Electron-beam Initiated Polymerization of Elemental Phosphorus

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Abstract: - The article discusses the results of the synthesis of polymer phosphorus from the elemental phosphorus in the aqueous medium under the electron-beam irradiation. The structure of the obtained high-molecular phosphorus-containing compounds was analyzed and compared with samples of commercially available red phosphorus by mass spectrometry with matrix-activated laser desorption/ionization.

Key-Words: - radiation chemistry, phosphorus, red phosphorus, radiation polymerization, phosphorus-containing polymers, electron accelerator

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1 Introduction

The modern state-of-art of chemistry of inorganic polymers, polymeric forms of phosphorus among them, is characterized by the development of fundamental and applied research aimed at obtaining target products with predictable properties. First of all, it should include modification of the structure and composition of inorganic polymers, variation of reaction initiation methods (e.g., chemical, thermal or high-energy initiation), as well as that of the reaction medium thus contributing to the formation of the desired structure of the final product. Recently, there has been an increased interest in the modification of red phosphorus, due to the significant expansion of the fields of application of this inorganic polymer [1-5].

2 Problem Formulation

Specific features of white phosphorus (high reactivity, fire and explosion hazards, toxicity) [6] make us look for milder conditions for obtaining red phosphorus. The use of high-energy radiation is one of the most interesting methods for initiating red phosphorus synthesis reactions. Its advantages and disadvantages can be identified in comparison with traditional thermal methods, however, it is obvious that only radiation initiation makes it possible to polymerize white phosphorus in various environments with the least fire risks.

Mendeleev University of Chemical Technologies of Russia has been developing this scientific direction for more than 40 years, the goal of which is to find alternative conditions for the conversion of white phosphorus into a polymer form, for example, under the influence of high-energy radiation [7-11]. Based on the obtained results and taking into account the experience of using electron beam radiation in polymer chemistry [12-17], it was decided to conduct a study of the polymerization process of elemental phosphorus under the influence of electron beam radiation in an aqueous medium in the presence of air.

3 Problem Solution

White phosphorus, purified with potassium bichromate, was placed in quartz glass tubes half filled with water, hermetically rolled up and irradiated at the electron accelerator "Electronics" UELV-10-10-S-70 (with magnetron MI-470). The irradiation was carried out by a beam of accelerated electrons with the energy of 7 MeV. Dosimetry was performed using a standard sample of the absorbed dose of proton and electron radiation SO PD(F)E-5/50. To isolate the resulting product, multiple purification in a Soxlet extractor was used, after which the samples were analyzed by MALDI-ToF technique using a mass-spectrometer Ultraflex II (Bruker) in the reflective mode on positive ions without the use of a matrix with an accelerating voltage of 25 keV. Desorption was performed by an Nd:YAG laser beam ($\lambda = 355$ nm). Also, the structure of the obtained phosphorus-containing polymers was characterized by X-ray fluorescent analysis (Bruker Kappa APEX DUO). The interpretation of the obtained spectra and the identification of individual peaks were carried out using the FlexAnalysis-3.3 program. The characteristics of the studied samples are presented in Table 1.

Table 1. Characteristics of the studied samples

№	Weight before irradiation, g	Reaction medium	Radiation absorbed dose, kGy	Yield, %
1	2,48	H_2O/air oxygen	100	3.9
2	2,50	H_2O/air oxygen	250	8.0
3	2,10	H_2O/air oxygen	500	11,5
4	2,55	H_2O/air oxygen	600	13,5

To identify the structure and composition of the obtained samples, their MALDI-TOF spectra were compared with the MALDI-TOF spectrum of commercially available red phosphorus ("Reachim", purity over 99%), Fig. 1.

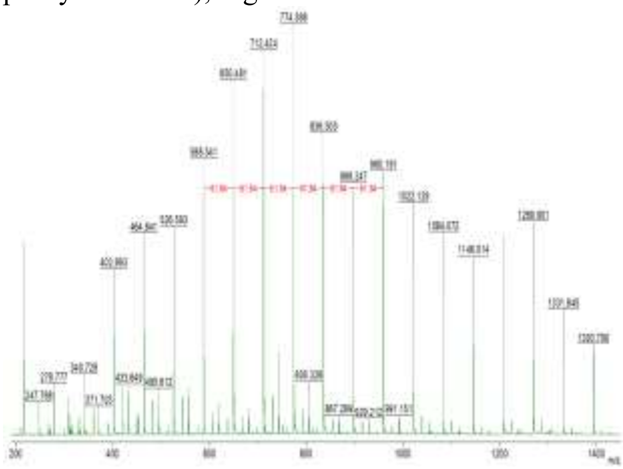

Fig. 1. MALDI-TOF spectrum of commercially available red phosphorus.

There is a series of intense signals in the spectrum (Fig. 1) that differs by 61.94 Da, which corresponds to two phosphorus atoms. The sample does not contain impurities, since the values of the signals correspond exactly to the masses of the fragments of the polymer chain, for example, the most intense signal with m/z = 774.368 corresponds to a fragment of the P_{25} chain with a calculated mass of 774.344 Da. The MALDI-TOF spectra of phosphorus-containing polymers obtained at different irradiation doses after irradiation at the electron accelerator are similar in many ways. For this reason, the discussion of the results will be conducted using Sample 4 as an example (Table. 1), obtained at the highest absorbed radiation dose of 600 kGy (Fig. 2).

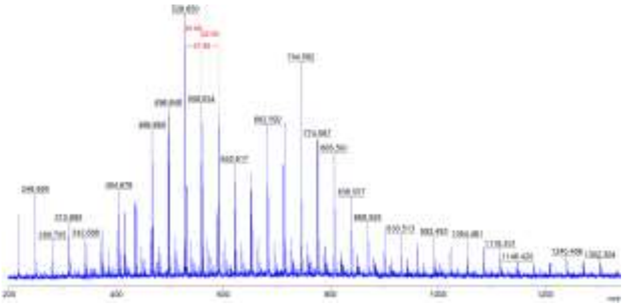

Fig. 2. MALDI-TOF spectrum of phosphorus-containing polymer obtained using an electron accelerator. The absorbed dose equals 600 kGy.

In the spectrum of the obtained phosphorus-containing polymers (sample No. 4), the difference in intense signals is also 61.95 Da, however, this value does not correspond to two masses of phosphorus atoms, but is divided into 32 and 30 Da, which indicates the presence of additional elements in the sample.

It is also worth paying attention to the mass of the most intense signal with m/z = 528.650. The polymer phosphorus fragment of the P_{17} chain has a calculated mass of 526.55 Da and is present in the red phosphorus spectrum (Fig. 1, 526.593 m/z signal), which differs by 2 Da from the fragment with a mass of 528.650 Da. Based on the combination of these two facts, it can be assumed that the signal with m/z = 528.650 corresponds to a fragment of the circuit with the formula $P_{15}O_4$, This fact is confirmed by the calculated data for such a structure: $M(P_{15}O_4)$ = 528.586 Da. The pattern of polymer fragmentation can be clearly observed as the result of the detailed examination of several intense spectrum signals (Fig. 3).

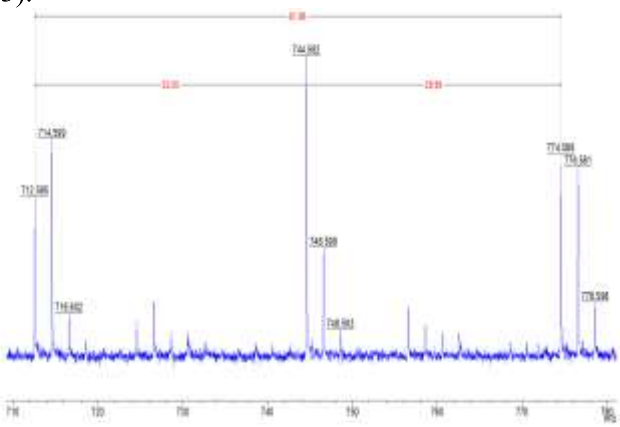

Fig. 3. MALDI-TOF spectrum (710 – 780 m/z).of phosphorus-containing polymer obtained using the electron accelerator. The absorbed dose equals 600 kGy.

The signal 712.565 m/z corresponds to a fragment P_{23} of the polymer chain, which differs by 61.95 Da from the fragment P_{25}. Signals 714.599 m/z and 716.602 m/z were registered from fragments $P_{21}O_4$ and $P_{19}O_8$, respectively, signals 744.582 m/z, 746.599 m/z, 748.593 m/z - $P_{23}O_2$, $P_{21}O_6$, $P_{19}O_{10}$, and signals 776.561 m/z and 778.598 m/z are present in the spectrum as a result of fragmentation of the oxidized polymer chain with the formation of structural components $P_{23}O_4$ and $P_{21}O_8$. The values of the signals differ by 2, which allows us to confidently consider these individual signatures as a set of sequences of fragments of various phosphorus-containing polymer chains, rather than single ensembles of signals with isotopic distribution, which is typical for samples with a high content of organic materials.

It is likely that the appearance of oxygen in the polymer chain of the obtained samples is associated with the air environment and oxygen dissolved in water, in which the polymerization was carried out. According to the results of X-ray fluorescence analysis, the atomic fraction of oxygen in the phosphorus-containing polymers equals about 20 %.

4 Conclusion

The polymerization of white phosphorus in an aqueous medium under the influence of an accelerated electron beam results in the formation of the high-molecular phosphorus containing compound. The results of the MALDI-TOF and X-ray fluorescence analysis of the samples obtained at different absorbed doses suggest the presence of long polymer chains of phosphorus in them, as well as fragments containing oxygen.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

Natalia Tarasova formulated the idea and edited the manuscript
Alexey Zanin has organized and executed the experiments of Section 3.
Efrem Krivoborodov analysed the experimental data and wrote the text of the manuscript.

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Conflict of Interest
The authors have no conflicts of interest to declare that are relevant to the content of this article.