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Novel cyclophosphazene monomers and their polymerization behavior

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SUMMARY

The starting material used for the synthesis of the derivatives presented in this Thesis is the ring compound hexachlorocyclotriphosphazene, $(\text{NPCl}_2)_3$ (Figure 1). Because the chlorine atoms on the phosphorus atom can be replaced easily by other groups this molecule has been the subject of extensive research. Another important topic of interest is the thermal ringopening polymerization of $(\text{NPCl}_2)_3$ which affords a reactive linear poly(dichlorophosphazene) $(\text{NPCl}_2)_n$. The properties of this polymer can be varied over a wide range by the introduction of suitable substituents on the inorganic backbone. These macromolecules belong to the class of hybrid inorganic-organic polymers.

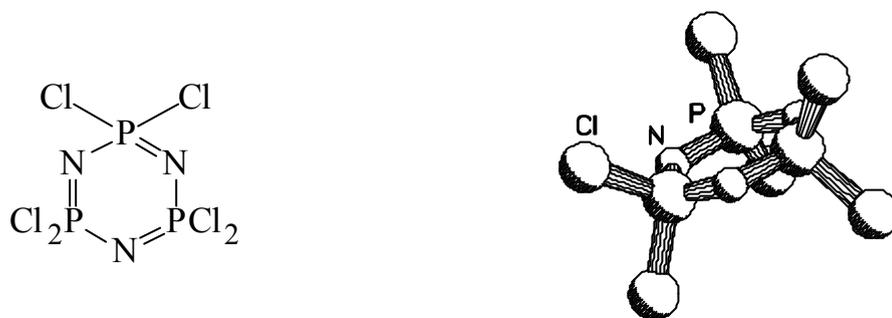


Figure 1 Hexachlorocyclotriphosphazene

A second route towards hybrid inorganic-organic polymers has been offered by the use of chlorocyclophosphazenes bearing an unsaturated side group. Homopolymerization or copolymerization reactions in the presence of an organic monomer as styrene or methyl methacrylate lead to polymers with the inorganic rings as substituents on the organic backbone. This route offers the possibility to transfer advantageous properties of inorganic components to traditional organic polymers.

Following these routes polymers have been synthesized with new and special properties which makes them suitable as e.g. flame retardant, photo resist or ceramic precursor.

This Thesis describes the synthesis and characterization of chlorocyclophosphazene derivatives which have an unsaturated group attached to the inorganic ring by a direct phosphorus-carbon bond. The substituents on the double bond cause steric and electronic perturbations of the olefin moiety. By investigating the behavior of these novel monomers (Figure 2) in radical polymerization reactions one can study to what extent these perturbations influence the reactivity of the olefin.

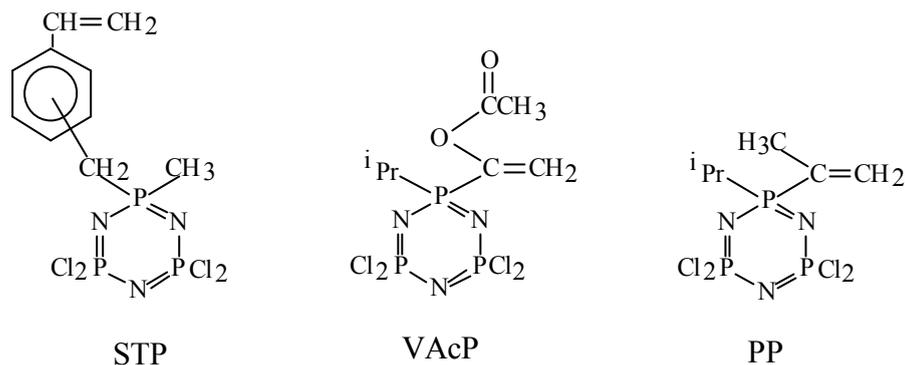


Figure 2 The novel inorganic precursors described in this Thesis

Chapter 1 gives a survey of the chemistry on (cyclo)phosphazenes and their use as monomer for the synthesis of polymers.

Chapter 2 describes the synthesis and characterization of three novel chlorocyclotriphosphazene monomers (Figure 2) and some interesting by-products.

The first synthetic route describes the reaction of vinylbenzylmagnesium chloride with $(\text{NPCl}_2)_3$. This reaction gives the styrene derivative, STP, in good yields.

The second route involves the nucleophilic addition of a hydrocyclophosphazene with a carbonyl group. Reaction of isopropylhydrocyclophosphazene with acetyl chloride in the presence of a base affords the vinyl acetate derivative, VAcP, or a bicyclopentatriphosphazene depending on the reaction conditions used.

The third monomer, PP, is prepared by a multi-step synthesis. Starting from $(\text{NPCl}_2)_3$ a hydroxyl substituted derivative is synthesized. Then the hydroxyl group is transformed in a sulphonium group. The last step is a base-catalyzed elimination reaction yielding PP. The overall yield for the preparation of this propene derivative is rather low.

The remaining chlorine atoms on the phosphazene ring are still susceptible for substitution reactions as is demonstrated by the reaction of dimethylamine with STP or PP. Complete substitution with dimethylamino groups can be achieved.

The crystal and molecular structures of a number of the compounds synthesized are discussed in Chapter 3. The sequence of N-P bond lengths in the molecules can be explained from the difference in electronegativity of the phosphorus centres. The bond angles within the PN-ring are understood in terms of steric constraints caused by the substituents.

Chapter 4 is concerned with the reactivity of the new inorganic precursors in radical polymerization reactions. The copolymerization reaction of methyl methacrylate (MMA) with

the styrene derivative STP can be described by the terminal model. From the calculated reactivity ratios it follows that STP possesses a reactivity equal to styrene.

Attempts to homopolymerize VAcP under radical polymerization conditions were unsuccessful. Copolymerizing with MMA yields copolymers with almost no inorganic monomer incorporated. The lower reactivity of VAcP in radical polymerization reactions is the result of the large steric hindrance at the double bond. In reactions with styrene a copolymer is obtained with a maximum amount of 20 mol% of VAcP incorporated. At feed ratios with 40 mol% of VAcP and higher no polymer is formed. From the results obtained in low conversion copolymerizations it is concluded that a penultimate model should be used to calculate the reactivity ratios. The reactivity ratios were estimated from a simulated data set.

The propene derivative, PP, shows a behavior similar to that of VAcP except that lower amounts of PP are incorporated at the same feed ratio as compared to VAcP. This can be explained by considering that VAcP has electron donating and withdrawing substituents which stabilize the newly formed radical more than when only an electron withdrawing group is attached to the double bond.

Finally, Chapter 5 deals with the thermal behavior of the hybrid inorganic-organic polymers synthesized. The thermal degradation behavior of the hybrid inorganic-organic polymers were studied in detail by Thermal Gravimetric Analysis (TGA) experiments. Further information about the decomposition process was gathered by analyzing the elemental composition of the residues with X-ray Photoelectron Spectroscopy (XPS). The homopolymer of STP shows in TGA a one step weight loss process. It also gives the highest char yield (64 wt%) of all polymer samples. Combined with the XPS analysis of the residue, several underlying decomposition processes can be discerned being: HCl elimination, phosphazene ring degradation and depolymerization.

Substitution of all chlorines with dimethylamino groups has no influence on the degradation behavior in TGA except that a lower char yield is obtained. As the elemental composition of the char is the same as that starting from the chloro analogue it is assumed that analogous degradation processes are operative except that in this case HNMe₂ elimination takes place.

Copolymers of STP and styrene show in TGA a similar behavior as the STP homopolymer. From this it is concluded that the same degradation path is followed for both homo- and copolymers.

The STP/MMA copolymers exhibit a two step degradation process. XPS scans show that complete loss of chlorine takes place in the first step and probably also depolymerization takes place. In the second step phosphazene ring degradation is observed, accompanied with further carbonization of the sample. A residue obtained in the TGA experiment under nitrogen

atmosphere has the same elemental composition as a polymer sample which was burnt in a flame. Combined with the observed self-extinguishing capabilities of the polymers it seems that the phosphazene ring intervenes in the oxidation process.

The VAcP/styrene copolymers decompose also via a two step process. These copolymers start to lose weight about 100 °C lower than the STP/MMA copolymers. The first step is most likely associated with breakdown of polymer chains at the C-C linkage between inorganic monomers. In the second step further depolymerization, HCl elimination and ring degradation occurs.

PP/styrene copolymers have in TGA lower char yields as VAcP/styrene copolymers with the same composition. This points to a decomposition mechanism in which depolymerization dominates.