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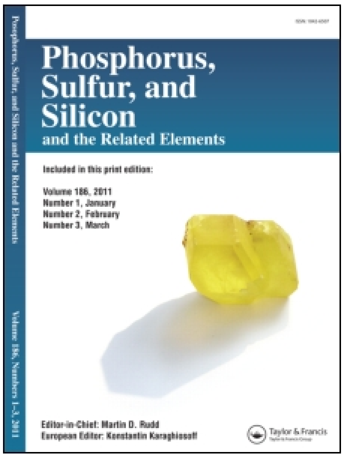

## Phosphorus, Sulfur, and Silicon and the Related Elements

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# Preparation and Polymerization of Styrene, Acrylate and Methacrylate Substituted Cyclophosphazenes

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# PREPARATION AND POLYMERIZATION OF STYRENE, ACRYLATE AND METHACRYLATE SUBSTITUTED CYCLOPHOSPHAZENES

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Abstract. Radical polymerization and copolymerization reactions involving olefin substituted cyclophosphazenes lead to hybrid inorganic-organic polymers and copolymers, which are characterized by a carbon-carbon backbone and pendant phosphazenic groups. The stability of the polymers prepared is related to their structures. The thermal behaviour of poly(cyclophosphazenemethacrylate) (PCPhMA), which appears to possess flame-retardant properties, is compared with that of poly(methylmethacrylate) (PMMA).

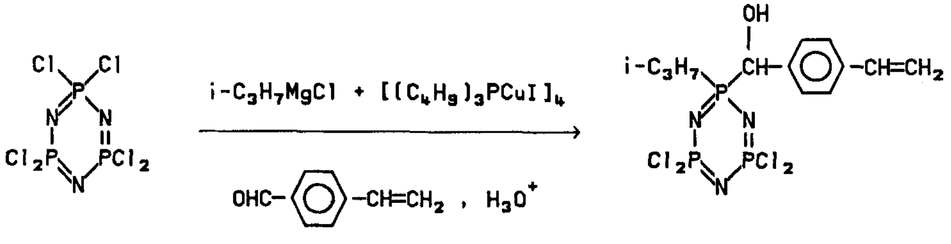
## INTRODUCTION

Organic polymers bearing pendant inorganic cyclophosphazene side-groups belong to the class of hybrid inorganic-organic polymers. They can be prepared by radical polymerization of olefin-substituted cyclophosphazenes. In order to avoid complications in the polymerization process the olefin has to be separated from the electron-withdrawing phosphazene moiety by an insulating spacer.[1,2]

Nucleophilic addition of phosphazenocuprates to aldehydes was used as a synthetic entry to suitable polymer precursors.[3] By this method alkyl(hydroxy)alkyl-substituted cyclophosphazenes were obtained, which could be applied directly in the polymerization experiments, providing the aldehyde used contained a polymerizable function, *viz.* *p*-formylstyrene. In a second approach the unsaturated moiety was introduced by esterification of the hydroxyl group with acrylic or methacrylic acid chloride. All these compounds readily undergo radical polymerization with AIBN as initiator. The thermal behaviour of one of the polymers prepared, poly(cyclophosphazene-methacrylate), is described in detail.

## SYNTHESIS OF PRECURSORS

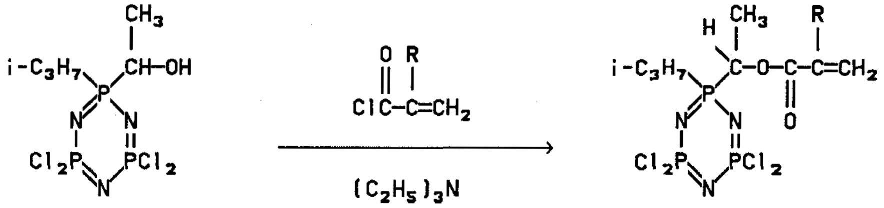
**Synthesis of $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7CHOH\text{-}p\text{-}C_6H_4CH{=}CH_2$ (2).** Starting from $(NPCl_2)_3$ (**1**) the synthesis of **2** was performed according to Scheme 1 in 66% yield.[3] Some care has to be taken in the recrystallization of **2** as thermal polymerization can take place, which lowers the yield and complicates the crystallization process.



(1) (2)

Scheme 1

**Synthesis of acrylates and methacrylates.** The synthesis of acrylate and methacrylate derivatives was achieved by esterification of $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7CH(OH)Me$ (**3**) (prepared from $(NPCl_2)_3$ and MeCHO [3]) with acryloyl or methacryloyl chloride under Schotten-Bauman conditions (Scheme 2).



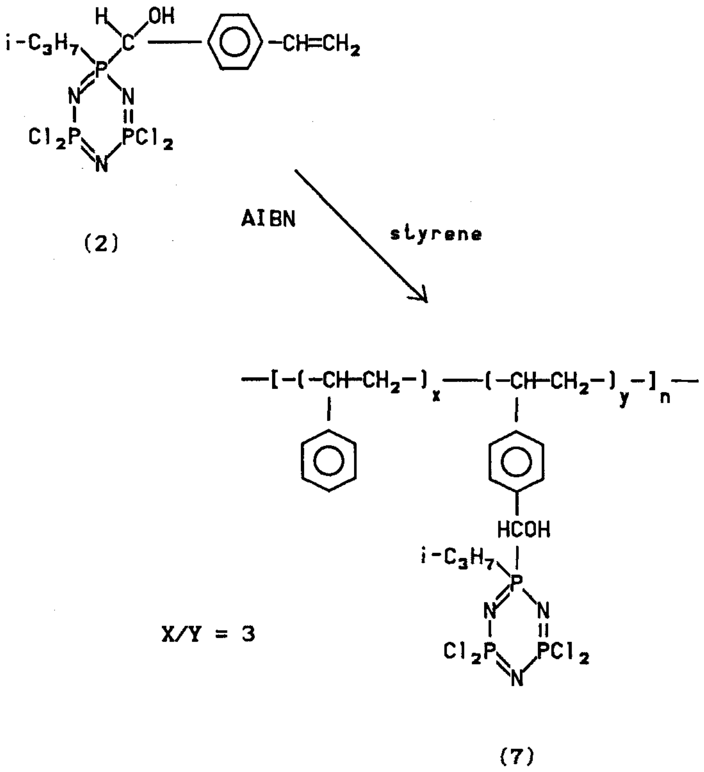
Scheme 2

The acrylate and methacrylate derivatives, **4** and **5**, were obtained as viscous oils in 55% overall yields starting from **1**. Compound **4** appeared to be unstable due to presence of an active proton at the double bond, and was not used in polymerization experiments.

## POLYMERIZATION EXPERIMENTS

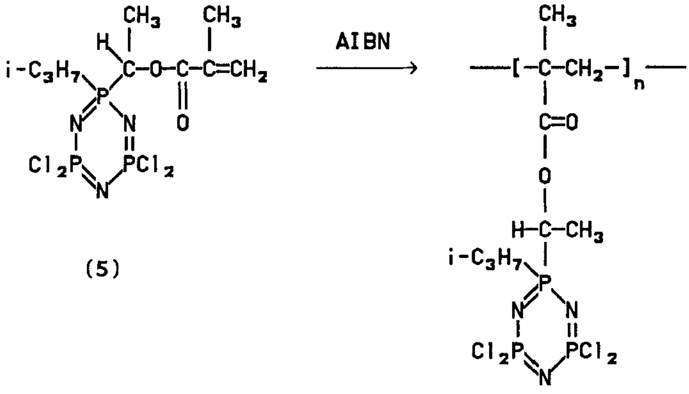
**Polymerization of $(NPCl_2)_2NP\text{-}i\text{-}C_3H_7CHOH\text{-}p\text{-}C_6H_4CH{=}CH_2$ (2).** Homopolymerization of **2** was carried out with azobisisobutyronitrile (AIBN) as initiator. The resulting polymer (**6**), though initially soluble in common organic solvents, became insoluble after one week.

This insolubility is almost certainly due to a gradual cross-linking, caused by intermolecular alcoholysis of P-Cl bonds with loss of HCl. Copolymerizing with styrene in a 1:1 feed ratio in the presence of AIBN afforded (Scheme 3) again a soluble polymer (7) which appeared to be stable for months. The "dilution" by styrene segments apparently prevents the cross-linking reactions. The molecular weight was determined relative to polystyrene standards by gel permeation chromatography (GPC): $\overline{M}_w = 4.0 \times 10^4$, $\overline{M}_n = 2.7 \times 10^4$, D = 1.5. Elemental analysis showed that 25% of the phosphazene comonomer was incorporated in the polymer chain.



Scheme 3

**Polymerization of $(NPCl_2)_2NPCHMeOC(O)CMe{=}CH_2$ (5).** Radical polymerization in benzene (AIBN as initiator) resulted in formation of poly(cyclophosphazenemethacrylate) (PCPhMA) (8) (Scheme 4).



(5)

PCPhMA (8)

Scheme 4

The molecular weight of PCPhMA (GPC, polystyrene standards) turned out to be $\overline{M}_w = 4.9 \times 10^5$, $\overline{M}_n = 2.6 \times 10^5$, D = 1.9.

The homopolymerization of 5 with AIBN in 2-xylene was monitored by differential scanning calorimetry (DSC). In these experiments the measured heat of polymerization ($\Delta H_p$) depends on the scan speed used.[4,5] Extrapolation to zero scan speed provided $\Delta H_{p,0}$, which amounted to $-57 \pm 4$ $kJmol^{-1}$ after correction for the heat of decomposition of AIBN. This value can be compared with those of other methacrylate esters which generally lie between -55 and -60 $kJmol^{-1}$. Combination of the $\Delta H_{p,0}$ value with the results obtained by isothermal kinetic measurements at 50 °C, using a Setaram Calvet-type twin microcalorimeter,[6,7] led to a kinetic order in monomer and initiator concentration of 1.0 and 0.40, respectively. These values suggest classical radical polymerization kinetics. Activation parameters were calculated as $E_a = 92 \pm 4$ kJmol$^{-1}$ and ln A (dm$^{3/2}$mol$^{1/2}$s$^{-1}$) = 26 ± 1.

## THERMAL ANALYSIS OF PCPhMA

The thermal properties of PCPhMA were studied by differential scanning calometry (DSC), a qualitative flame retardancy test and thermal gravimetric analysis (TGA).

From a DSC scan the glass transition temperature ($T_g$) was determined to be 146 °C.

The crude flame retardancy test was performed by placing about 5 mg of PCPhMA on a spatula and holding it into a Bunsen burner flame. On heating, the polymer did not ignite, although inflammation of the gaseous decomposition products was observed. After a short heating period, a black brittle residue was formed, which could be heated until glowing without any visible changes. It should be mentioned that poly(methylmethacrylate) (PMMA) ignited readily in this test and burned away completely. Moreover, on heating (and burning) PMMA liquefies, which is one largest hazards in fires involving polymer materials. PCPhMA did not show any sign of liquefaction on heating.

The observations during the flame retardancy tests are confirmed by the TGA measurements. As may be seen from Fig. 1 (upper part) PCPhMA loses mass to form a black material with 30% of its initial mass. This corresponds well with the PN content of the polymer (31%), indicating that the material is probably phosphorus nitride. The black material is remarkably stable up to 600 °C. PMMA starts to decompose at 270 °C (Fig. 1, lower part) and this decomposition continues until all the sample has been consumed. From the TGA analysis of PCPhMA it becomes clear that no cross-linking occurs with loss of HCl, as was observed for the homopolymer of $N_3P_3Cl_5(OCH=CH_2)$.[8]

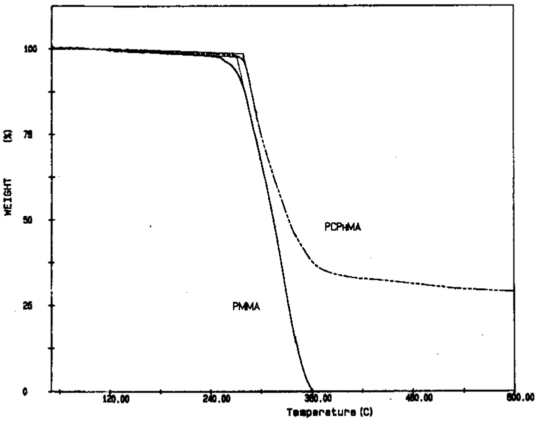


Figure 1. TGA scans of PCPhMA (upper) and PMMA (lower).

Such an intramolecular cross-linking would result in a two step decomposition of the polymer, while only one transition is observed for PCPhMA.

The thermal properties, discussed in this section, demonstrate that PCPhMA is excellently suited for application as flame retardant.

## ACKNOWLEDGEMENTS

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