

Synthesis and research of functional oligoaryloxycyclotriphosphazenes

Abstract

In recent years, there are more and more applications for oligomeric and polymeric phosphazenes and their derivatives. High chemical versatility and functionality make it possible to obtain organophosphazenes with desired properties that meet the requirements. Phosphazenes can be used in various fields of science and technology, from the creation of modifiers for industrial resins to the components for dental filling compositions.

The polycondensation products of chlorocyclophosphazenes with diatomic phenols - hydroxyaryloxycyclotriphosphazenes (HARP) - are of interest both for the synthesis of various types of phosphazene-containing polymers (polyesters, phenol-formaldehyde and epoxy resins), and for the modification of ordinary organic polymers.

Therefore, it seems relevant to improve the synthesis of HARP and their derivatives and expand the possible directions of their practical application.

The overall goal of this work is the synthesis of oligomeric hydroxyaryloxycyclotriphosphazenes of reduced functionality, their epoxy derivatives and the determination of possible ways of using the obtained compounds. To achieve this goal, it was necessary to solve the following tasks:

- to optimize methods for the synthesis of partially substituted aryloxychlorocyclotriphosphazenes based on hexachlorocyclotriphosphazene (HCP) with isolation and identification of the corresponding derivatives of phenol or paracetamol;
- to develop optimal methods for the preparation of mixed hydroxyaryloxycyclotriphosphazenes based on these compounds and resorcinol;

- establish the basic laws of epoxidation of mixed hydroxyaryloxycyclotriphosphazenes with epichlorohydrin, as well as the structure and composition of epoxy oligomers formed on phosphazene-containing epoxy.

Scientific novelty

Phenoxychloro- (PCP) and p-acetamidophenoxychlorocyclotriphosphazenes (ACP) were synthesized and synthesized using ^{31}P NMR, ^1H spectroscopy and MALDI-TOF mass spectrometry.

Two new methods have been developed for the synthesis of mixed hydroxyaryloxycyclotriphosphazenes by the reaction of PCP or ACP with resorcinol in a heterogeneous mixture of cyclohexane-pyridine and in acetonitrile medium with the acceptance of potassium carbonate formed by HCl.

The optimal conditions for the epoxidation of PCP-based HARF by the reaction with epichlorohydrin in excess of the latter in the presence of KOH were established, epoxycyclotriphosphazenes with an epoxy number from 6 to 11 were obtained and characterized.

The occurrence of adverse reactions during the epoxidation of mixed hydroxy-m-phenoxy-p-acetamidophenoxycyclotriphosphazenes was revealed, leading to crosslinking and destruction of the resulting products.

Theoretical and practical significance of the dissertation results

An analysis of the effect of the ratio of PCP (ACP): resorcinol on the composition and structure of hydroxyaryloxycyclotriphosphazenes formed during their interaction showed a deviation of the indicated reaction from the theory of three-dimensional polymerization of Flory. This deviation is explained by the influence of steric factors during the replacement of the last chlorine atoms in the triphosphazene cycle.

The synthesized epoxy phosphazene-containing oligomers based on resorcinol are recommended for the production of limited combustible or completely non-combustible polymer composite materials.

Protection provisions

- methods for the synthesis of hydroxyaryloxyphosphazenes based on a mixture of aryloxychlorocyclophosphazenes and resorcinol;
- synthesis of epoxyphosphazenes based on a mixture of chlorocyclophosphazenes, resorcinol and phenol or p-acetamidophenol;
- patterns of the formation of hydroxy and epoxyphosphazene oligomers.