New polymeric fireproofing agent based on tertiary phosphine

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One of the most effective methods for lowering the flammability of polymeric materials is to use unsaturated phosphorus-containing compounds for their synthesis. The introduction of chemically combined phosphorus into the composition of high molecular weight compounds by methods of polymerisation, copolymerisation, and polymer-like transformations of phosphorus-containing monomers with industrial large-tonnage monomers makes it possible to produce polymers with unique application properties [1].

Recently, in order to produce materials with reduced flammability, a vast number of phosphorus-containing reactive compounds have been synthesised and investigated as fireproofing agents: vinyl, allyl, diene, and acrylic derivatives of phosphorus acids [2].

Of particular interest are phosphorus-containing quaternary compounds based on the interaction of tertiary phosphines with appropriate alkyl halides [3].

The aim of the present work was to study the laws governing the radical homopolymerisation and copolymerisation of previously uninvestigated phosphorus-containing allyl halide derivatives, to establish the influence of the structure of the monomers and the polymerisation conditions on the properties of the polymers, and to determine the possibilities of their use to produce polymeric materials of reduced flammability.

Para-trisphosphate allyltriphenylphosphonium halides (p-TPATPPHs) were synthesised by the interaction of triphenylphosphine with an allyl halide (allyl chloride and allyl bromide respectively) in an inert solvent, and subsequent phosphorylation using Friedel–Crafts catalysts. The synthesised product was purified by recrystallisation.

The structure of the monomers was confirmed by data of elemental analysis, MR, values, data of IR, NMR, and UV spectroscopy, and, in a number of cases, the results of mass spectrometry.

In an investigation of the radical polymerisation of the synthesised monomers it was established that the remoteness of the phosphorus-containing fragments from the double bond of its structure has an effect on the polymerisation rate. Along with this feature of polymerisation, higher activity of trivalent phosphorus derivatives is observed during polymerisation, other conditions being equal. One of the reasons for this is the higher viscosity of p-TPATPPHs, which leads to inhibition of the diffusion of the active ends of growing macroradicals and, consequently, to a reduction in the rate constant of chain rupture. Owing to this, earlier onset of the gel effect (collapse) is also observed for monomers of the examined class.

It was established that the rate of the process of polymerisation increases with increasing polarity of the medium \(\varepsilon\), i.e. tetrahydrofuran < dioxane < DMPA < dimethylsulphoxide.

It was established that the total polymerisation rate of p-TPATPPHs in the chosen solvent increases with increasing monomer and initiator concentration and temperature, which indicates that the polymerisation process fully obeys the laws of complex radical processes.

Investigations of the viscous characteristics of the polymers obtained showed that they are typical polyelectrolytes.

It was then of interest to study the thermal and fireproofing characteristics of the polymers synthesised.
Differential thermal analysis of the polymers was carried out under identical heating conditions (V = 5 K/min) on a Paulik–Paulik–Erdei derivatograph.

The kinetic curves of thermo-oxidative decomposition of the polymers are S-shaped, which seems to be due to the slower reduction in weight of the specimens at the start of thermal degradation, while acceleration in a relatively narrow range is subsequently observed. Acceleration of the process of decomposition is probably connected with the accumulation of structures with end unsaturated groups which, with increase in temperature, promote acceleration of the degradation process.

To assess the fireproofing characteristics of the polymers synthesised, use was made of the method of determining the oxygen index, the rate of ignition, and the self-extinguishing of specimens. When a small amount (up to 3%) of synthesised polymers is introduced into the composition of industrial polymers – ED-20 epoxy resin, ABS plastics, polymethyl methacrylate – there is a marked increase in the oxygen index (OI = 26%). Furthermore, it was revealed that, simultaneously with the reduction in flammability, there is a reduction in smoke during combustion.

It was established that the inhibition of combustion of polymers is due to the appearance of fireproofing characteristics mainly in the gas phase.

Thus, the possibility of the synthesis and radical polymerisation of a new allyl phosphonium monomer with high fireproofing characteristics has been established.

REFERENCES