Synthesis and thermal transformations of polyphosphosiloxane based on trimethyl phosphate and (3-aminopropyl)triethoxysilane

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A method for the synthesis of polyphosphosiloxane by the thermal condensation of an equimolar mixture of trimethyl phosphate and (3-aminopropyl)triethoxysilane at 200 °C was developed. The reaction affords ethanol and polyphosphosiloxane $-\{Si(OEt)[(CH_2)_3NR^1R^2]-O-P(O)(OMe)-O\}_n-$ (R^1 = H, Me; R^2 = Me), whose composition and structure were confirmed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, IR spectroscopy, and elemental analysis. The scheme of polymerization involving the intermediate formation of methyl- and dimethylphosphoric acids and their condensation with ethoxysilanes was proposed. The calcination of the obtained polyphosphosiloxane *in vacuo* at 350 °C results in the elimination of the amino groups and alkoxide substituents, and a spatially cross-linked polymer is formed as an amorphous powder. Its further thermolysis at 600 and 1000 °C gives crystalline phosphosilicates $Si_5O(PO_4)_6$ or SiP_2O_7. Their amorphous and crystalline samples were characterized by IR spectroscopy, X-ray diffraction analysis, and solid-state ^{13}C and ^{31}P spectroscopy.

Key words: trimethyl phosphate, (3-aminopropyl)triethoxysilane, condensation, polyphosphosiloxane, phosphosilicates, thermal transformations, amorphous and crystalline phases, organosilicon compounds.

Amorphous and crystalline phosphosilicates possess unique physicochemical properties and structural characteristics and are used in various applied areas. The acidic catalysts based on silicon phosphates are used in olefin hydrogenation and oligomerization.[1,2] Phosphosilicate glasses subjected to the corresponding treatment are interesting for the preparation of biologically active materials[3,4] and ionic semiconductors used for the creation of fuel cells and chemical sensors.[5—9] Crystalline phosphosilicates and glasses of various composition are interesting from the viewpoint of studying specific features of the coordination environment of the silicon and phosphorus atoms.[10—12]

Two widely used methods were developed for the synthesis of phosphosilicates. One of them is co-fusion of solid reactants, being, as a rule, SiO_2 and P_2O_5 or orthophosphoric acid.[13,14] This method requires high temperatures, which can decrease the phosphorus content in the product due to the volatility of P_2O_5. The obtained samples are characterized by a small surface area. Another method is based on the sol—gel process.[15] For instance, the phosphosilicate glasses of various composition were prepared using $Si(OMe)_4$ or $Si(OEt)_4$ are the source of silicon, H_3PO_4 or $POCl_3$ was the phosphorus source, and the silicon-containing component was pre-hydrolyzed.[5—7,11,12,16,17] These materials possess high specific surface and high porosity. A substantial shortcoming of the method is a strong dependence of the synthesis conditions (for example, pH of the solution, nature of the starting reactants, their stoichiometric ratios and concentrations in the mixture, temperature of gel formation) on the properties of the final product.

Various mono-, oligo, and polymeric silyl esters of phosphorus acids are prepared by the interaction of organochlorosilanes with phosphorus acids and their esters and salts and by the reactions of alkoxy-, acyloxy-, and hydroxysilanes with phosphorus acids, their chlorides, and

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phosphorus pentaoxide. The reactions of aminosilanes and hexaalkyldisilazanes with phosphoric acid also afford silyl esters.[18,19] In all listed reactions, the phosphorus-containing component bears the acid moiety, whereas the reactant containing silicon is generally neutral. The direct interaction of full esters $Si(OR)_4$ and organoalkoxysilanes $R'_nSi(OR)_{4-n}$ with trialkylphosphates $(RO)_3P{=}O$ is not used in the synthesis of compounds with the Si—O—P bonds. The hydrolytic condensation of $Si(OMe)_4$ or $Si(OEt)_4$ with phosphoric acid esters is impeded because of a great difference in the hydrolysis rates. The alkoxy derivatives of silicon rapidly react with water, while phosphates are hydrolyzed too slowly to be used in the sol—gel process.[20]

The purpose of the present investigation is to develop a non-hydrolytic method for the synthesis of polyphosphosiloxane from trimethyl phosphate (TMP) and (3-aminopropyl)triethoxysilane (APTES) and to study its thermal transformations.

Results and Discussion

Heating of APTES and TMP results in the formation of a viscous liquid, which after evacuation is transformed into a hygroscopic white powder insoluble in organic solvents.

The IR spectra of the resinous (curves *1* and *2*) and solid (curve *3*) products of the reaction of APTES and TMP are presented in Fig. 1. They contain a broad intense absorption at 3500—2500 cm^{-1} (stretching vibrations of the N—H bonds). The character of the N—H bond absorption changes on the reaction step. It is seen that in the resin obtained at 100 °C the amino group exist as ions, for instance, $Si(CH_2)_3N^+H_2Me$ with the corresponding set of bands at 2700—2500 cm^{-1}. After the reaction completion (resin heated to 190 °C), the final product contains free amino groups, because an intense band appears at 3400—3100 cm^{-1}. The N—H bending vibrations are presented by a broadened band at 1643 cm^{-1}. Upon the appearance of the charged amino groups in the resinous products, an additional band of bending vibrations of the N—H bond appears at 1543 cm^{-1}, whose intensity decreases with an increase in the temperature of the synthesis. This band is completely absent in the spectrum of the solid reaction product. The set of bands in the 2980—2870 cm^{-1} interval is attributed to the C—H stretching vibrations. The narrow low-intensity bands in a range of 1490—1390 cm^{-1} correspond to the bending vibrations of the C—H bonds. The band at 1230 cm^{-1} characterizing the P=O bond is shifted in the spectrum of the resin relative to the band of the starting TMP (1280 cm^{-1}) due to hydrogen bonding with the amino groups at the intermediate reaction steps. However, in the spectrum of the solid product this band lies at 1300 cm^{-1}, which is characteristic of polyphosphosiloxanes.[16] The band at 1011 cm^{-1} and the shoulder at 1175 cm^{-1} can be assigned to the asymmetric stretching vibrations of the Si—O—P bond (see Ref. 16). The vibrations of the Si—O—C and P—O—C bonds are also concentrated in this region. The intense absorption at 1200—1000 cm^{-1} is caused by the superposition of the bands characterizing the P—O—Me (1052 cm^{-1}) and Si—O—Et (1163, 1103, 1077, and 961 cm^{-1}) moieties. The band at 790 cm^{-1} can be ascribed to stretching vibrations of the Si—C bond.

The ^1H, ^{13}C, and ^{31}P NMR spectra of the solid product of the reaction of APTES with TMP were measured in D_2O. The hydrolysis to the Si—O—P bonds affords a mixture of silanols, alcohols, and phosphoric acid derivatives.

The ^1H NMR spectrum of the hydrolysis product (Fig. 2) contains a series of signals belonging to the protons of moieties of molecules of the starting reactants. The intense singlet at δ 2.99 corresponds to the protons of the methoxy group. The triplet (δ 1.12, ^3J = 7.1 Hz) and quadruplet (δ 3.51, ^3J = 7.1 Hz) with the intensity

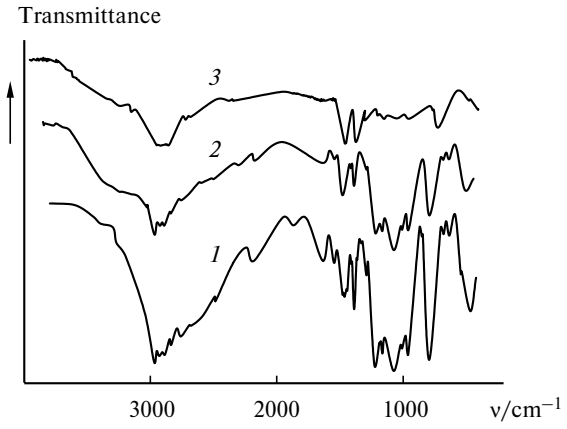


Fig. 1. Transformation of the IR spectrum of a mixture of APTES with TMP during the reaction: 100 (*1*), 190 (*2*), and 200 °C (*3*); *1*, *2* for liquid films and *3* for a suspension in Nujol.

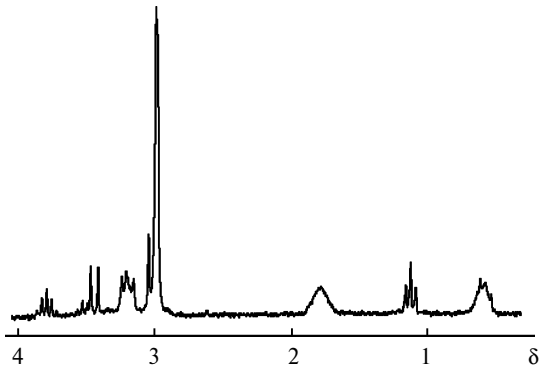


Fig. 2. ^1H NMR spectrum (200 MHz) of polyphosphosiloxane formed by the thermal condensation of TMP and APTES in D_2O.

ratio 3 : 2 belongs to the methyl and methylene protons of the ethoxy group, respectively. These groups belong to methanol and ethanol formed by the hydrolysis of the Si—OEt and P—OMe bonds in D_2O, respectively. The multiplet signals at δ 0.6 and 1.8 with equal intensity characterize the protons of the first and second methylene groups related to the silicon atom in the $SiC\underline{H}_2C\underline{H}_2CH_2N$ fragment. In addition to the coupling on adjacent protons, the additional broadening of these signals can be explained by the presence of the β-isomer of aminopropyltriethoxysilane with the $SiCH_2CH(Me)N$ group. Several of multiplets at δ 3—4 correspond to protons of various groups bound to the nitrogen atom. The doublet at δ 3.44 (^3J = 11.0 Hz) is assigned to the methyl group of the $CH_2NHC\underline{H}_3$ moiety, and the multiplet at δ 3.80 is attributed to the $CH_2N\underline{H}CH_3$ proton; the integral intensities of these signals are in a ratio of 3 : 1. The singlet at δ 3.05 characterizes the protons of the methyl groups in the $CH_2N(C\underline{H}_3)_2$ moiety. The broad band in the δ 3.16—3.25 interval corresponds to the methylene groups bound to the nitrogen atom and represents a superposition of the signals split on adjacent protons, namely, the triplet of $CH_2C\underline{H}_2NMe_2$ and the multiplet of $CH_2C\underline{H}_2NHMe$. In this case, an additional broadening can take place due to the superposition of the signal from the methine proton bonded to the nitrogen atom in the β-isomer of aminopropyltriethoxysilane.

Analogous conclusions can be drawn for the assignment of lines in the ^{13}C NMR spectrum (Fig. 3) of the same sample.[21] The methoxy group is characterized by a signal at δ 52.76. Two signals of approximately equal intensity at δ 16.35 and 68.37 corresponding to the methyl and methylene fragments can be ascribed to the ethoxy group. These chemical shift values are characteristic of the carbon atoms of methanol and ethanol, respectively. Two high-field signals at δ 8.15 and δ 8.52 are assigned to the carbon atoms bound to the silicon atom in the $Si\underline{C}H_2CH_2CH_2NMe_2$ and $Si\underline{C}H_2CH_2CH_2NHMe$ groups. The second methylene groups in these fragments ($SiCH_2\underline{C}H_2CH_2NMe_2$ and $SiCH_2\underline{C}H_2CH_2NHMe$) appear at δ 15.55 and 16.76, respectively. The signals at δ 62.06 and 57.40 characterize the methylene groups bonded to the nitrogen atom ($SiCH_2CH_2\underline{C}H_2NMe_2$ and $SiCH_2CH_2\underline{C}H_2NHMe$). The carbon atoms of the methyl groups $SiCH_2CH_2CH_2N(\underline{C}H_3)_2$ and $SiCH_2CH_2CH_2NH\underline{C}H_3$ resonate at δ 55.21 and 52.50.

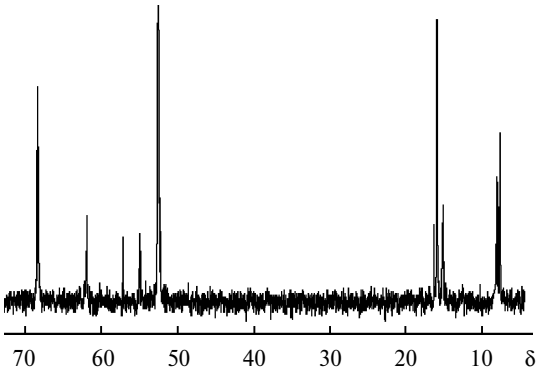


Fig. 3. ^{13}C NMR spectrum (50 MHz) of polyphosphosiloxane formed by the thermal condensation of TMP and APTES in D_2O.

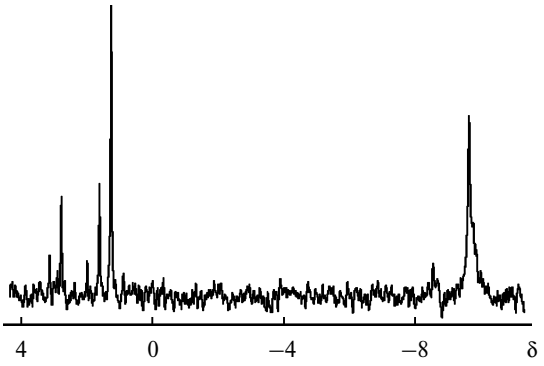


Fig. 4. ^{31}P NMR spectrum (80 MHz) of polyphosphosiloxane formed by the thermal condensation of TMP and APTES in D_2O.

Thus, the analysis of the ^1H and ^{13}C NMR spectra shows that the hydrogen atoms in the amino function of an APTES molecule are substituted for the methyl group to form the NHMe and NMe_2 moieties.

The signals in the ^{31}P NMR spectrum (Fig. 4) are localized in the chemical shift region close to zero, indicating the presence of several phosphoric acid derivatives in solution.[22] Orthophosphoric acid and its ions has the following signals: D_3PO_4 (δ 1.27), $D_2PO_4^-$ (δ −9.65), DPO_4^{2-} (δ −9.79), and PO_4^{3-} (δ −9.84). The intensities of lines related to the ions decrease sharply on going from $D_2PO_4^-$ to PO_4^{3-}, which agrees with the values of the dissociation constants of phosphoric acid by three steps.[23] Methyl esters are present in solution as both nondissociated molecules and ions. The signal at δ 3.14 corresponds to dimethylphosphoric acid $(MeO)_2P(O)OD$, and the signal at δ 2.77 corresponds to its ionized form $(MeO)_2P(O)O^-$. The signals at δ 2.00, 1.66, and −8.55 belong to methylphosphoric acid $MeOP(O)(OD)_2$ and ions formed by its dissociation by the first ($MeOP(O)ODO^-$) and second ($MeOP(O)O_2^{2-}$) steps, respectively. The comparison of the line intensities suggests that the major component in the mixture is phosphoric acid formed due to methylphosphate hydrolysis.[24]

$$MeOP(O)(OD)_2 + D_2O \rightleftharpoons D_3PO_4 + MeOD$$

Dimethylphosphoric acid is hydrolyzed to a less extent[24]; however, this two-step process also occurs.

$$(MeO)_2P(O)OD \overset{+D_2O}{\rightleftharpoons} MeOP(O)(OD)_2 + MeOD \overset{+D_2O}{\rightleftharpoons} D_3PO_4 + MeOD$$

Thus, we can believe that in the final product of the reaction of APTES with TMP the majority of phosphorus atoms are bound to one methoxy group only. The other P—O—Si bonds are much less stable to hydrolysis than the P—O—Me ester bonds in the initial compound. It is known[20] that TMP is not cleaved by water for a long time.

Orthophosphoric acid, which is formed by the dissolution of the solid reaction product in water, is easily titrated with alkali. It follows from this that the interaction of the neutral component (TMP) with APTES, being a base, gave a compound with acidic properties. The titration of the reaction mixture at different temperatures suggests the course of the process (Fig. 5). Mixing of the reactants at ambient temperature (20 °C) produces the alkaline medium. The quantity of sulfuric acid consumed in the titration is equivalent to the content of APTES in the mixture. The alkaline character is retained on heating to 60 °C, whereas the aqueous solution becomes virtually neutral upon storing of the mixture at 80 °C. The further temperature rise is accompanied by a gradual increase in acidity of the reaction mixture and a parallel increase in its viscosity due to oligomer formation. Phosphoric acid that neutralizes the amino groups is formed due to the hydrolysis of these oligomers. Therefore, the longer is the —(Si—O—P)— chain, the more acidic is the solution. When the process is completed at the step of polymer formation, the amount of titrated acid is equivalent to the amount of APTES taken for the reaction.

The acidity of a solution of the powder obtained after evacuation at 200 °C is higher than a solution of the untreated resin. This is related to the removal of ethanol (due to which the weight of the sample decreases) and a minor amount of organic amines, which neutralized some fraction of the acid.

The acid-base titration made it possible to find out one more interesting feature of the process under study. The acidity of the reaction mixture, which is a function of the conversion of the starting reactants, remains unchanged for a long time at each chosen temperature and changes only with the temperature rise. Thus, the components of the mixture are equilibrated under these external conditions. The temperature rise shifts the equilibrium toward the formation of the final products.

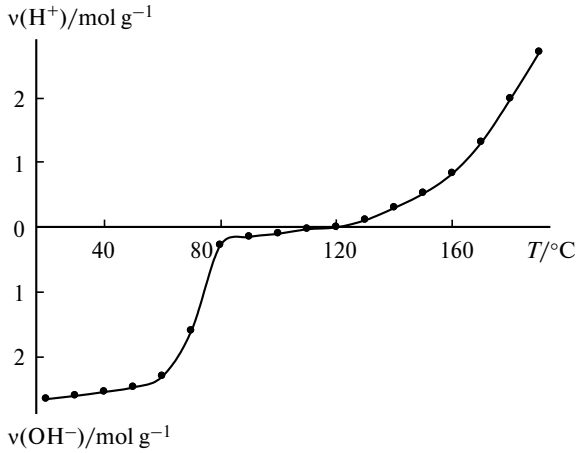


Fig. 5. Change in the acidity of the reaction mixture of APTES with TMP on heating.

Based on the obtained experimental results, the sequence of transformations that occur in an APTES—TMP system can be presented by Scheme 1. Since TMP has high methylating ability[24] and APTES, being a bifunctional compound, contains the primary amino group, the components of the reaction mixture can interact without preliminary hydrolysis of the reactants.

The reactions of phosphoric acid esters with primary amines afford hydrogen bonds between the phosphoryl and amine groups.[23] In the case of TMP and APTES, this is confirmed by the shift of the absorption bands of the P=O and N—H bonds by 10 cm^{-1} toward lower frequencies in the IR spectrum obtained by mixing of the reactants. In addition, a weak band with a maximum at 420 nm appears in the electronic absorption spectrum of a mixture of APTES and TMP (Fig. 6). This band results in the appearance of a yellow color at the beginning of the reaction. As can be seen from the data in Fig. 6, the molar absorption coefficient is characterized by an inverse temperature, which is typical of charge-transfer complexes.[25] The proton is transferred to the phosphoryl group and the methyl group migrates to the nitrogen atom, resulting in the formation of quaternary ammonium phosphate salt[24] (see Scheme 1, reaction (1)). The salt is equilibrated with dimethylphosphoric acid (**1**) and 3-(methylamino)propyltriethoxysilane (**2**) (see Scheme 1, reaction (2)).

This conversion affords the acidic hydroxy group capable of cleaving the Si—OEt bond to evolve ethanol (see Scheme 1; reactions (3), (4), and (7)). Monomeric

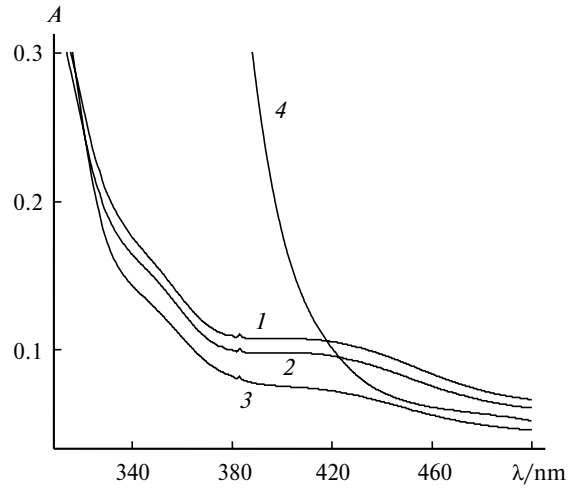
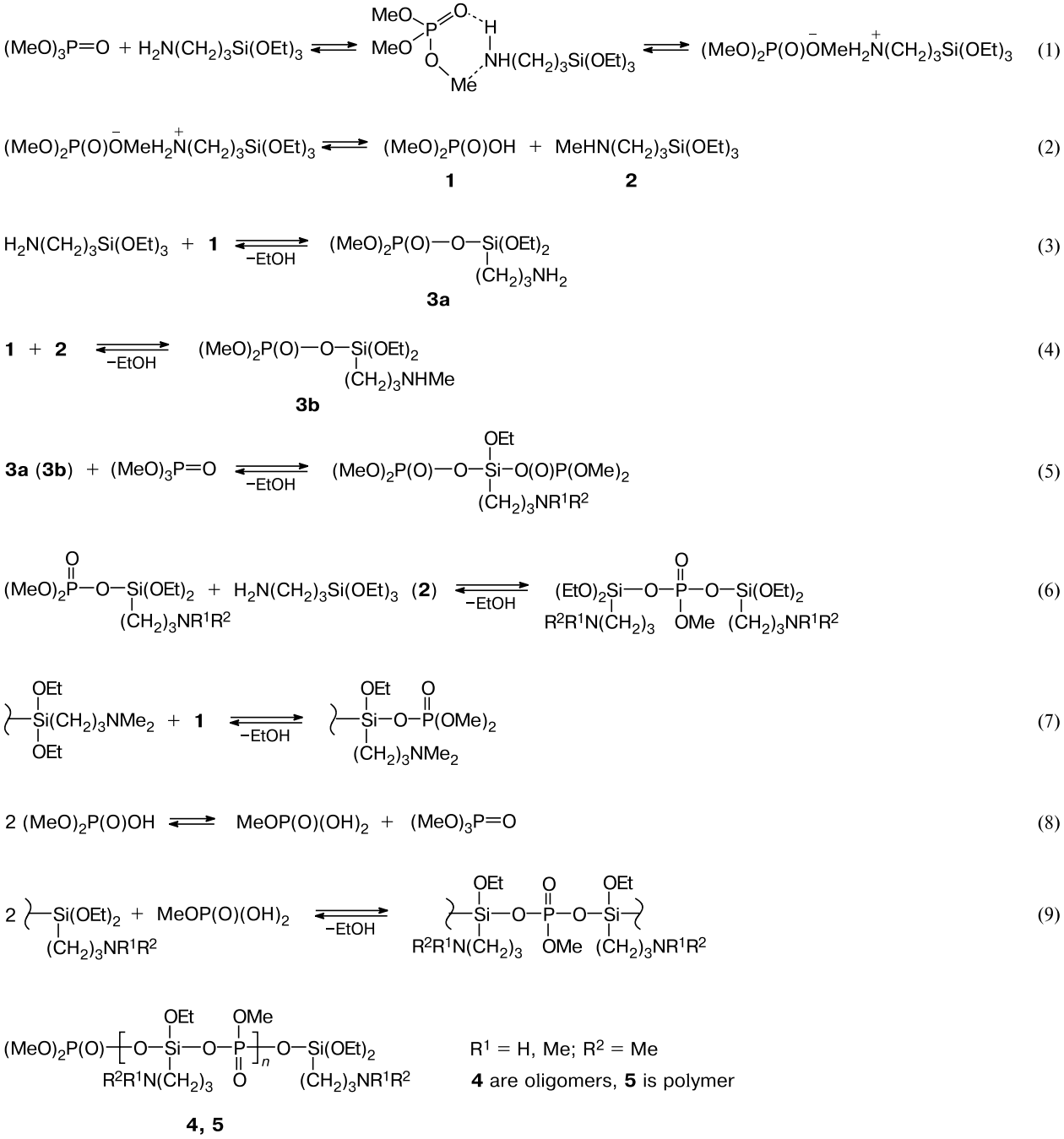


Fig. 6. Electronic absorption spectrum of the reaction mixture of APTES with TMP on heating: 20 (*1*), 40 (*2*), 60 (*3*), and 90 °C (*4*).

Scheme 1



compounds bearing the Si—O—P bonds (**3a,b**) are formed in this step. Compounds **3a,b** can react with both TMP (see Scheme 1, reaction (5)) and APTES or its methylated derivative **2** (see Scheme 1, reaction (6)). In addition, dimethylphosphoric acid can disproportionate to form TMP and methylphosphoric acid (see Scheme 1, reaction (8)). The latter can also react with alkoxy derivatives, resulting in an additional cross-linking of the silicon-containing fragments (see Scheme 1, reaction (9)). The chain growth occurs by the multiple repetition of the transformations shown in Fig. 1 and affording oligomers **4**. All these condensation reactions are reversible[26] and rather efficient only if volatile ethanol is removed. Therefore, resin is transformed into solid polymeric product **5** only upon heating above 200 °C *in vacuo*.

The presented scheme agrees well with the changes observed during the process. The absorption band characteristic of hydrogen bonding appears in the electronic

spectrum at temperatures below 60 °C. At a higher temperature, the thermal motion weakens the intermolecular interaction but the chemical reaction affording new compounds with Si—O—P bonds becomes possible. In this case, the boundary of absorption in the electronic spectrum shifts toward the visible region (see Fig. 6, curve *4*). The presence of oligomers formed in the reaction mixture upon further heating induces nonuniform light dispersion on particles of different size, which is reflected in the electronic spectrum. The absorption boundary becomes flatter, thus shifting to the visible spectral region. Therefore, the yellow—brown color of the mixture is enhanced, which is especially noticeable in the absence of stirring when polydispersity of oligomeric molecules is higher.

The temperature effect on the system under study can be explained as follows. It is most likely that the reactivity of phosphate $(MeO)_2P(O)OR$ depends to a great extent on the nature of the R substituent. The starting reactants begin to interact at relatively low temperature (80—90 °C) when the content of the active methylating agent TMP in the mixture is high. If one methyl group is substituted for the silicon-containing moiety (compounds **3a,b**), the reactivity decreases. Therefore, the temperature should be gradually increased to continue the process.

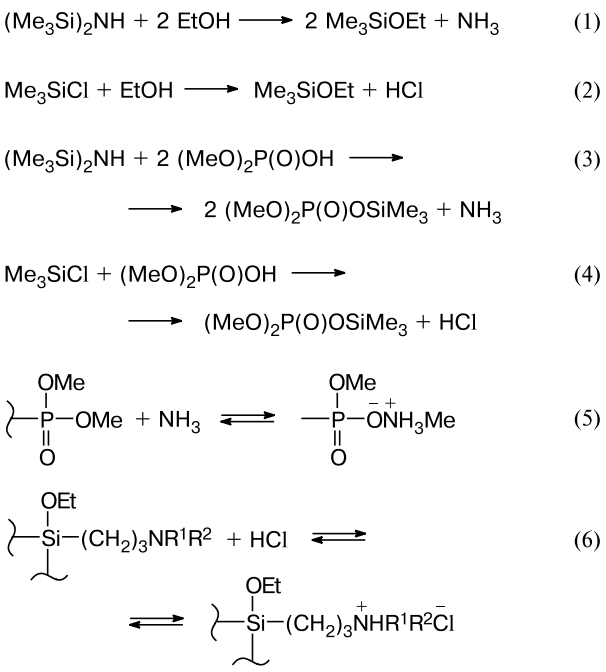
Comparing the data of the IR spectra and NMR spectra to the structural formula of polyphosphosiloxane **5**, one can conclude unambiguously that the spectral characteristics correspond to the structure of the synthesized compound. The quantitative composition of the product is also confirmed by elemental analysis.

Attempts to isolate dimethylphosphoric acid as its trimethylsilyl ester failed. For this purpose, hexamethyldisilazane or chlorotrimethylsilane was introduced into the reaction mixture both at the beginning of the process and at the substantial extent of conversion. However, in all cases, the additives used vigorously reacted with ethanol to form ethoxytrimethylsilane in almost quantitative yield (2 moles per 1 mole of APTES). A white precipitate was also formed at a considerably lower temperature (100—120 °C) due to ethanol binding and shift of the equilibrium condensation reactions toward the final products. After it was heated *in vacuo* at 150 °C and volatiles were removed, a hygroscopic powder was obtained, being, according to the IR spectroscopy and elemental analysis data, identical to polymer **5**. According to the GLC data, $(MeO)_2P(O)OSiMe_3$ is observed as an admixture in the amount lower than 5% in a mixture of the trapped products. The solid polymeric product interacts with neither $(Me_3Si)_2NH$, nor Me_3SiCl even on heating for a long time (12 h).

The transformations that occurs in the presence of the additives are shown in Scheme 2.

Ammonia and hydrogen chloride evolved in reactions (1), (3) and (2), (4), respectively, can partially be absorbed. Ammonia is capable of binding with the phosphate component (see Scheme 2, reaction (5)), and HCl can react with the amino groups in the composition of the organosilicon component (see Scheme 2, reaction (6)). The ammonium salts that formed decompose readily upon thermal treatment, because the acidity of the polymeric products obtained both in the presence and absence of additives do not substantially differ.

Scheme 2



It follows from the transformations shown in Schemes 1 and 2 that the condensation reactions occur rather rapidly. Introduced additives have no time to react with dimethylphosphoric acid but efficiently bind ethanol. Otherwise the single products of the reaction of APTES with TMP in the presence of hexamethyldisilazane or trimethylchlorosilane would be dimethyl trimethylsilyl phosphate and 3-(methylamino)propyltriethoxysilane rather than the polymer.

The thermal decomposition of polyphosphosiloxane **5** was studied in a temperature interval of 40—1000 °C. The TGA curves obtained in an inert gas flow are presented in Fig. 7. The sample is highly hygroscopic and contains some amount of adsorbed water, which is removed at temperatures from 100 to 200 °C. The main weight loss, being ~40—50%, occurs in the 300—350 °C interval. Under these conditions, the amine groups are eliminated almost completely and the spatially cross-linked polymer is formed by the condensation of the ethoxy and methoxy groups. Then at 450 °C residues of organic substituents are removed and crystalline phosphosilicate starts to form. The weight loss is low in this step, being 10—15%. After this the sample weight remains virtually unchanged up to 1000 °C.

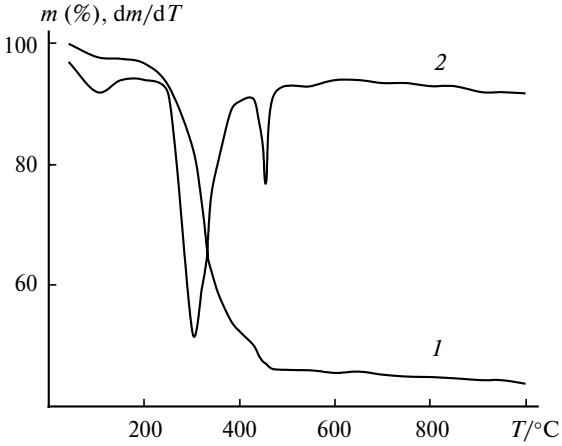
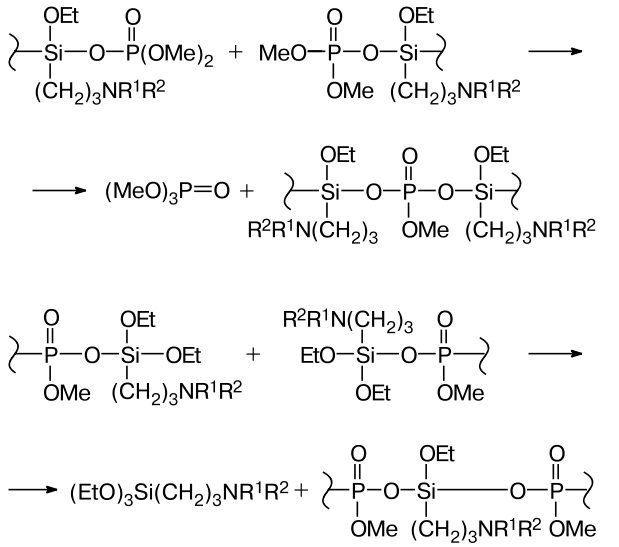


Fig. 7. Integral (*1*) and differential (*2*) TGA curves of polyphosphosiloxane formed by the thermal condensation of TMP and APTES.

To establish the nature of the products formed at different temperatures, we carried out the consecutive thermal treatment of compound **5** synthesized in the reaction of APTES with TMP. Heating in an evacuated ampule with simultaneous defrosting of volatiles results in the formation of a friable white mixture, which gradually turns grayish upon further calcination (350 °C, 4 h). After cooling this mixture is easily broken to form a powder with a lower hygroscopicity than that of the starting polymer. Its solubility in water also decreases, but the acidity of this solution increases. In addition to gaseous and highly volatile products, such as organic amines and alkoxy derivatives, TMP, APTES, and its methylated analogs are eliminated in this process (GC-MS data). Their content in the distillate is low, being totally ≤5—10%. Molecules of these compounds can be formed due to the thermocondensation reactions[19] shown in Scheme 3.

The powder obtained was further calcined successively at 600 and 1000 °C (5 h) in a quartz ampule in air and in oxygen and argon flows. The samples obtained under these conditions are not hygroscopic and poorly soluble in water. At 600 °C in an inert atmosphere a black powder containing carbonaceous materials is formed. Already at a higher temperature (1000 °C) these materials are sublimed or burn in air or in an oxygen flow. Therefore, white or slightly grayish powders are formed, as a rule, in an argon medium at 1000 °C. According to the X-ray diffraction data, calcination at 350 °C produces an amorphous phase and the further thermal treatment makes it possible to obtain crystalline samples, and the fraction of the amorphized component decreases with the temperature rise. During pyrolysis phosphosilicates are formed as either hexagonal ($Si_5O(PO_4)_6$, $R\bar{3}H$, a = 7.89 Å, c = 24.02 Å), or cubic (SiP_2O_7, $Pa3$, a = 7.47 Å) phases, and the latter can also exist in other structural modifications. In addition, the calcination of the sample, from which SiP_2O_7 crystallized, at 600 °C gave a mixture containing in addition to the phosphosilicate indicated a phase that can be identified as crystalline silicon Si136 (136 atoms in the cell, cubic, $Fd3m$, a = 14.62 Å).[27] Literature data concerning the conditions of preparation of this or another compound are rather contradictory.[12—14,16] In our case, it turned out that such factors as the ratio of the reactants (APTES and TMP), temperature (600 and 1000 °C), calcination time (0.5—5 h), and hydrolysis of the starting polymer or its preparation in the presence of hexamethyldisilazane or trimethylchlorosilane exert no effect on that which of two phosphosilicates is formed. In the predominant majority of the performed experiments $Si_5O(PO_4)_6$ crystallized. However, we succeeded to establish that a $Si_5O(PO_4)_6$ additive to the sample, from which the SiP_2O_7 phase was formed, at the calcination stage at 350 °C made it possible to shift the process toward the first of them. Probably, the formation of phosphosilicate of certain composition depends on the fact what crystal nucleates in a medium of amorphous polyphosphosiloxane and is determined by the mutual arrangement of chains and networks in the supramolecular structure of the cross-linked polymer.

Scheme 3



The X-ray diffraction patterns and IR spectra reflecting the formation of crystalline phosphosilicates from the amorphous powder with the temperature rise are shown in Figs 8 and 9. The spectral characteristics of $Si_5O(PO_4)_6$ and SiP_2O_7 agree with published data.[13]

The ^{13}C and ^{31}P NMR spectra in the solid phase were obtained for the amorphous and crystalline samples calcined at 350 and 1000 °C. Unfortunately, we failed to detect the solid-phase ^{29}Si NMR spectrum. Probably, this is related to the cross polarization effect due to which the carbon signal is enhanced and the resonance from ^{29}Si is suppressed.

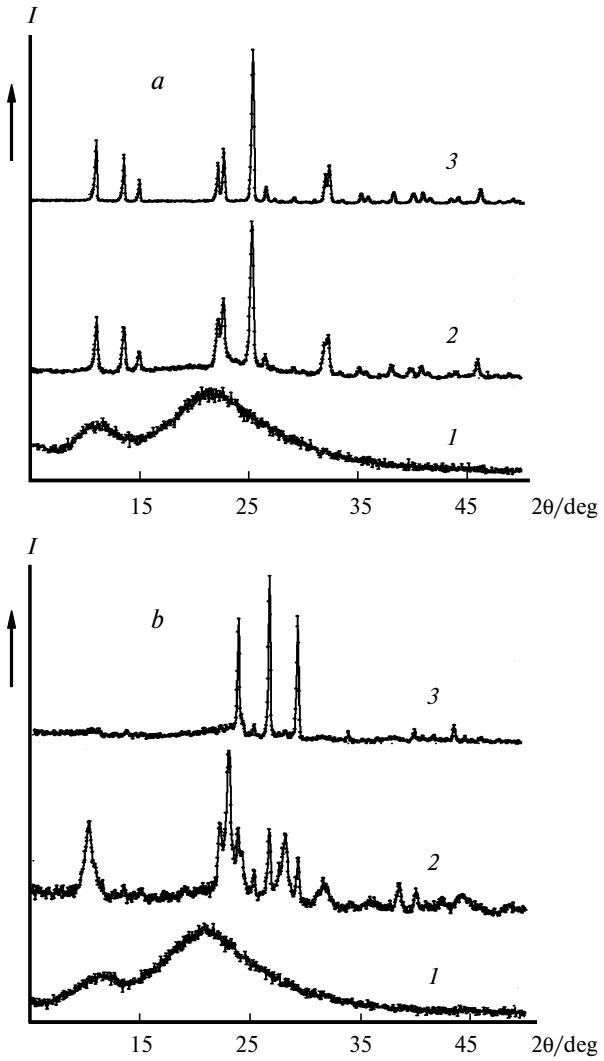


Fig. 8. Transformation of the X-ray diffraction pattern upon the formation of phosphosilicates $Si_5O(PO_4)_6$ (*a*) and SiP_2O_7 (*b*): 350 (*1*), 600 (*2*), and 1000 °C (*3*).

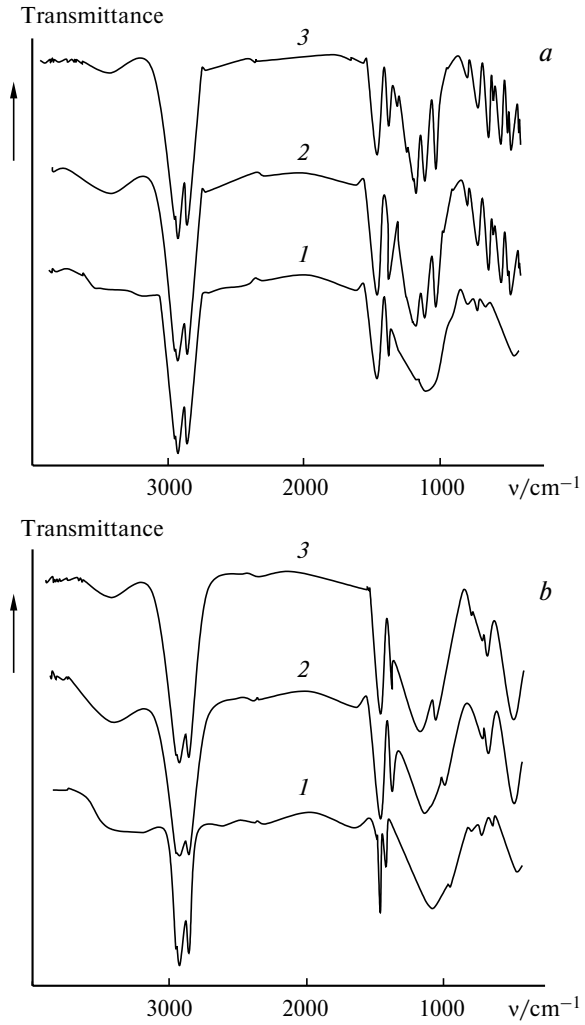
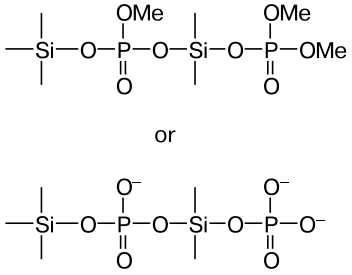


Fig. 9. Transformation of the IR spectrum upon the formation of phosphosilicates $Si_5O(PO_4)_6$ (*a*) and SiP_2O_7 (*b*): 350 (*1*), 600 (*2*), and 1000 °C (*3*).

The poorly resolved signals from the carbon atoms bound to the oxygen atoms in the methoxy (δ 56) and ethoxy (δ 53) groups appear in the ^{13}C NMR spectrum of the powder calcined at 350 °C (Fig. 10, curve *1*). The broadened signal at δ 46 corresponds to the carbon atoms bonded to the nitrogen atoms in the $\underline{C}H_2N(\underline{C}H_3)_2$ and $\underline{C}H_2NH\underline{C}H_3$ groups. The weak signals at δ 12—17 characterize the C atoms of the methylene groups in the $Si\underline{C}H_2\underline{C}H_2$ fragments and the methyl C atom in the ethoxy group ($\underline{C}H_3CH_2O$). The ratio of line intensities indicates that the silicon-containing fragments mainly undergo thermal decomposition at this stage: the amino groups are eliminated and spatial cross-linking occurs due to silicon alkoxide. The ^{31}P NMR spectrum (Fig. 11, curve *1*) exhibits a signal at $\delta \approx 0$ corresponding to orthophosphoric acid, which was probably formed due to hygroscopicity and affinity of polyphosphosiloxane to hydrolysis, and two signals attributed to the terminal (δ −16) and intrachain (δ −27) phosphorus-containing groups.[12] These lines are rather broad, indicating different structures of the phosphates, which can contain organic substituents or constitute the inorganic phase.



The appearance of broad poorly intense bands in the region of positive chemical shifts (δ 40—60) is caused by the fact that the position of polymeric chains and

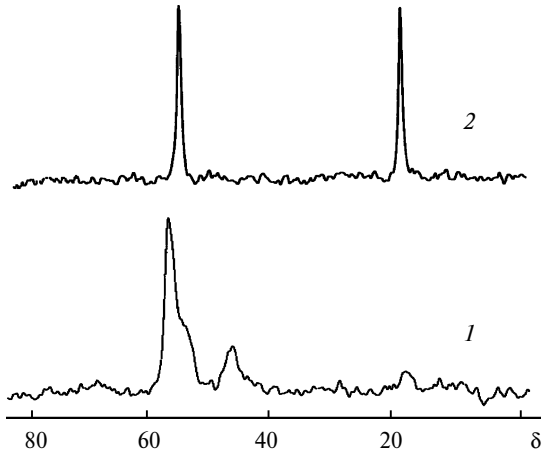


Fig. 10. Solid-state ^{13}C NMR spectra of the thermally treated samples: 350 (*1*) and 1000 °C (*2*).

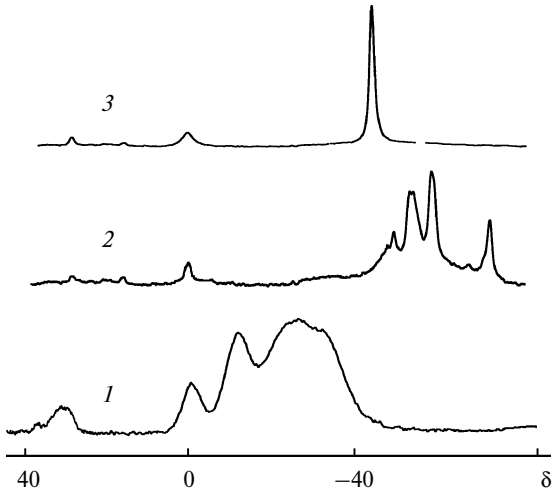


Fig. 11. Solid-state ^{31}P NMR spectra of the thermally treated samples: 350 (*1*) and 1000 °C (*2*, *3*); *1*, *2* for SiP_2O_7 and *3* for $Si_5O(PO_4)_6$.

networks in the polyphosphosiloxane structure is rigidly fixed.[12]

The signals of the methylene (δ 53) and methyl (δ 17) carbon atoms of the ethoxy groups appear in the solid-phase ^{13}C NMR spectrum of the crystalline sample calcined at 1000 °C (see Fig. 10, curve *2*). Perhaps, this is related to their residual content in the amorphized moiety of the sample. The ^{31}P NMR spectra of crystalline phosphosilicates are also shown in Fig. 11. The both compounds contain a minor amount of orthophosphoric acid (δ ≈ 0). The lines in the negative region of chemical shifts describe the corresponding phosphosilicates. The single signal at δ −44 is assigned to $Si_5O(PO_4)_6$ (see Fig. 11, curve *3*). The superposition of signals of several structural modifications of SiP_2O_7 is observed in the chemical shift interval from −80 to −45 ppm (see Fig. 11, curve *2*): δ −47 and −49 for monoclinic; δ −47 and −54 for tetragonal; δ −53 for hexagonal; δ −47, −49, −59, and −74 for cubic modification.[1]

In summary, the studies showed a principal possibility to carry out the reaction of TMP with APTES (bifunctional organosilicon compound) without preliminary hydrolysis of the components. The hydroxy group capable of interacting with silicon alkoxide appears due to the interaction of TMP with the amino group. The polymer product with the Si—O—P bonds is formed due to the thermal condensation of the starting reactants. The further thermal treatment of polyphosphosiloxane produces phosphosilicates of different composition: $Si_5O(PO_4)_6$ and SiP_2O_7. The crystalline phase begins to form on heating at temperatures above 500 °C, and the fraction of the amorphous component decreases with the temperature rise. Polycrystalline samples of phosphosilicates SiP_2O_7 in several structural modifications and $Si_5O(PO_4)_6$ were obtained at 1000 °C.

Experimental

IR spectra were recorded on a FSM-1201 FTIR spectrometer. Liquid and resinous substances were supported as a film between KBr plates. A suspension in Nujol was prepared to record the spectra of the solid samples. Electronic absorption spectra of the reaction mixture during the process were measured on a Perkin—Elmer Lambda 25 spectrophotometer in a quartz cell 5 mm thick. The ^1H, ^{13}C, and ^{31}P NMR spectra of the samples dissolved in D_2O were recorded on a Bruker Avance DPX-200 instrument (200, 50, and 80 MHz, respectively); internal standard for ^1H and ^{13}C being Me_4Si and for ^{31}P being 85% H_3PO_4. Solid-phase ^{13}C, ^{31}P, and ^{29}Si NMR spectra were detected on a Bruker AM-300 instrument.

X-ray diffraction analysis was carried out on a DRON-3M diffractometer coupled with a computer (Cu-Kα radiation) with a graphite monochromator using a diffracted beam.

Thermogravimetric analysis was carried out on a Perkin—Elmer Pyris 6 TGA instrument. A polymer sample (10 mg) was heated with a rate of 5 deg min^{-1} from 40 to 1000 °C in a nitrogen atmosphere.

(3-Aminopropyl)triethoxysilane (Slavgorod Production Association "Altaikhimprom") was rectified *in vacuo* on a column 1×50 cm packed with nichrome wire coils; before use TMP was distilled under reduced pressure, and hexamethyldisilazane and trimethylchlorosilane were subjected to standard distillation.

Analysis of APTES was carried out on a Tsvet-530 gas chromatograph on a stainless steel column (0.3×200 cm) packed with the Chromaton-N-AW-DMCS solid support with the 5% XC-2-1 liquid phase; katharometer as the detector; helium as the carrier gas; temperature of the thermostat was 160 °C, and the temperature of the detector and injector was 220 °C. The content of isomeric 2-aminopropyltriethoxysilane was 2.1%. To analyze liquid products of the condensation of APTES with TMP and compounds obtained when the reaction was carried in the presence of hexamethyldisilazane or trimethylchlorosilane, a column 0.3×200 cm packed with 5% SE-30 on Chromaton-N-AW was used; katharometer as the detector; helium as the carrier gas; the temperature of the thermostat was 60 °C (for

low-boiling substances) and 130 °C (for high-boiling substances), and the temperature of the detector and injector was 200 °C.

Mass spectra were obtained on a Trace GC Ultra LC-MS spectrometer with a Polaris Q mass analyzer (capillary chromatographic column TR-5MS, 30 m × 0.25 mm, thickness of the stationary phase film 0.25 μm; temperature of the injector 250 °C; helium as the carrier gas, flow rate 1.5 mL min^{-1}; programmed temperature increase from 40 to 250 °C; mass analyzer with an ion trap; ionization potential 70 eV; temperature of the ion source 300 °C; detected mass range 40—400). Chromatograms were recorded using total ion current. The analyzed mixture was dissolved in CH_2Cl_2. The sample volume was 1 μL. The NIST MS Search 20 library was used to interpret the mass spectra.

Elemental analyses were carried out at the Analytical Center of the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences.

Reaction of APTES with TMP. A round-bottom flask equipped with a stirrer and a reflux condenser was loaded at room temperature with APTES (4.43 g, 0.02 mol) and TMP (2.80 g, 0.02 mol). The light yellow color appeared upon mixing of the reactants. The reaction vessel was gradually heated to 150 °C and stored for 2 h at this temperature and continuous stirring. The vigorous interaction started at 80—100 °C. It was accompanied by the evolution of ethanol, whose vapors were condensed in a reflux condenser. The viscosity of the mixture increased and the yellowish color was enhanced. The viscosity of the mixture increased sharply during 20—30 min at 120—140 °C without stirring. The resin turned yellow-brown after the reaction mixture was stored under these conditions for 2 h. Then heating was continued to 200 °C *in vacuo* without stirring. At 180—190 °C the resin foamed. Upon further evacuation and heating (200 °C, 3 h) the white foam congealed occupying the whole volume of the flask. The solid fragile mixture was easily broken to form a hygroscopic powder.

All procedures with the obtained polymer product were carried out in a dry argon atmosphere. The IR spectrum of polyphosphosiloxane **5** is presented in Fig. 1. The elemental analysis corresponds to the structural formula (see Scheme 1). Found (%): C, 32.46; H, 7.21; N, 4.26; Si, 10.20; P, 11.25. Calculated (%): C, 34.35; H, 7.25; N, 5.34; Si, 10.69; P, 11.83 (for the polymer containing the same amount of the NMe_2 and NHMe groups). The insignificantly lower results for carbon and nitrogen are explained by the removal of a minor amount of volatile organic amines on heating of the polymer *in vacuo* at high temperature.

Upon evacuation of the resin, 2.05 g of a liquid was collected in the trap. According to the GLC data, the liquid contained 94.8% low-boiling compounds and the starting reactants as admixtures (TMP (2.3%) and APTES (2.9%)). Volatile condensation products consisted of ethanol (97.8%), methanol (1.7%), and a minor amount of organic amines (0.2 and 0.3%). The IR spectrum of the compounds removed from the reaction mixture *in vacuo* corresponded to ethanol and contained several additional low-intensity absorption bands belonging to methanol and amines. Ethanol evolved in this process in an amount of 2 moles per 1 mole of APTES taken in the reaction.

Reaction of APTES with TMP in the presence of hexamethyldisilazane or chlorotrimethylsilane additives. A round-bottom flask equipped with a stirrer and a reflux condenser was loaded at ~20 °C with APTES (4.43 g, 0.02 mol), TMP (2.80 g, 0.02 mol), and hexamethyldisilazane (3.22 g, 0.02 mol) or chlorotrimethylsilane (4.34 g, 0.04 mol). The reaction mixture was gradually heated with continuous stirring. At 80—100 °C the components began to interact vigorously to form a white precipitate, and ethoxytrimethylsilane vapors condensed in the condenser. In the first case, ammonia vapors evolved, whereas in the second case hydrogen chloride vapors were formed. An indicator paper placed in a reflux condenser showed a strongly alkaline or strongly acidic medium, respectively. If stoichiometric amounts of $(Me_3Si)_2NH$ or Me_3SiCl to the resin obtained at the intermediate stage and cooled to ambient temperature, the same changes were observed in the reaction mixture with further heating and stirring. After evacuation at 150 °C the white solid transformed into a hygroscopic powder.

The IR spectra of the products obtained in the presence of the additives are completely identical to the IR spectrum of polymer **5** (see Fig. 1). The quantitative composition of these powders is also virtually the same as that of polymer **5**. Found (%): C, 32.25; H, 7.18; N, 4.32; Si, 10.65; P, 11.78 and C, 32.40; H, 7.27; N, 4.41; Si, 10.40; P, 11.48 for the products obtained upon the addition of $(Me_3Si)_2NH$ and Me_3SiCl, respectively.

According to the GLC data, the liquid collected in the trap consisted of Me_3SiOEt (93.9 and 94.2%), $(MeO)_2P(O)OSiMe_3$ (4.1 and 3.5%), insignificant admixtures of the starting reactants TMP (0.8 and 0.9%) and APTES (0.5 and 0.4%), and additives (0.7 and 1.0%) in the case of hexamethyldisilazane and chlorotrimethylsilane, respectively. Me_3SiOEt was identified by the physical properties (b.p. 75—76 °C, n_D^{25} 1.3711; see Ref. 28: b.p. 75.7 °C, n_D^{25} 1.3712). The found dimethyl trimethylsilyl phosphate and ethoxytrimethylsilane are identical to authentic samples obtained using known procedures.[26]

Acid-base titration. Stoichiometric quantities of APTES and TMP were mixed at ~20 °C in a round-bottom flask equipped with a stirrer and a reflux condenser. Then the temperature was gradually raised with stirring to 190 °C with an increment of 10 °C, storing the reaction mixture for 20 min at each temperature. A sample was taken with a capillary at an interval of 20 min and weighed. A weighed sample (0.05—0.10 g) was dissolved in distilled water and left for 20—30 min for hydrolysis completion. Then the indicator (1% alcoholic solution of phenolphthalein) was added, and the solution was titrated with a 0.1 *M* solution of KOH or a 0.1 *N* solution of H_2SO_4, depending on the pH of the medium. Acidity of the samples was estimated by the amount of the acidic (H^+) or basic (OH^-) groups based on 1 g of the hydrolyzed substance. Aqueous solution of the solid samples were titrated similarly. Acidity of the powders obtained in the reactions of APTES with TMP expressed in the amount of H^+ was $4.61 \cdot 10^{-3}$ mol g^{-1}; in the presence of $(Me_3Si)_2NH$ it was $4.55 \cdot 10^{-3}$ mol g^{-1}; in the presence of Me_3SiCl it was $4.69 \cdot 10^{-3}$ mol g^{-1}. Acidity of the calcined samples is higher, because the amine groups are eliminated upon the thermal treatment. For the amorphous sample it is ~$7.5 \cdot 10^{-3}$ mol g^{-1}, whereas for crystalline phosphosilicates it reached values corresponding to the content of the PO_4^{3-} phosphate ions: $16.53 \cdot 10^{-3}$ and $19.80 \cdot 10^{-3}$ mol g^{-1} for $Si_5O(PO_4)_6$ or SiP_2O_7, respectively. However, to estimate the latter, prolong (10—15 days) hydrolysis of the samples in an alkaline medium is needed.

Thermal treatment of polyphosphosiloxane. ***A.*** A weighed sample of polymer **5** (2.0—2.5 g) was evacuated for 30 min, and

the ampule was sealed and heated for 4 h at 350 °C. Volatile products, being a colorless transparent liquid, were frozen into a trap and then analyzed by the LC-MS method. At this step the amino groups were eliminated as organic amines with methyl and propyl substituents. The thermal condensation of polymer molecules gave TMP, APTES, and its liquid analogs. The content of these compounds in the distilled-off liquid was low and totally at most 5—10%. Amines, TMP, and APTES were identified by the mass spectra available from the data base. In addition, the chromatogram contained two peaks, whose retention times were higher than that for APTES. As a whole, the mass spectra of these compounds differ slightly from the spectrum of APTES and contained the ions characteristic of APTES. Therefore, we assumed that these substances were 3-(methylamino)propyltriethoxysilane and 3-(dimethylamino)propyltriethoxysilane.

B. Weighed samples (0.1—0.2 g) of the powder calcined at 350 °C in quartz ampules 7×100 mm in size were placed in broad vertical quartz tube and left in air under atmospheric pressure or were blown with oxygen or argon. Then the ampules were heated in an electric oven to 600 or 1000 °C, stored for 5 h, and cooled to ~20 °C.

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