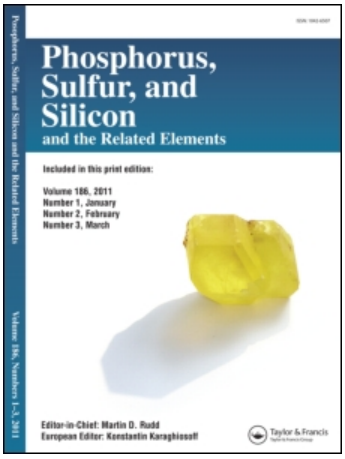

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Radiation-Induced Synthesis of Polymers on the Basis of Elemental Phosphorus

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Radiation-Induced Synthesis of Polymers on the Basis of Elemental Phosphorus

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The use of red phosphorus in different branches of industry (synthesis of materials for electronics, nonferrous metallurgy, production of flame retardants for polymers, defense applications, and precursors in the synthesis of organophosphorus compounds) specifies the search for the simple and easily controlled processes of the synthesis of this polymer of elemental phosphorus with the predictable properties. The studies of the radiation-induced synthesis of the polymers based on the elemental phosphorus have been carried out. The use of methods of radiation chemistry made it possible to solve a number of problems, traditional in the synthesis of the red phosphorus. The qualitative and quantitative characteristics of the process and those of the end products obtained are discussed.

Keywords Phosphorus; polymers; radiation

INTRODUCTION

The use of red phosphorus in different branches of industry (synthesis of materials for electronics, nonferrous metallurgy, production of flame retardants for polymers, defense applications, and precursors in the synthesis of organophosphorus compounds) specifies the search for the simple and easily controlled processes of the synthesis of this polymer of elemental phosphorus with the predictable properties.[1] We have carried out the studies of the radiation-induced synthesis of the polymers based on the elemental phosphorus. The use of methods of radiation chemistry made it possible to solve a number of problems, traditional in the

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high-temperature synthesis of the red phosphorus:

1) the reduction of the temperature of the beginning of the reaction of the formation of red phosphorus from the white one and the enlargement of the temperature interval of the process;
2) the variation of the conditions of the initiation of the reaction by the ionizing radiation makes it possible to govern the composition and the structure of phosphorous-containing polymer; and
3) the methods of the synthesis of high molecular mass compounds (polymerization, polymerization in the solution and emulsion polymerization) being applied to the inorganic monomer—the white phosphorus—made it possible to obtain phosphorus-containing polymers (PCPs) of different structures.

RESULTS AND DISCUSSION

The general scheme of radiation-induced polymerization of white phosphorus is shown in Figure 1. Depending on the mass content of the white phosphorus in the reaction system, the initiating radicals might be formed through the direct action of the radiation on the phosphorus molecules (high content of the white phosphorus) or through the formation of the radicals from the reaction media-solvent, additives, and so on (low content of the white phosphorus). It possible to obtain:

- using the radiation-induced balk polymerization, the analogs of thermal red phosphorus with the low degree of polymerization, the red phosphorus with the desirable radiation, thermal, and doped defectiveness;

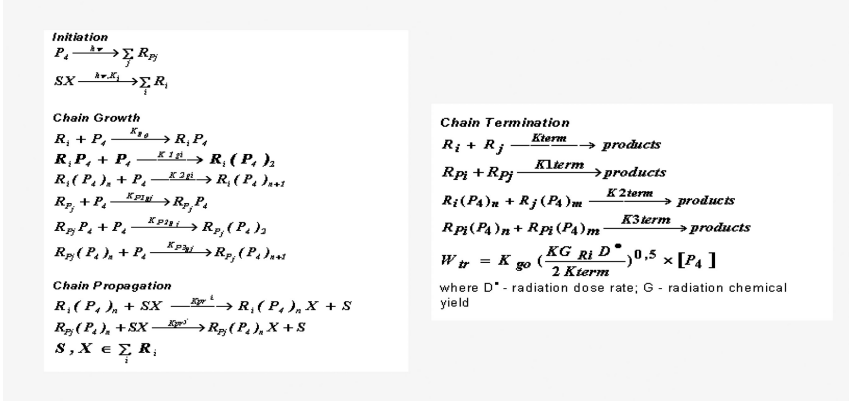

FIGURE 1 General Scheme of polymerization.

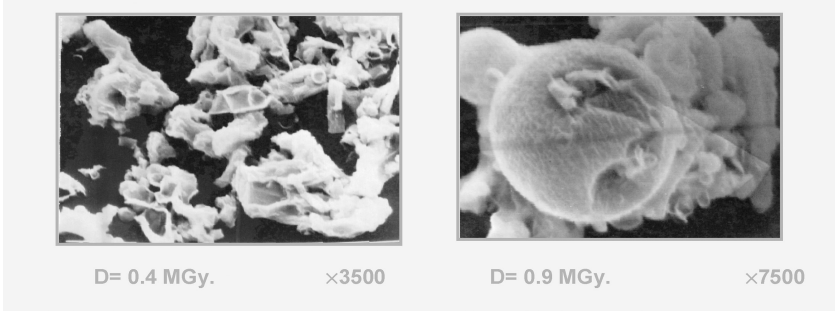

FIGURE 2 Influence of the absorbed radiation dose on the structure of PCP, obtained by radiation emulsion polymerization. Microphotography of the PCP sample, obtained in the emulsion, stabilized by sodium salt of the carboxymethyl cellulose. T = 318K, $D^* = 1.64$ Gy/s.

- using the polymerization in solution-phosphorous-containing polymers with the low degree of polymerization. The polymeric products contain the fragments of the solvents (RO, C_6H_5, CCl_3, C_2H_5O, etc.). The reactivity of the synthesized PCPs is comparable with that of the white phosphorus; and
- using the polymerization of white phosphorus in the dispersed state (water emulsions) it is possible to obtain phosphorous-based polymers in the shell-growth process (Figures 2 and 3).

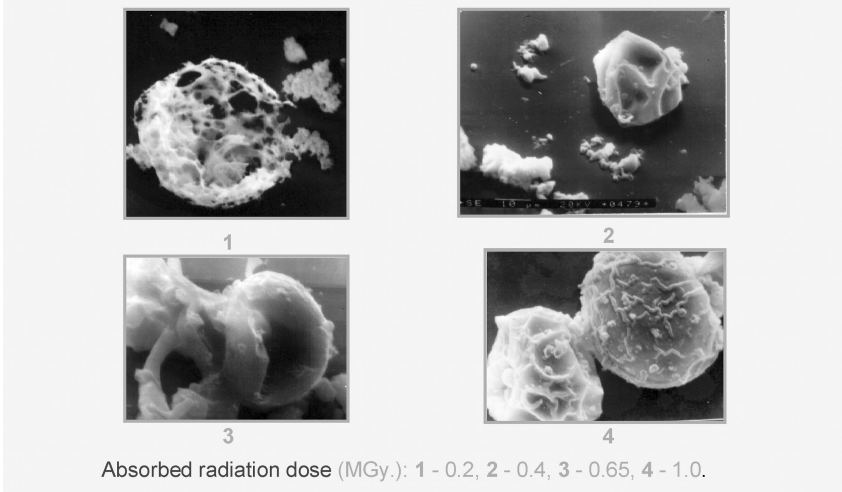

FIGURE 3 Electronic microphotography of PCP samples, obtained in 10 mass. % emulsions of elemental phosphorus in the presence of Al(OH).

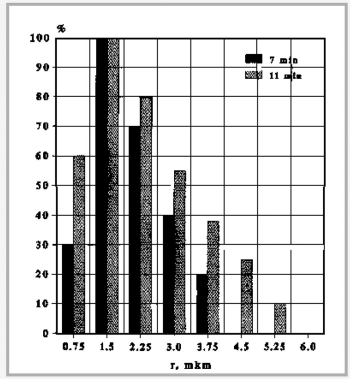

FIGURE 4 Histogram of PCP particle sizes distribution. Radiation polymerization in the benzene solution in the presence of atmospheric oxygen. $D' = 0{,}26$ Gy/s, $T = 303$ K. $[P_4]_0 = 0{,}02$ M.

The method of the radiation-induced polymerization makes it possible to regulate the size of polymeric particles, porosity, and reaction ability of the polymer (Figures 4, 5 and 6).

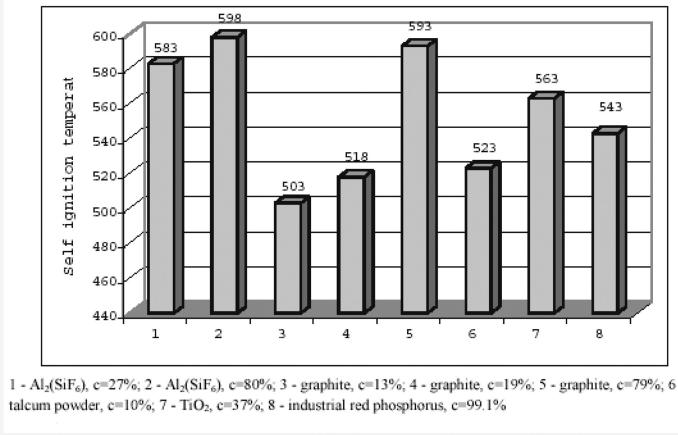

FIGURE 5 Self ignition temperature as function of modification additive type. Thermo-radiation induced bulk polymerization. C - the conversion of white phosphorus.

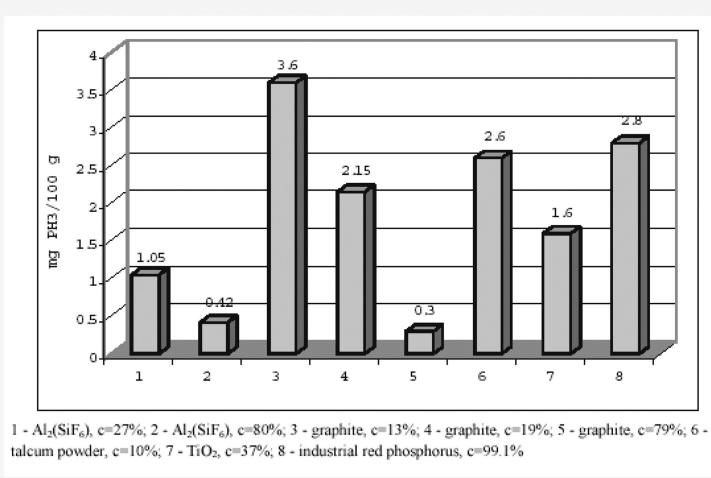

FIGURE 6 The amount of phosphine formed at 448 K as function of modification additive type thermo-radiation induced bulk polymerization. C - the conversion of white phosphorus.

Future trends in the development of studies in the field of new materials and processes, based on the radiation chemistry of elemental phosphorus might be seen as follows:

- Synthesis of the copolymers of phosphorus and inorganic "monomers" (S, As, etc.);
- Use of ionic liquids for "greening" the processes of the synthesis of polymeric forms of phosphorus;
- Synthesis of the polymeric forms of phosphorus with the controlled defectiveness for the applications in the organophosphorus synthesis;
- search for the fullerene-like structures of elemental phosphorus and it's co-polymers; and
- quantum-chemical calculations of phosphorus cluster structures and the estimation of its reactivity.

EXPERIMENTAL

Gamma-radiation of Co-60 (energy 1,25 MeV) was used for the initiation of polymerization of white phosphorus. Absorbed dose rate varied in the interval 0,5–4 Gy/s. The temperature of the polymerization varied

from 288K to 673K. The other details of the reaction procedures might be found in.[2–5]

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