Translated from *Uspekhi Khimii*, 52 1173-1195 (1983) U.D.C. 678.7

Phosphorylation of Carbochain Polymers

A.P.Khardin, O.I.Tuzhikov, and S.N.Bondarenko

The methods for the chemical modification of carbochain polymers by various phosphorylating agents are examined. The possible ways of utilising macromolecular compounds with phosphorus-containing groups in the side chain are surveyed. The bibliography includes 186 references.

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I. INTRODUCTION

The polymer analogue reactions of macromolecular compounds constitute one of the most important methods for the introduction of new functional groups into polymer side chains[1]. One of the most promising versions of this method involves the phosphorylation of carbochain polymers. The interest in this procedure can be readily accounted for because the introduction of a phosphorus atom into the side chains of the macromolecules of various polymers makes it possible not only to improve important properties of the initial high-molecular-weight compounds, such as fire resistance, hydrophilic properties, and thermal stability, but also (depending on the type of phosphorus-containing functional groups introduced) to obtain polymeric materials capable of ion exchange and sorption of transition metal ions from solutions and to synthesise polymers with oxidation-reduction properties and biological activity. Virtually all the macromolecular compounds modified by various phosphorylating agents are produced in large amounts and some of the products are manufactured on an industrial scale[2].

Extensive experimental data have now accumulated on the phosphorylation of carbochain polymers but there are no publications in the literature which survey adequately questions associated with this problem. The available monographs and review publications[3-11] only partially fill the gap in the systematic description and survey of data concerning this branch of the chemistry of macromolecular compounds and the chemistry of phosphorus.

II. OXIDATIVE CHLOROPHOSPHORYLATION OF CARBOCHAIN POLYMERS

One of the effective methods of phosphorylating carbochain polymers involves their treatment by phosphorus halides and oxygen—the oxidative chlorophosphorylation of hydrocarbons. Phosphonyl chloride groups can then be introduced into the polyethylene side chain[12-17] in accordance with the mechanism[9-15]

$$\ldots -CH_2-CH_2-CH_2- \ldots + PCl_3 + {}^1/_2O_2 \rightarrow \ldots -CH_2CHCH_2- \ldots + HCl\,.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad POCl_2$$

The reaction is carried out at 60–80 °C, whereupon polyethylene forms a solution in phosphorus trichloride. The rate of phosphorylation is determined by the rate of dissolution of oxygen in the mixture. When air is used instead of oxygen, the above reaction proceeds at a lower rate. The derivatives obtained contain up to 16% of phosphorus. With increase of the degree of phosphorylation, the crystallinity of the product diminishes relative to the initial polyethylene[12]. Under analogous conditions, the $POCl_2$ functional groups have also been introduced into the polypropylene macromolecule[18-20]:

$$\ldots -CH_2-\underset{CH_3}{CH}-CH_2-\underset{CH_3}{CH}- \ldots + PCl_3 + {}^1/_2O_2 \rightarrow \ldots -CH_2-\overset{CH_3}{\underset{POCl_2}{C}}-CH_2-\underset{CH_3}{CH}- \ldots + HCl\,.$$

It has been suggested that the phosphonyl chloride groups are linked mainly to a tertiary carbon atom in the polymer chain. With increase of the degree of phosphorylation, the hardness and rigidity of the polymer decrease. The phosphorus content reaches 7% in the final product.

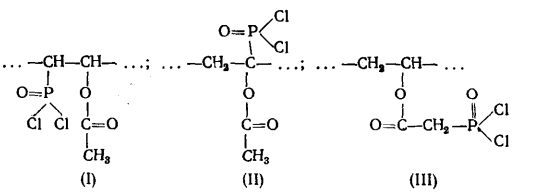
By treating the ethylene–propene copolymer with phosphorus trichloride and oxygen, Leonard et al.[21] and Weiss[22] obtained phosphorus-containing elastomers.

The heterogeneous oxidative chlorophosphorylation of polyethylene and ethylene–propene copolymers has also been investigated[23-29]. When thin films of polyethylene are treated with phosphorus trichloride vapour and oxygen, reactions of first order with respect to phosphorus trichloride and with 0.5 order with respect to oxygen take place. Phosphorylation takes place preferentially in the amorphous phase of the polymer.

Depending on the structure of the polyolefin chains, various reaction centres participate in the process. For branched polymers, such as high-pressure polyethylene and ethylene–propene copolymers, the main reaction centres are the hydrogen atoms at tertiary carbon atoms.

The phosphonyl chloride groups in polyolefins are highly reactive and undergo hydrolysis, alcoholysis and phenolysis and also interact with amines and metal salts. The hydrolysis of chlorophosphorylated polyolefins leads to the corresponding polymeric phosphonic acids[12].

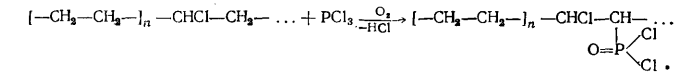
The oxidative chlorophosphorylation of poly(vinyl acetate), which resulted in the formation of copolymers containing units with different structures, has been investigated[30]:



(I) (II) (III)

It was suggested[30] that phosphorus enters mainly the polymer chain with formation of fragments (I) and (II).

It has been shown[31-33] that an analogous reaction takes place also when chlorinated polyolefins are used. For chlorinated polyethylene, this can be represented schematically in the following manner:



The phosphorus content in chlorinated polyethylene and atactic polypropylene increases with decrease of the chlorine content in the initial polymers and reaches 7.8 and 11.4% respectively.

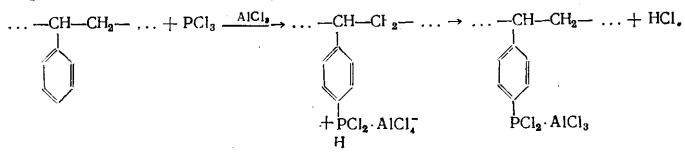
In a number of instances alkyl- and aryl-dichlorophosphines were used in the reaction instead of phosphorus trichloride[34-36]. This yielded polymers containing in the side chain groups characteristic of derivatives of dialkyl- or alkylaryl-phosphinic acids.

It is noteworthy that polyisobutylene, poly(methyl methacrylate), and polystyrene are degraded on phosphorylation, the final degradation product containing an insignificant amount of phosphorus[12]. A number of workers[37,38] believe that the oxidative phosphorylation can be classified as a process proceeding via a free-radical mechanism.

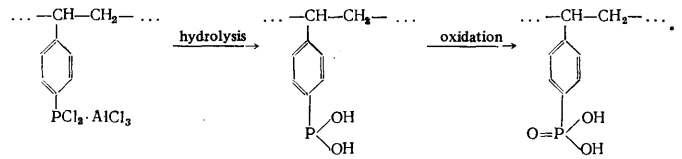
III. PHOSPHORYLATION VIA THE FRIEDEL–CRAFTS AND CLAY–KINNEAR–PERREN REACTIONS

A considerable proportion of the publications of the phosphorylation of carbochain polymers are associated with the employment of the Friedel–Crafts reaction. The phosphorylation of the copolymers of styrene with aromatic divinyl compounds has been studied in greatest detail[39-47]. Aluminium trichloride, titanium tetrachloride, tin tetrachloride, and zinc chloride have been recommended as catalysts. Aluminium trichloride has been used in most investigations, although it has been shown[48] that a more active catalyst, namely aluminium tribromide, would be more effective by increasing the degree of phosphorylation and reducing the reaction temperature.

The mechanism of the phosphorylation reaction can be represented schematically as follows:



The complex of the dichloride of polystyrylphosphonic acid with aluminium trichloride can subsequently hydrolyse and undergo consecutive oxidation reactions:

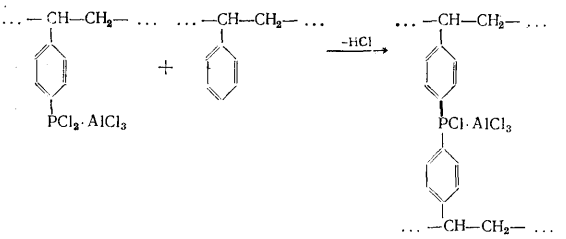


Nitric acid, SO_2Cl_2, and $SO_2–Cl_2$ and $Cl_2–P_2O_5$ mixtures, as well as other reagents are used as oxidants.

The interaction of cross-linked polystyrene with phosphorus trichloride followed by treatment of the resulting polystyrylphosphonic acid dichloride with a Grignard reagent led to the synthesis of monofunctional cation-exchange resins[50]. It has been stated that the substitution of two chlorine atoms in polystyrylphosphonic acid dichloride takes place stepwise as a result of steric hindrance. Under severe conditions, 85% of chlorine can be substituted to give the disubstituted derivative when ethylmagnesium bromide is used. Depending on the structure of the Grignard reagent, the degree of conversion decreases from 54 to 35% in the following sequence of substituents: $C_2H_5 > C_3H_7 > C_4H_9 > CH_3$.[51]

A detailed study of the influence of the reaction conditions on the degree of conversion of styrene–divinylbenzene copolymers[42] established that the latter depends on a series of parameters: the amount of aluminium trichloride and phosphorus trichloride, the reaction time, the degree of cross-linking of the copolymers, and their porosity.

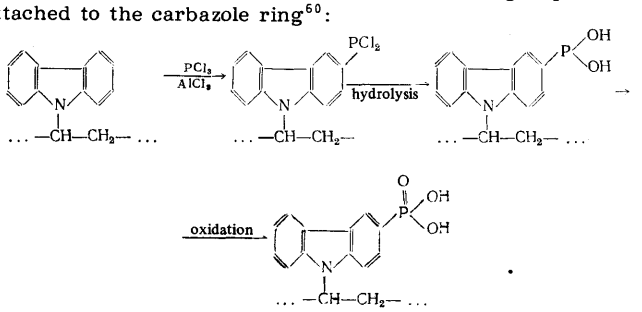
It has been noted that the macromolecules are cross-linked under the reaction conditions[49]:



The study of the kinetics of the phosphorylation of styrene–divinylbenzene copolymers established[45] that the principal rate-limiting stage is diffusion of the phosphorylating agent through the film of liquid adjoining the surface of the grain. The diffusion of the phosphorylating agent within the copolymer grains as well as its concentration in the swollen copolymer can also have a definite influence on the rate of phosphorylation. The conclusion that the phosphorylation process has an external diffusion mechanism is consistent with data[47] according to which the phosphorylation front migrates from the surface to the centre of the grain and the degree of phosphorylation depends on the depth to which the phosphorylating agent penetrates into the copolymers. With increase of the degree of cross-linking of the copolymers, the rate of reaction falls, but, for copolymers with a macroporous structure, obtained in the presence of an inert solvent, the rate of reaction increases sharply[52,53].

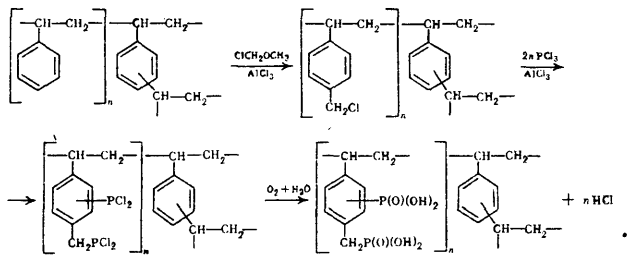
The phosphorylation of polystyrene grafted to polyethylene or polypropylene films has been achieved in a number of studies[54,55]. The phosphorylation was carried out at 40 to 65 °C by treatment with phosphorus trichloride in the presence of aluminium trichloride. On subsequent hydrolysis and oxidation with nitric acid, ion-exchange membranes with satisfactory electrochemical characteristics were obtained.

Modified copolymers with ion-exchange properties, a good mechanical strength, and an increased porosity and thermal stability have been obtained by the phosphorylation of macroporous ternary copolymers of styrene, divinylbenzene (1 to 20%), and acrylonitrile or ethyl, methyl, or butyl acrylate with phosphorus trichloride in the presence of aluminium trichloride[56-59]. The simultaneous treatment of poly-*N*-vinylcarbazole with phosphorus trichloride and aluminium trichloride yielded a product with the phosphonic acid group attached to the carbazole ring[60]:



The interaction was carried out in ethyl chloride with molar ratios polyvinylcarbazole : catalyst-phosphorylating agent of 1 : 2.5 : 10 in the temperature range 20–140 °C. Among phosphorylating agents, PCl_3 and PBr_3 proved to be the most effective and aluminium trichloride was the best catalyst. The degree of phosphorylation increased with temperature and reached a maximum (11.4% of phosphorus) at 76 °C (phosphorus trichloride) and 140 °C (phosphorus tribromide). The phosphorylated poly-*N*-vinylcarbazole has ion-exchange properties and does not dissolve in the usual organic solvents.

Polymers with phosphonic acid groups in the side chain have been obtained by treating chloromethylated vinyl derivative–aromatic compound copolymers with phosphorus trichloride in the presence of $AlCl_3$ in accordance with the scheme[61]



In this case substitution can take place via the Friedel–Crafts reaction in the benzene ring or via the Clay–Kinnear–Perren reaction in the chloromethyl group. Thus it has been suggested[62,63] that both reactions take place. Studies by Kinnear and Perren[64] showed that, when benzyl chloride interacts with PCl_3 and $AlCl_3$, phosphorylation takes place either in the chloromethyl group or in the aromatic ring, while simultaneous introduction of two phosphonic acid groups into the same benzene ring is unlikely.

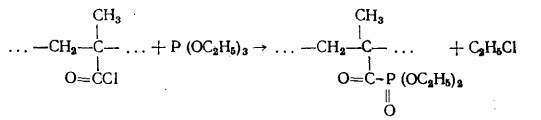
The phosphorylation of the chloromethylated styrene–divinylbenzene copolymer gives rise to lower degrees of conversion, compared with the phosphorylation of the non-chloromethylated copolymer, which can be explained by the greater ability for swelling of the latter in phosphorus trichloride[33].

Phosphonic acid cation-exchange resins can be obtained by the chloromethylation of condensed aromatic petroleum processing products followed by their phosphorylation with phosphorus trichloride in the presence of Friedel–Crafts catalysts and oxidation[65]. In terms of their activity, the catalysts can be arranged in the sequence $SnCl_4 > FeCl_3 > AlBr_3 > AlCl_3 > ZnCl_2$. The maximum degree of phosphorylation is attained when the ratio of the chloromethylated asphaltide to PCl_3 or $SnCl_4$ is 1 : 10, at a temperature of 35 to 60 °C, and for a process time ranging from 1 to 2 h. By virtue of their structure, which resembles that of graphite, they withstand more effectively the effects of small and large doses of γ-radiation compared with phosphonic acid cation-exchange resins based on styrene–divinylbenzene copolymers.

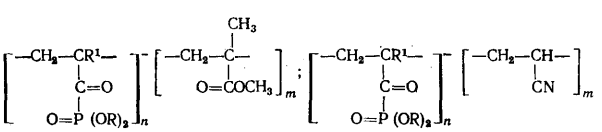
Nitrogen- and phosphorus-containing polymers with ion-exchange properties have been synthesised by polymer analogue reactions of the copolymers of styrene with divinyl compounds[66]. The initial and chloromethylated macronetwork copolymers of styrene and divinyl compounds were phosphorylated with phosphorus trichloride in the presence of $AlCl_3$. The divinyl compounds employed were ethylene-, hexamethylene-, and decamethylene-dimethacrylamides, dimethacrylate esters of di(hydroxyphenyl)sulphone and di(hydroxyphenyl)sulphoxide, and the dimethacrylamides derived from *m*-phenylenediamine, di(aminophenyl)ether, di(aminophenyl)methane, and di(aminophenyl)sulphide. In the synthesis of nitrogen- and phosphorus-containing amphoteric ion-exchange resins, the unsubstituted CH_2Cl groups in the partially phosphorylated chloromethylated copolymer were aminated with various isomers of pyridinedicarboxylic acids and their nitriles in dimethylformamide at 100 °C.[67] The presence of amide, ester, sulphoxide, sulphide, pyridinecarboxylic acid, and nitrile groups promoted an increase of the selectivity of the ion-exchange resins in relation to the sorbed ions.

IV. PHOSPHORYLATION OF CARBOCHAIN POLYMERS WITH THE AID OF THE ARBUZOV REARRANGEMENT

In one of the first studies of the Arbuzov rearrangement of macromolecular compounds, poly(vinyl chloroacetate), poly-α-chloroacrylate, poly(vinyl chloride), and the polymeric acrylic and methacrylic acid chlorides were used as the polymeric matrices[68]. The reaction was carried out in solution in dioxane at 100–150 °C using polymeric methacrylic acid chloride; it took place in accordance with the mechanism



When the chlorine atom is linked directly to a carbon atom of the main chain of the macromolecule, the degree of phosphorylation is insignificant. Best results were obtained in the reaction of triethyl phosphite with poly(vinyl chloroacetate). The resulting polymers were elastic and hygroscopic, did not support combustion, were resistant to acids, and exhibited an effective adhesion to glass. Polymers with analogous properties have been obtained by the reaction of triethyl phosphite with the copolymers of acryloyl or methacryloyl chloride and methyl methacrylate or acrylonitrile[69]:



Phosphorus-containing vinyl copolymers have been synthesised by the reaction of phosphonate esters with halogenomethyl groups in the copolymer and subsequent hydrolysis of the ester groups. The product had ion-exchange properties[70]. A cation-exchange resin has also been obtained by treating halogenomethylated copolymers of mono- and polyfunctional compounds with triethyl or trimethyl phosphite[71].

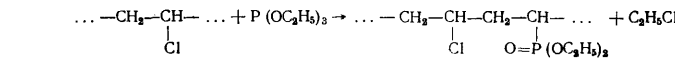
In order to improve the stability and non-combustibility of vinyl chloride polymers and copolymers, it has been suggested that they be treated with trialkyl phosphites[72,73]. The introduction of phosphonoethyl groups into the side chain of the copolymer of vinyl chloride with acrylonitrile is accompanied by an increase of its thermal stability and resistance to acids and organic solvents with retention of its non-combustibility.

Phosphorus-containing polymers with improved technological properties and strength parameters have been obtained by the reaction of trimethyl phosphite with chlorosulphonated polyethylene[74].

Several studies have been devoted to the reaction of poly(vinyl chloride) with mixed alkyl(aryl)phosphites[75–77]. According to the authors of these investigations, the reaction is accompanied by the Arbuzov rearrangement, which entails the appearance of phosphorylated units in the initial polymer. In the course of modification at 200 °C, the dehydrochlorination of the polymer with formation of polyconjugated double bonds was observed together with the main

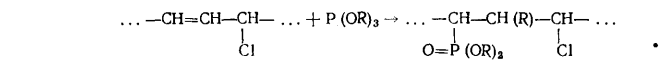
reaction. The specimens acquire a colour as a consequence of such modification.

The interaction of triethyl phosphite with poly(vinyl chloride) at 80–200 °C via the mechanism

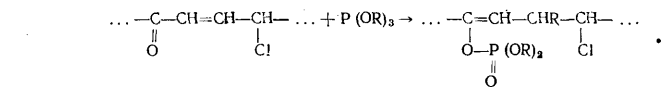


has been investigated[77]. The reaction was followed from the change in the chlorine and phosphorus contents in the final product. The polymers were amorphous powders soluble in organic solvents. At reaction temperatures up to 180 °C, there is no degradation of the polymer but on further increase of temperature a three-dimensional structure is formed.

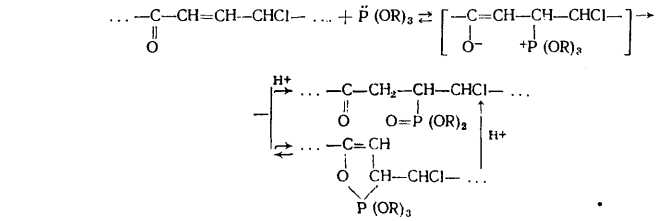
A detailed study of the mechanism of the interaction of poly(vinyl chloride) with trialkyl phosphites showed[79] that the hypothesis that phosphorus-containing compounds add to the double bond in poly(vinyl chloride) [78] is incorrect:



Thus the interaction of tributyl phosphite with 4-chloropent-2-ene does not entail the reaction with inner β-chloroallyl groups. The main process is the dehydrochlorination of 4-chloropent-2-ene. If the hydrogen chloride evolved in this process is not bound, tributyl phosphite is dealkylated with formation of dibutylphosphorus acid[79]. Data on the ozonolysis of poly(vinyl chloride) subjected to a preliminary treatment with a phosphorus-containing compound[81] indicate the absence of unsaturated C=C bonds in the main polymer chain and therefore cast doubt on the probability of the reaction of trialkyl phosphites with the carbonyl–allyl groups of macromolecules via the Perkow mechanism to form unsaturated phosphites[80]:



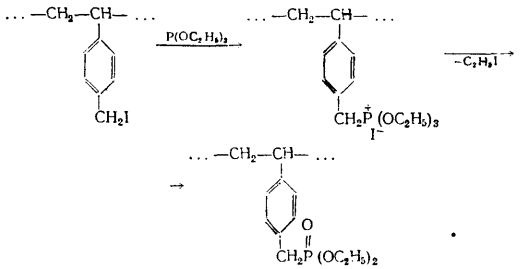
This effect may be attributed to the nucleophilic addition reaction in the presence of proton donors under the conditions of the stabilisation of poly(vinyl chloride) by organic phosphites involving attack by the latter on the β-carbon atom of the conjugated system of the carbonylallyl group followed by the protonation of the dipolar ion and the formation of a stable ketophosphonate[81]. Thus the reaction of organic phosphites with poly(vinyl chloride) under comparatively mild conditions leads to the quantitative opening of the inner unsaturated C=C bonds present in the polymer macromolecules with formation of single C–C bonds, which is due to the interaction of organic phosphites with the carbonylallyl groups of the polymer via the mechanism[82]



The occurrence of this interaction has been confirmed by the method of the competing reactions of trialkyl, alkyl, and aryl phosphites with a 1:1 mixture of methyl vinyl ketone (a model of the carbonylallyl group) and 4-chloropent-2-ene (a model of the β-chloroallyl group). Organic phosphites react selectively with methyl vinyl ketone, while 4-chloropent-2-ene is recovered unchanged from the reaction (apart from its dehydrochlorination products).[79]

Chloromethylated polystyrene and its copolymer with vinylidene chloride as well as poly(2,6-dimethyl-1,4-phenylene oxide), containing bromine in the side chain or in the benzene ring, are phosphorylated by triethyl phosphite (on refluxing in the presence of diethylmethanol) with formation of non-cross-linked polymers having phosphonate side groups[83]. The polyphosphonates are hygroscopic; the adsorbed water, whose amount increases with increase of the phosphorus content, influences the glass points of the polymers. The polyphosphonates can be combined with a large number of polymeric systems and may form "true" polymer alloys with acetylcellulose.

Iodomethylated derivatives of polystyrene are more readily phosphorylated by organic phosphites[84,85]:



At a temperature above 70 °C, the Arbuzov rearrangement with participation of macromolecules is accompanied by the isomerisation of triethyl phosphite under the influence of the ethyl iodide evolved in the reaction. It has been shown[84] that the rate constants for the Arbuzov rearrangement of triethyl phosphite in the presence of iodomethylated polystyrene decrease in the course of the reaction and that the apparent activation energy has different values at high and low temperatures.

Products containing phosphonate groups in the side chain have been obtained by treating hydroxystyrene polymers with a phosphinate ester[86].

Dialkoxyphosphonomethylpolystyrenes have been obtained by the reaction of chloromethylpolystyrene with mixed alkyl phosphites having the general formula $(RO)_2POR^1$ (where $R = C_{3-7}$ alkyl and R^1 = methyl or ethyl) at 20–30 °C for 5–24 h and then at 170–190 °C for 10–20 h.[87]

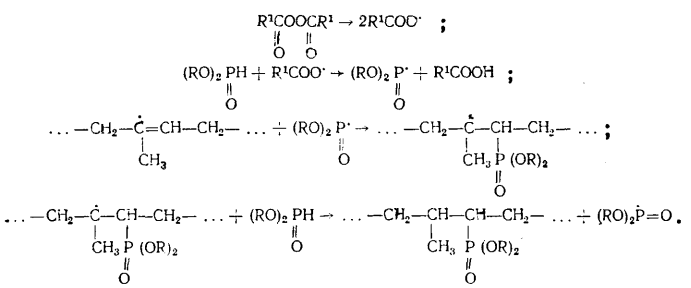
Insoluble polymers containing polyalkylphosphonium groups in the side chain have been obtained by the reaction of PR_3 with diene, olefin, and alkylhalogeno-olefin polymers[88].

V. ADDITION OF PHOSPHORUS-CONTAINING COMPOUNDS WITH A MOBILE HYDROGEN ATOM TO UNSATURATED BONDS IN MACROMOLECULES

The addition of partially esterified phosphorus acids, initially investigated in relation to individual unsaturated compounds[89], was subsequently studied also in relation to polymers. The reaction was achieved for natural rubber by treatment of the latter with dialkyl phosphites[90] and somewhat later also for isoprene rubber[91]:

Investigation showed that, when various dialkyl phosphites are allowed to interact with natural rubber in the presence of benzoyl peroxide, it is possible to introduce up to 9–10% of phosphorus into the rubber, which corresponds to the addition of dialkyl phosphites to 60% of all the double bonds in the rubber. The vulcanised specimens obtained have reduced combustibility. With increase of the length of the

alkyl group in dialkylphosphorous acids, the content of the bound phosphorus in the polymer falls. A possible mechanism of such addition of dialkyl phosphites can be represented by the following scheme:

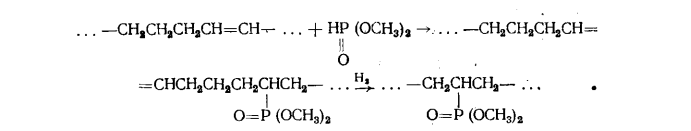


The polymers obtained do not dissolve in organic solvents and merely swell in them, which is apparently associated with the cross-linking resulting from the recombination of macroradicals.

The possibility of the addition of dialkyl phosphites to a dehydrochlorinated vinyl chloride–acrylonitrile copolymer has been demonstrated[92]. However, the phosphorus content in the final product was small (1.6 wt.%).

A method has been proposed for the synthesis of a phosphorus-containing polyallene by treating polyallene with dialkyl phosphites in the presence of organic peroxides as a result of irradiation with γ-rays at 20–140 °C.[93] The interaction of diorganophosphites with the product of the esterification of poly(vinyl alcohol) with the chloride of cinnamic acid has been investigated[94] and the influence of the nature of the initiator on the structure of the polymers obtained has been demonstrated. Structure formation was observed for peroxy-compounds, while in the presence of azobisisobutyronitrile the formation of a three-dimensional network was not observed. An increase of temperature to 120 °C increases the degree of phosphorylation but the final product ceases to be soluble. The introduction of phosphono-groups plasticises the initial polymer, reduces the softening temperature by 40–65 °C, increases the intrinsic viscosity, and imparts self-extinguishing properties to the polymer.

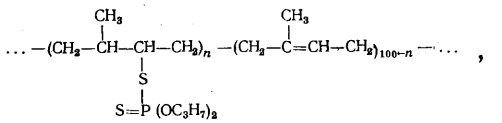
Phosphorylated derivatives of polycyclopentene containing 5–10 mole % of dimethylphosphonate groups have been obtained by the addition (initiated by peroxy-compounds) of dimethyl phosphite to the double bonds of polycyclopentene containing 82% of *trans*-double bonds, 17% of *cis*-double bonds, and 1% of vinyl side groups at 85–90 °C in solution in toluene with subsequent hydrogenation of the residual unsaturated bonds by toluene-*p*-sulphohydrazide at 145 °C:[95]



Dehydrated poly(vinyl alcohol) fibre containing 32–90% of double bonds is phosphorylated by dialkyl phosphites via the addition of the latter to the double bonds[96].

Phosphorylated raw rubbers for technical rubber articles have been obtained by the interaction of unsaturated raw rubbers in the form of aqueous latexes, stabilised by hydroxyethylated alkylphenols or higher alcohols, with dialkyl phosphites at 80–90 °C in the presence of radical initiators[97].

The reaction of *cis*-1,4-polyisopropene with di-isopropylphosphorodithioic acid in the presence of a catalyst led to the synthesis of a phosphorus-containing polymer having the structure[98]

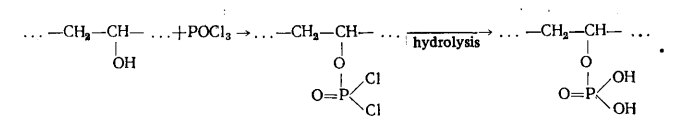


where n = 5–63. The polymer contains 0.7–6.9 wt.% of phosphorus and 0.9–16.6 wt.% of sulphur. The addition of certain other esters of dialkylphosphorodithioic acids to unsaturated elastomers has been carried out under analogous conditions[99,100]. The reaction takes place readily in the presence of benzoyl peroxide or isopropylphenyl hydroperoxide. The products contain 0.3–8 wt.% of phosphorus and 0.5–20% of sulphur and are readily soluble in organic solvents.

Phosphorus acids have been used in some investigations[101–104] as phosphorylating agents for carbochain polymers. Thus a phosphorus-containing polyallene has been obtained by treating polyallene with hypophosphorous acid in the presence of radical initiators in an inert gas atmosphere[103]. The final product contains 11 wt.% of phosphorus and is of interest for the formation of fire-resistant polymeric materials. Hypophosphorus acid proved to be the best phosphorylating agent in the hydrophosphorylation of polymers containing allyl groups in the side chain[101]. Polymers containing from 4 to 11% of phosphorus and having self-extinguishing properties have been obtained by this reaction.

VI. OTHER METHODS

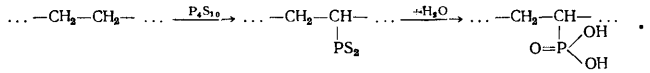
Phosphoryl chloride is an effective phosphorylating agent for hydroxyl-containing polymers. Phosphorylated derivatives of poly(vinyl alcohol) have been obtained by reaction with $POCl_3$.[105–107] After phosphorylation, the polymer loses its solubility in water and the phosphorus content in the final product reaches 14.7%. The potentiometric titration curve for the hydrolysed product has the form characteristic of dibasic acids. The reaction proceeds via the mechanism



The degree of conversion of the poly(vinyl alcohol) units in the phosphorylation reaction reaches 30–35%, which corresponds to one phosphoric acid group for each three hydroxy-groups in the polymer.

A series of ion-exchange materials have been synthesised by treating with phosphoryl chloride the fibres, fabrics, and films obtained from poly(vinyl alcohol).[108–110] It has been shown that an analogous reaction can also be achieved for other hydroxyl-containing polymers, for example, polyhydroxystyrene[111] and polydimethylethynylmethanol[112]. Phosphorus-containing poly(vinyl alcohol) has also been obtained by the reaction of poly(vinyl alcohol) with phosphoric acid in the presence of *N*-methylpyrrolidinone[113]. The phosphorylation of macromolecular compounds with phosphorus sulphide has been investigated in relation to polyethylene, polypropylene, polystyrene, polyacrylonitrile, and synthetic rubbers.

Polyethylene is phosphorylated in solution in chlorobenzene at temperatures in excess of 100 °C under a normal or excess pressure. The main reaction and subsequent hydrolysis of the PS_2 groups proceed via the mechanism[114]

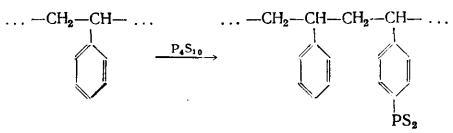


Depending on the reaction conditions and the reactant ratio, the phosphorus content in the product can vary from 3 to 10%.

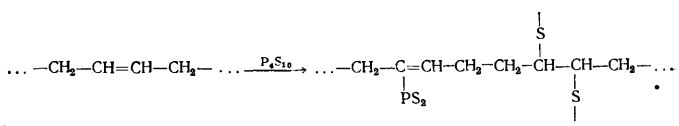
Polypropylene has been phosphorylated at normal and enhanced pressures and temperatures from 132° to 200 °C in an autoclave. The phosphorus content in the product did not exceed 1%. The low reactivity of polypropylene has been explained by the shielding of the tertiary carbon atoms by methylene groups[114]. The phosphorylated polypropylene contains up to 1% of sulphur, which corresponds to one sulphur atom for 75 elementary units of the polymer.

In the phosphorylation of polyacrylonitrile with phosphorus sulphide, it was possible to introduce only 0.5% of phosphorus into the polymer. As for polypropylene, despite the enhanced reactivity of the tertiary carbon atom, access to the latter is sterically hindered. Phosphorylation under more severe conditions makes it possible to increase the phosphorus content to 7.3%. When an attempt was made to hydrolyse the PS_2 groups in the phosphorylated polyacrylonitrile, the hydrolysis of the nitrile groups to carboxy-groups was noted at the same time.

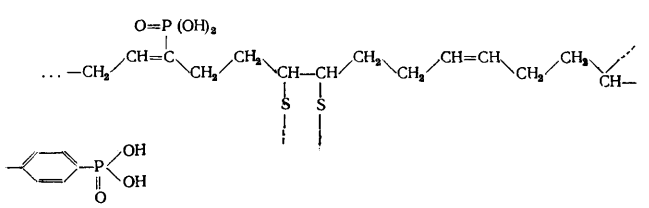
A study has also been made of the phosphorylation of polystyrene. This resulted in products in which a phosphorus atom is present in each second, fourth, or tenth elementary unit of the polymer depending on the conditions. The PS_2 groups enter preferentially into the *para*-position in the benzene ring[10]:



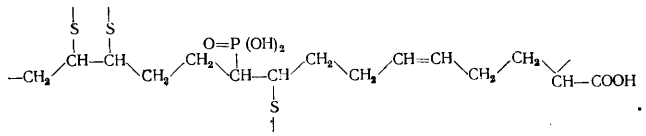
The phosphorylation of various raw rubbers has also been studied[115]. The phosphorylation of butadiene rubber proceeds via the mechanism



When the SKS-30 rubber was phosphorylated in solution in chlorobenzene at 132 °C, it was shown by infrared spectroscopy that the reaction involves both the carbon atoms of the main macromolecular chain and the phenyl substituent. The final product contains 11.5% of phosphorus and 22.7% of sulphur and has the structure



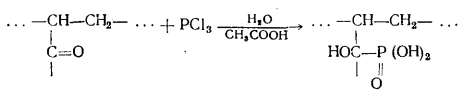
The phosphorylation of butadiene-nitrile rubbers proceeds with greater difficulty than that of butadiene–styrene rubbers. After hydrolysis, the products have the structure



All the phosphorus-containing polymers obtained are plastics insoluble in water, acids, alkali, and organic solvents. They melt at 200–300 °C and have ion-exchange properties.

A method of synthesis of polyphosphonothioic acid with a high molecular weight by the reaction of polyisobutylene with phosphorus pentasulphide in the presence of sulphur and followed by hydrolysis of the reaction product has been proposed[116]. Phosphorus-, sulphur-, and halogen-containing polymers, distinguished by an enhanced resistance to acids, have been synthesised by the reaction of polymers of aliphatic hydrocarbons (or their copolymers with vinyl acetate or vinyl chloride) with phosphorus trihalides and sulphur at temperatures exceeding 140 °C.[117]

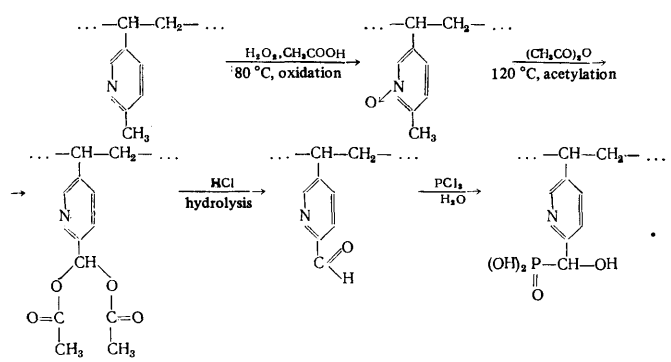
The reactions of carbonyl-containing polymers with phosphorus trichloride yielded polymers containing α-hydroxyphosphonic acid groups[118]:



The substrates can be both aliphatic polymers [for example, poly(methyl vinyl ketone)] and aromatic polymers (for example, acylated polystyrene).[119,120] The reaction also proceeds when an acylated styrene–divinylbenzene copolymer is used[121]. Treatment with phosphorus trichloride of a grafted *cis*-butadiene rubber–acrolein copolymer results in the formation of a structured product containing 0.5–0.7% of phosphorus and exhibiting an enhanced fire resistance[122]. The interaction of low-molecular-weight polybutadiene containing the OH and COOH groups with PCl_5 results in the phosphorylation of the polymer not only in the functional groups but also in the double bonds[123].

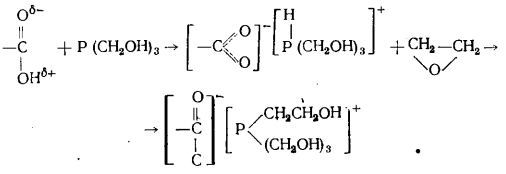
Phosphorus-containing polymers with ion-exchange properties have been obtained in the phosphorylation of polyacrolein[124] and acrolein-divinylbenzene copolymers by treatment with phosphorus trichloride[125].

Consecutive transformations of the copolymers of 2-methyl-5-divinylpyridine with divinylbenzene and di-isopropenylbenzene led to the synthesis of new phosphorus-containing pyridine polymers with ion-exchange properties[126]:

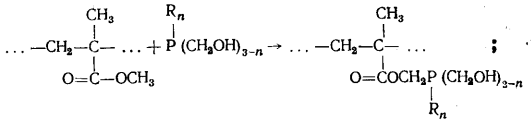


The products contain 8–9% of phosphorus and 5–6% of nitrogen and exhibit the maximum selectivity in relation to indium and uranyl ions.

The possibility of synthesising phosphorus-containing polymers by treating polyacrylic and polymethacrylic acid and also of copolymers containing carboxy-groups with tri(hydroxymethyl)phosphine (in the presence of epoxyethane) has been demonstrated[127]. The phosphorylation of polyacrylic and polymethacrylic acids was carried out using water as the solvent. The phosphorylation of carboxylate rubbers and methacrylic acid–styrene copolymers was performed in benzene or toluene. In the case of polymethacrylic acid in the presence of a threefold excess of phosphine, the degree of phosphorylation of the functional groups reaches 91%. For polyacrylic acid, the degree of phosphorylation is 59.8%. The properties of the products vary as a function of the amount of phosphorus introduced. Whereas the phosphorylated polyacrylic acid is a powdered product, polymethacrylic acid can be rubber-like after phosphorylation. The following reaction mechanism has been proposed:



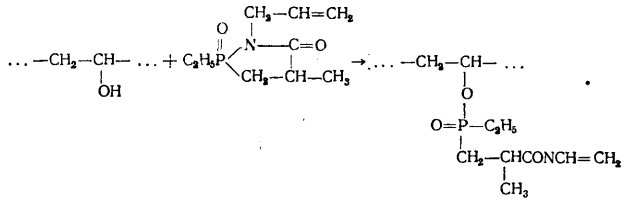
An attempt has been made to carry out the transesterification of poly(methyl methacrylate) by treating it with various phosphine derivatives[128]:



$R = CH_3$; C_3H_7; $C_6H_5CH_2$; $n = 0-2$

However, it was not possible to introduce phosphorus into the polymer, which the authors believe[128] can be explained by the influence of the substituent at the α-carbon atom, which hinders the transesterification.

Azophospholan has been used as the phosphorylating agent for polyhydroxy-compounds[129,130]. The interaction of azophospholan with poly(vinyl alcohol) proceeds analogously to its interaction with low-molecular-weight alcohols:

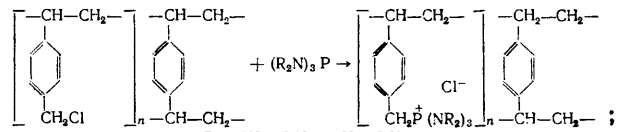


Up to 6.1% of phosphorus is introduced into the final product.

Phosphorus-containing derivatives of polyhydroxy-compounds have also been obtained using the anhydride of 4-hydroxy-4-oxo-4-phosphocaproic acid[131], 1-chloro-3-methyl-1-oxo-phosphocyclopentane[132], and acetyl phosphites[133] as phosphorylating agents.

Diethylphosphonoacetals of poly(vinyl alcohol) have been obtained by the reaction of diethylphosphonoacetaldehyde with partially acylated poly(vinyl alcohol).[134] The products synthesised are soluble in water and contain up to 8% of phosphorus.

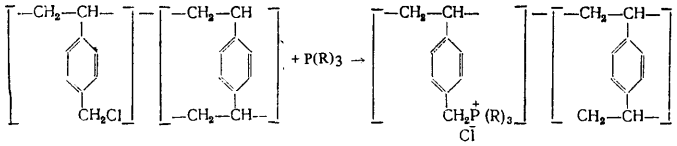
The reaction of the chloromethylated styrene–divinylbenzene copolymer with phosphorous acid amides yielded[135] the corresponding high-molecular-weight polymeric quasi-phosphonium salts:



$R = CH_3$; C_2H_5; C_3H_7; C_4H_9.

In order to increase the degree of phosphorylation, the reaction is carried out without a solvent in the presence of an excess of phosphorous acid amides in an argon atmosphere. The degree of phosphorylation is influenced not only by the reaction conditions but also by the structure of the groups in the amides, the degree of phosphorylation decreasing with increase of the bulk of such groups. It has been established that the maximum degree of phosphorylation is attained when the reaction is carried out at 120 °C for 10 h. The quasi-phosphonium salts are stable substances which do not change on refluxing ror 15 h in solution in aqueous dioxane in the presence of 0.1 *N* sodium hydroxide and in concentrated hydrochloride acid.

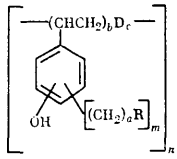
Phosphorus-containing polymers having the structure



$R = C_3H_7$; C_6H_5; CH_3OH

have been obtained by phosphorylating chloromethylated styrene–divinylbenzene or styrene–divinyl copolymers by various phosphines (in the presence of anhydrous aluminium trichloride as the catalyst or in its absence).[136,137]. Polymeric quaternary phosphonium salts containing more than 80% of phosphorus have been synthesised by the reaction of triethyl phosphite with chloromethylated styrene copolymers at 100–140 °C.[138]

Hydroxystyrene polymers, which incorporate phosphonium groups of the type



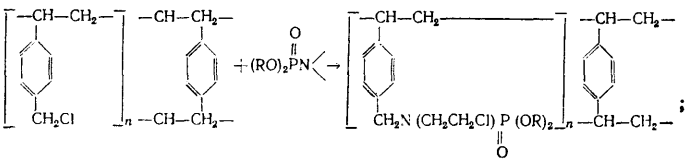
where $a = 0$ or 1, $m = 0-2$, $n > 3$, b is an integer, $c = 0$ or is an integer, D is a copolymer unit, $R = \overset{+}{P}(OR^1)_p \cdot (R^2)_{3-p}X^-$, $p = 1$, 2, or 3, $R^1 = C_{1-20}$ alkyl, $R^2 = H$ or C_{1-20} alkyl, and X = Cl, Br, or I, are formed when halogenated polyhydroxystyrene interacts with the triester $P(OR^1)_pR^2_{3-p}$.[139]

A method for the preparation, by an analogous reaction, of homogeneous ion-exchange membranes by phosphorylating with triphenylphosphine a chloromethylated polystyrene grafted to vinylidene fluoride–chlorotrifluoroethylene copolymer films has been described[140]. The membranes have a high exchange capacity and are incombustible.

According to Gorbunov et al.[141], phosphorus-containing polymers are formed when tri(hydroxymethyl)phosphines interact with the homopolymers and copolymers of unsaturated acid fluorides. The final products contain up to 12% of phosphorus and exhibit an enhanced fire resistance.

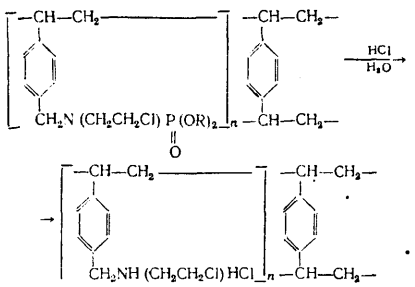
Water-soluble resins have been obtained as products of the reactions of a styrene–halogenomethylstyrene copolymer with a trisubstituted phosphine at 60 °C for 6 h.[142]

The interaction of the ethyleneamides of dialkylphosphoric acid with a chloromethylated styrene–divinylbenzene copolymer is accompanied by the cleavage of the ethyleneimine ring with formation of *N*-iminoethylation products[135]:

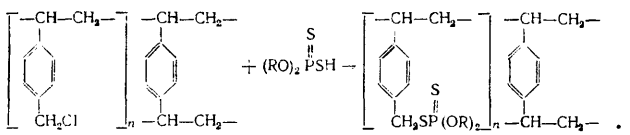


$R = CH_3;\ C_2H_5;\ C_3H_7$.

The *N*-phosphonaminoethylation products are unstable in an acid medium and are readily cleaved at the N–P bond with formation of dialkylphosphoric acid and the copolymer of the hydrochloride of (β-chloroethyl)vinylbenzylamine and divinylbenzene:

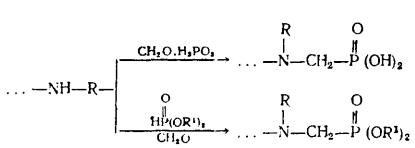


When a chloromethylated styrene–divinylbenzene copolymer is heated at 150 °C with *O,O*-dialkyl esters of phosphorodithioic acid in the absence of a hydrogen chloride acceptor or in its presence, copolymers of *O,O*-dialkyl *S*-(*p*-vinylbenzyl) esters of phosphorothioic acid and *p*-divinylbenzene are formed[143]:



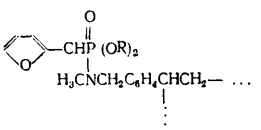
The degree of phosphorylation of the chloromethylated styrene–divinylbenzene copolymer depends on the size of the alkyl group in the *O,O*-dialkyl phosphorodithioic acid molecule and reaches 99.2%. With increase of the bulk of the hydrocarbon group, the degree of phosphorylation falls. The final product contains 3.9–9.6% of phosphorus and 8.7–19.7% of sulphur. The copolymers of *O,O*-dialkyl *S*-(*p*-vinylbenzyl) esters of phosphorothioic acid and *p*-divinylbenzene readily alkylate aliphatic and aromatic amines with formation of the salts of the corresponding tertiary amines and the copolymers of *O*-alkyl *S*-(*p*-vinylbenzyl) esters of phosphorothioic acids.

Primary and secondary amino-groups, introduced into the structure of the macroporous methacrylate–divinylbenzene copolymer by aminolysis with ethylenediamine and hexamethylenediamine condense with formaldehyde and phosphorous acid or its alkyl esters[144]:

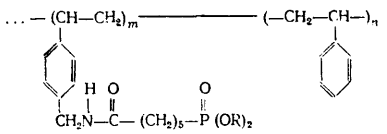


The phosphorylation of the aminated styrene–divinylbenzene copolymer proceeds via an analogous mechanism[145–147].

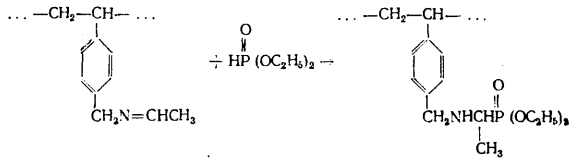
An anion-exchange resin, the elimination of the ester residue of which gives rise to an ampholyte with the *N*-methylamino-2-furylmethylphosphonic acid groups, has been synthesised by the amination of the chloromethylated polystyrene skeleton with the diethyl ester of *N*-methyl-α-amino-2-furylmethylphosphonic acid[148]:



A self-extinguishing polymer has been obtained by introducing a phosphorus-containing group into the *para*-position in the polystyrene molecule as a result of treatment of the polymer with 2-diethylphosphono-*N*-hydroxymethylacetamide, 2-dipropylphosphono-*N*-hydroxymethylacetamide, etc. in the presence of Friedel–Crafts catalysts[149]:



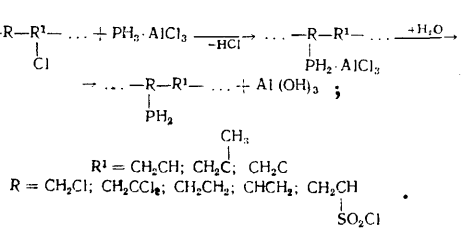
A polymeric complexone containing 8–9% of phosphorus and 5–7% of nitrogen has been synthesised by the condensation of dialkyl phosphites with the products of the interaction of aminomethylpolystyrene and acetaldehyde[150]:



Polymers containing phosphino-groups have been synthesised by the reaction of halogen-containing polymers [chloromethylated polystyrene, brominated polybutadiene, poly(vinyl chloride), and poly-*p*-bromostyrene] with metal phosphides in an inert solvent at temperatures from 40° to 200 °C.[151]

A self-extinguishing polystyrene containing the CH_2CH. $.[C_6H_4–CH_2P(O)(OR)_2]$ units, where R = alkyl or C_{1-8} cyclic alkyl, have been obtained by the interaction of alkali metal dialkyl phosphites with a partially chloromethylated polystyrene[152]. The reaction takes place at 40–90 °C for 6–8 h and the final product contains 5–10% of phosphorus.

The copolymer of chloromethylated polystyrene and divinylbenzene interacts with (β-diphenylphosphinoethyl)phenylphosphine treated with potassium in tetrahydrofuran, giving rise to three-dimensional products with diphosphine side groups[153]. Carbochain polymeric phosphines have been synthesised by phosphorylating halogen-containing carbochain polymers with a complex of phosphine and aluminium trichloride[154]:



The interaction is accompanied by a side reaction involving the elimination of hydrogen chloride and the consequent formation of polyene structures in the main macromolecular

chains. The degree of phosphorylation is greatly influenced by the temperature, the nature of the initial halogen-containing carbochain polymer and the Lewis acid. Depending on the reaction conditions, up to 18% of phosphorus is introduced into the treated polymers.

A mixture of red phosphorus and iodine can be used as the phosphorylating agent for chloromethylated styrene–divinylbenzene copolymers[155].

VII. APPLICATIONS OF PHOSPHORYLATED CARBOCHAIN POLYMERS

As mentioned above, phosphorylated carbochain polymers have found a wide variety of applications. Thus, phosphorylated styrene–divinylbenzene polymers containing phosphoric acid groups and exhibiting ion-exchange properties are widely used in the sorption of transition metal ions from solutions of alkali metal and ammonium orthophosphates, from chloride solutions with a complex salt composition, and from phosphoric acid[156–159]. Polyampholytes containing both nitrogen and phosphorus are capable of sorbing tellurium[160], beryllium[161], and nickel[162] ions from electrolyte solutions constituting the waste from the metal treatment industry and its waste water. Nitrogen- and phosphorus-containing amphoteric ion-exchange resins with aminomethylphosphonic acid groups can be used for the joint sorption of copper and zinc from sulphuric acid solutions[163], while polymers with hydroxyethylidenephosphinic acid have been recommended for the elimination of iron from phosphoric acid and electrolytes[164].

Ampholytes based on network copolymers of 2-methyl-5-vinylpyridine, combining in a single elementary unit of the network matrix both the pyridine and α-aminomethylphosphono-groups, are selective in relation to copper in the presence of cobalt, nickel, and iron[165]. Phosphorus-containing polymers with hydroxyaminoalkylphosphono- and ethylenediaminephosphono-groups sorb uranium from carbonate-containing solutions[166]. Carbochain polymers with difluoroalkyl phosphate groups in the side chain also exhibit complex-forming properties[167].

Phosphorylated copolymers of styrene with vinylphenols or the glycidyl ethers of vinyl phenols have been used as phosphorus-containing polymeric catalyst carriers, which are characterised by a pronounced ability to swell in hydrocarbon solvents and an enhanced stability[168]. Polymeric ligands for metal complex catalysts have been obtained by treating phosphorylated polymers containing aromatic rings with organometallic compounds[169]. Pyridinephosphineiridium complexes fixed on macroporous polystyrene–divinylbenzene polymers with phosphine groups have shown a high activity in the hydrogenation of olefins[170] and the hydridocarbonyltris(triphenylphosphine)rhodium complex on a styrene–divinylbenzene copolymer is an effective catalyst of the hydroformylation of propene[171].

Phosphorylated carbochain polymers have been used as stabilisers of the ageing of high-molecular-weight compounds. It has been shown for polyethylene that they are effective inhibitors of thermo-oxidative degradation[172] and can be used as anti-ageing agents for cured rubbers based on synthetic raw rubbers[173–175].

The products of the interaction of tri(hydroxymethyl)phosphine with carboxyl-containing chloroprene and nitrile elastomers have been used as adhesives for the attachment of various types of rubbers to metals[176], while cured rubbers based on phosphorylated carboxylate raw rubbers exhibit an enhanced resistance to benzene[177]. Phosphorus-containing ethylene–propene rubber increases the thermal stability and improves the working properties of lubricating oils[178]. The product of the interaction of low-molecular-weight polypiperylene with di-isopropylphosphorodithioic acid has been used as a polyfunctional additive to lubricating oils with effective antioxidant, antiwear, and antidrag properties[179]. Phosphorus-containing oligoisobutylene exhibits analogous properties[180].

The polyphosphonates obtained by phosphorylating polystyrene, poly(2,6-dimethyl-1,4-phenylene oxide), or the styrene–vinylidene chloride copolymer has been used to prepare semipermeable membranes capable of sorbing selectively individual organic liquids from their mixtures with other liquids[181].

The product of the interaction of the acrylic copolymer with phosphorus pentoxide has been used as a reactive organic phosphate catalyst for thermoreactive varnish coatings[182]. Phosphorus-containing polystyrene combined with carbon tetrachloride has been used in peptide synthesis[183]. Certain phosphorylated carbochain polymers exhibit bactericidal properties[184]. They have been used as polymerisation initiators[185], for the prevention of the formation of scale, and also as flocculants[186].

Thus the study of the phosphorylation of synthetic carbochain polymers is undoubtedly of both theoretical and applied importance and the search for new phosphorylating agents and the expansion of the assortment of polymers used in this process will create even greater possibilities for the practical utilisation of such products.

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