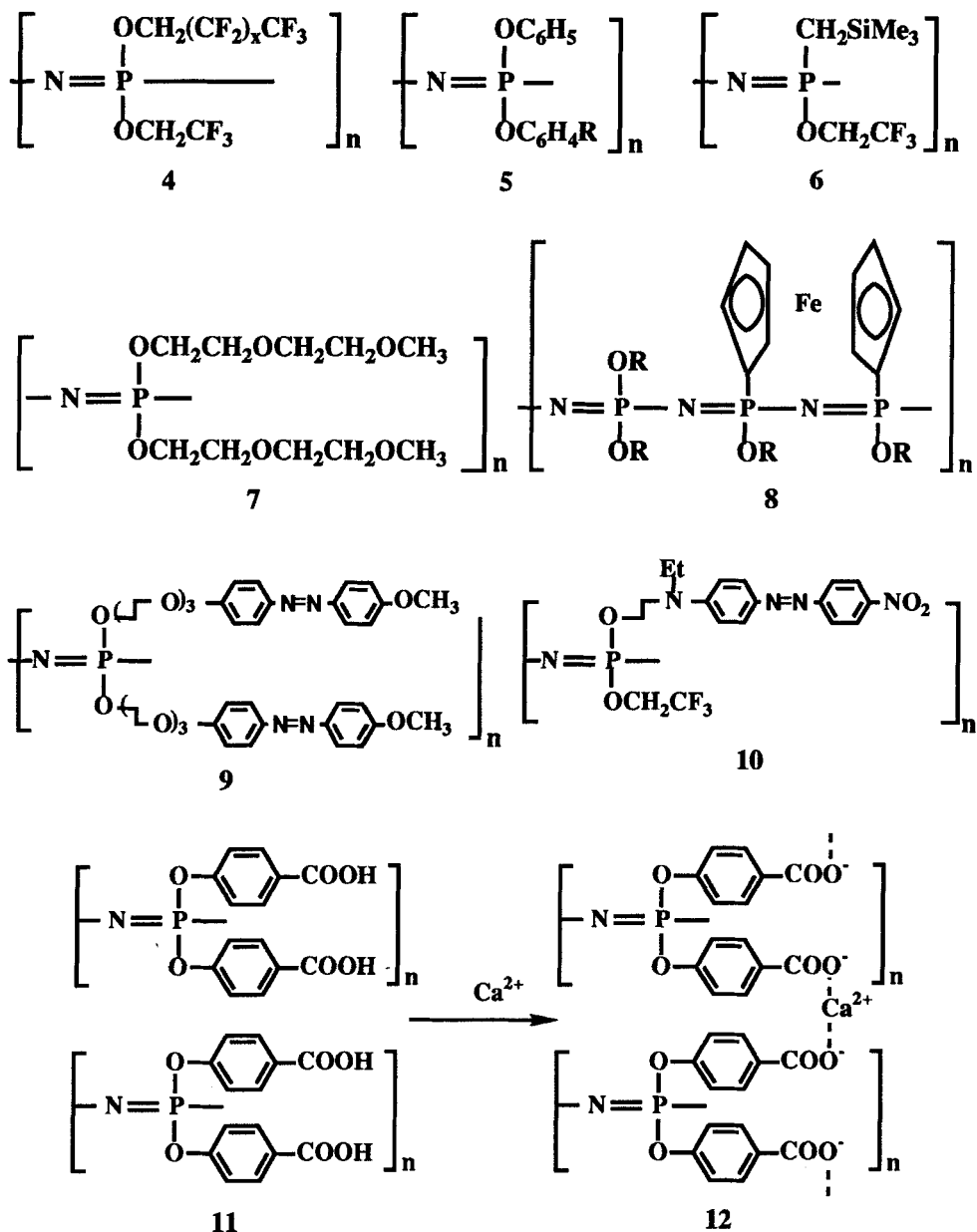
Elastomers

Structures 4-7 in Chart 1 illustrate side group combinations that allow sufficient molecular reorientation at room temperature to permit the emergence of elastomeric character. Polymers 4 and 5 are produced commercially for this purpose. Species 7 (known by the acronym, MEEP) is being investigated widely as a polymeric matrix for solid ionic conduction and as a biomedical hydrogel material. It is one of the most interesting and important polyphosphazenes yet synthesized.

Side Groups that Generate Semiconductive, Liquid Crystalline, Ferroelectric, or NLO Properties

Recent advances have led to the synthesis of a new family of polyphosphazenes with metallocenyl side groups, of which 8 is a representative structure. These species are

Chart 1



electron-hopping semiconductors. Polymers 9, 10, and analogues with chiral side groups are liquid crystalline, ferroelectric, or NLO materials. Species 8 has one of the highest second harmonic NLO values of any polymer.

Biomedical Hydrogels

Finally, radiation crosslinked polymer 7 and ionically crosslinked polyphosphazene 11 have valuable properties for use in biology and medicine. Crosslinked matrix 12 has been used as a biocompatible coating for hybridoma mammalian cells for prospective use in devices such as the artificial liver or in biotechnology for the production of proteins.

UNDERLYING BASIC SCIENCE

Underlying all of these properties and uses are fundamental questions about the nature of the phosphorus-nitrogen bond and its influence on the unique properties of these polymers. Also of fundamental importance are questions about the mechanisms of the substitution reactions shown in Scheme I, in which typically 30,000 substitutions take place on one molecule, with the reactions influenced in a complex way by the steric and electronic characteristics of the nucleophiles and the structure of the partly substituted polymers. Approaches to the study of these aspects include synthetic, mechanistic, and structural studies on small-molecule cyclic and linear short chain phosphazenes, molecular mechanics calculations, and attempts to understand molecular interactions in the solid state. Thus, this subject provides unusual opportunities for directly relating mechanisms and molecular structures to useful properties and advanced applications.

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