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N. P. GRECHKIN

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Abstract

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N. P. GRECHKIN

COPOLYMERIZATION OF DIETHYLENEAMIDES OF PHOSPHORUS ACIDS WITH BIFUNCTIONAL ORGANIC COMPOUNDS

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In our previously published works, the reaction of N-phosphonoaminoethylation of organic compounds was described ([1–3]).

This reaction consists in the addition of ethyleneamides of phosphorus acids, with opening of the ethyleneimine ring, to various organic compounds containing suitable functional groups: NH_2, HNR, SH, OH, CH_2Cl, COOH, etc.

It has recently been shown ([4]) that diethyleneamides of phosphorus acids also enter into the above reaction, the addition proceeding at both ethyleneimine rings with their opening, for example:

$$EtOP(=O)[N(CH_2CH_2)]_2 + 2HNEt_2 \longrightarrow EtOP(=O)[NH{-}CH_2{-}CH_2NEt_2]_2.$$

The realization of this reaction led us to the idea that, upon interaction of diethyleneamides of phosphorus acids with bifunctional organic compounds possessing the listed groups—diamines, dicarboxylic acids (or with dibasic inorganic acids), dimercaptans, etc.—linear copolymers containing phosphorus in the chain can be obtained. Schematically, these reactions may be represented as follows:

1. $HOOC(CH_2)_{nCOOH} + (EtO)P(=O)(NCH_2CH_2)_2 + HOOC(CH_2)_{nCOOH} + (EtO)P(=O)(NCH_2CH_2)_2 + \cdots$
$\longrightarrow \cdots OC(CH_2)_{nCOOCH}2CH_2NH{-}P(=O)(OEt){-}NHCH_2CH_2OC(CH_2)_{nCOCH}2CH_2NH{-}P(=O)(OEt){-}N$

2. $H_2N(CH_2)_{nNH}2 + (EtO)P(=O)(NCH_2CH_2)_2 + H_2N(CH_2)_{nNH}2 + (EtO)P(=O)(NCH_2CH_2)_2 + \cdots$
$\longrightarrow \cdots NH(CH_2)_{nNHCH}2CH_2NH{-}P(=O)(OEt){-}NHCH_2CH_2NH(CH_2)_{nNHCH}2CH_2NH{-}P(=O)(OEt){-}NH$

3. $\cdots HS(CH_2)_{nSH} + (EtO)P(=O)(NCH_2CH_2)_2 + HS(CH_2)_{nSH} + (EtO)P(=O)(NCH_2CH_2)_2 + \cdots$
$\longrightarrow \cdots S(CH_2)_{nSCH}2CH_2NH{-}P(=O)(OEt){-}NHCH_2CH_2S(CH_2)_{nSCH}2CH_2NH{-}P(=O)(OEt){-}NHCH_2CH$

Fig. 1

Figure 1: Fig. 1

4. $\cdots \mathrm{ClCH_2{-}C_6H_{10}{-}CH_2Cl} + \mathrm{(EtO)P(=O)(NCH_2CH_2)_2} + \mathrm{ClCH_2{-}C_6H_{10}{-}CH_2Cl} + \mathrm{(EtO)P(=O)(NCH_2C}$
$\longrightarrow \cdots \mathrm{CH_2{-}C_6H_{10}{-}CH_2{-}N(CH_2CH_2Cl){-}P(=O)(OEt){-}N(CH_2CH_2Cl){-}CH_2{-}C_6H_{10}{-}CH_2{-}N(CH_2CH_2}$

The alternation of atoms in the chains written above we infer with sufficient confidence from previously studied reactions of the monomeric type.

As the experiments we carried out showed, diethyleneamides of phosphorus acids do indeed copolymerize with dicarboxylic acids, diamines, *n*-dichloromethylaryls, and other bifunctional compounds. Thus, for example, when equimolecular amounts of the diethyleneamide of isopropylthiophosphoric acid and sebacic acid are heated to 110–120°, an exothermic reaction occurs, as a result of which a rubber-like substance with a high coefficient of extension is formed.

In the copolymerization of diethyleneamide of ethylphosphonic acid with benzidine (taken in molar ratios), upon heating to 125–130°, as a result of an exothermic reaction there is formed a solid transparent polymer the color of strong tea. In studying the thermomechanical properties (on an apparatus designed by B. Ya. Teitelbaum and M. P. Dianov) of the latter polymer, it showed the presence of a highly elastic state in the temperature interval from 150 to 220° (Fig. 1). In the viscous-flow state, the polymer at 300° can be drawn into threads.

Fig. 1

A whole series of other experiments carried out by us also leads to the formation of polymeric materials, the study of which is currently under way. The property of diethyleneamides of phosphorus acids to add to functional groups of organic compounds can be used to obtain grafted and cross-linked phosphorus-containing polymers. With their aid it is possible to cross-link: 1) polyamide chains, irrespective of the nature of the end groups, since both amino and carboxyl groups equally readily undergo the reaction of N-phosphonoaminoethylation; 2) polyester chains possessing carboxyls as end groups.

In an analogous manner, monoethyleneamides of phosphorus acids can be used for grafting phosphonic groups onto active terminal or branched groups of polymer molecules. Experiments carried out in this direction also led to positive results.

In simultaneous copolymero-polycondensation, carried out by heating to 180° at normal pressure (and to 230° in vacuum) sebacic acid (1 mol) with tetramethylene glycol (0.9 mol) and diethylamide of ethylphosphonic acid (0.1 mol),

an opaque wax-like polymer with a low melting temperature (about 60°) was obtained.

In amide copolymero-polycondensation of sebacic acid (1 mol) with benzidine (0.9 mol) and diethylamide of ethylphosphonic acid (0.1 mol), by heating in a stream of nitrogen to 220°, a solid, opaque, horn-like polymer was obtained. The physicochemical properties of the polymers obtained are being studied.

Thus, a new method has been proposed for obtaining phosphorus-containing polymers by means of the reaction of N-phosphonoaminoethylation.

Chemical Institute
of the Kazan Branch of the Academy of Sciences of the USSR

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.