Synthesis and structure of the grafted layer on silicas chemically modified by aminophosphonic acids

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The synthesis and properties of three representatives of a new class of chemically modified silicas containing aminophosphonic acids, namely, (*N*-methyl-*N*-propylamino)methylenephosphonic, *N*-propylaminodi(methylenephosphonic), and *N*-[2-(propylamino)ethyl]-*N*,*N*-di(methylenephosphonic acids), covalently grafted on the silica surface are reported. The modified silicas were obtained by the two-step Kabachnik—Fields reaction in high yields. The concentrations of the grafted groups were determined by elemental analysis and pH-titration. The new materials were characterized by IR and ^{31}P and ^{13}C high resolution solid state NMR spectroscopy. The hydration of the modified silicas was found to result in a significant change in the structure of the grafted layer and to increase the mobility of the grafted groups.

Key words: chemically modified silicas, grafted aminophosphonic acids, solid state NMR spectroscopy, structure of the grafted layer.

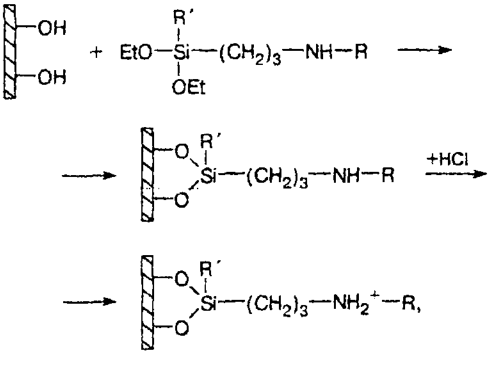
Phosphate-grafted cation exchangers based on organic synthetic polymers[1] are known to possess high sorption properties and increased selectivity toward multicharged ions of heavy metals. However, such materials have some disadvantages that are typical of all ion exchangers based on resins: slow sorption equilibration, swelling, and low mechanical, thermal, and radiation stability. These disadvantages can be avoided by using porous highly despersed silicas as a matrix for immobilization.[2] Previously[3—6] attempts to synthesize silicas with phosphonic acid groups covalently grafted were undertaken. However, they resulted in either arylphosphonic acids[4] labile for hydrolysis or multifunctional (that is containing a mixture of various grafted groups) materials with a low content of grafted phosphonic acids.[3]

This work deals with development a method for synthesis and study of the structure of a new class of complex-forming chemically modified silicas (CCMS) containing derivatives of aminomethylphosphonic ($R_2N—CH_2PO_3H_2$) acid on their surface. Introducing amino groups to the molecule of phosphonic acid improves its complexing ability and widens the synthetic potentialities, allowing one to obtain various types of grafted diphosphonic acids. According to their complexing characteristics, these grafted groups can be assigned to the class of phosphorus-containing complexones.[7]

Results and Discussion

Grafting aminophosphonic acids was carried out by the method of assembling them on the surface in two stages. At the first stage, the aminopropyl ($SiO_2—NH_2$), methylaminopropyl ($SiO_2—NHMe$), or *N*-propyl-1,2-diaminoethane ($SiO_2—En$) groups were covalently grafted by treating SiO_2 with 3-aminopropyl(methyl)diethoxysilane, [3-(methylamino)propyl]triethoxysilane, or *N*-[3-(diethoxymethylsilyl)propyl]ethylenediamine, respectively (see Scheme 1).

Scheme 1



R = H, R′ = Me; R = Me, R′ = OEt; R = C_2H_4—NH_2, R′ = Me

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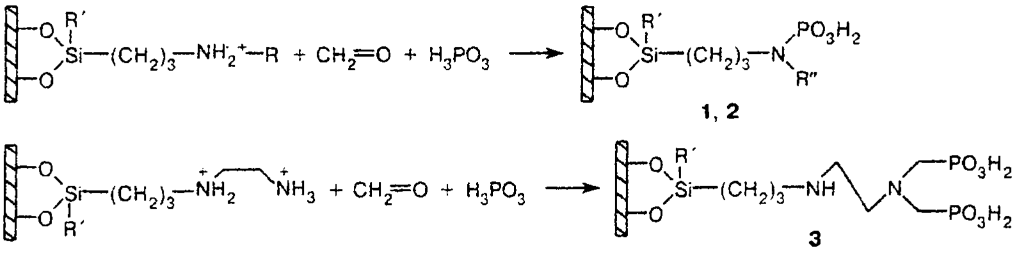
Scheme 2



R″ = $CH_2PO_3H_2$ (**1**), Me (**2**)

At the second stage, the grafted amine was condensed with H_3PO_3 and paraform by the Kabachnik—Fields reaction[8] (Scheme 2).

As a result, three aminophosphonic acids were immobilised and *N*,*N*-bis[(dihydroxyphosphoryl)methyl]-aminopropylsilica (**1**), 3-{*N*-(dihydroxyphosphoryl)-methyl-*N*-methyl]aminopropylsilica (**2**), and 3-*N*-2-{*N*,*N*-[bis(dihydroxyphosphoryl)methyl]amino}ethyl-aminopropylsilica (**3**) were obtained.

The surface reactions are known to possess a number of peculiarities, and one of them is a low degree of conversion of grafted groups into other moieties.[9] To optimize the conditions for the synthesis of grafted aminophosphonic acids and to reveal the main factors controlling the degree of the surface reaction, we used silicas with various porous structures: (**a**) macroporous Silochromes (SCh), (**b**) nonporous Aerosils (AS), and (**c**) mesoporous silica gel (SG). We also varied the molar ratio of the starting components and the nature and concentration of the grafted silane (see Table 1) in the synthesis of CCMS.

Silica was treated with ninhydrin for the express analysis of conversion of the grafted groups.[10] The absence of coloration of the solid phase attests to the absence of residual aminopropyl groups on the CCMS surface. This reagent turns the starting silicas and the polyfunctional phases to a blue color. This approach turned out to be rather effective, because it enabled optimization of the chemical process without chemical analysis of the reaction products.

The immobilization of the organophosphorus ligand on the silica surface was proved by the elemental analysis data (Table 2) and ^{31}P and ^{13}C high resolution solid phase NMR and IR spectroscopy.

As the modified silica can have a polyfunctional composition, the use of the elemental analysis data for determination of the concentration of the grafted groups needs a specific approach.[9] First of all, we found the increment of the content of an organic substance on the surface by comparison of the elemental analysis data for initial silica with that for the product of its phosphorylation. Based on the assumption that the increase in the C, H, and P content on CCMS is a result of grafting the $CH_2PO_3H_2$ fragment on aminosilica, we calculated the concentration of the grafted aminophosphonic groups C_L/mmol g^{-1} from the formula:

$$C_L = 10P_E/An_E,$$

where n_E is the number of atoms of the element under determination in the grafted fragment, A is the element atomic mass, and P_E is the percentage of the element.

The elemental analysis data confirmed the proposed mechanism of the modification reaction. As the reaction

Table 1. Some characteristics of silicas used in the synthesis of grafted aminophosphonic acids and the reaction conditions

CCMS	Matrix type	S /m^2 g^{-1}	d/nm	Concentration of the grafted amino groups		Molar ratio of the reagents —NHR : H_3PO_3 : CH_2O
				mmol g^{-1}	μmol m^{-2}	
1a$_1$	Fractosil	130	20	0.25	1.92	1 : 2 : 2
1a$_2$	Fractosil	130	20	0.25	1.92	1 : 2.4 : 3.3
1a$_3$	CX-80	80	100	0.13	1.62	1 : 6.6 : 5.1
1b	A-200	200	0	0.35	1.75	1 : 4.4 : 6.3
1c	Silasorb	300	6	0.25	0.83	1 : 5.4 : 8
2b	A-200	200	0	0.53	2.65	1 : 1.4 : 1.6
3b	A-200	200	0	0.50	2.50	1 : 3.6 : 3.6

Table 2. Elemental analysis data for CCMS (C_l (%)) and calculated concentrations of the grafted groups (C_L/mmol g^{-1})

CCMS	Yield (%)	Element content								C_L(CCMS)	
		C		H		P		P (oxidative decomposition)		Elemental analysis	pH-Titration
		C_l	C_L	C_l	C_L	C_l	C_L	C_l	C_L		
1a$_1$	80	1.49	0.26*	0.39	0.37*	1.23	0.2	—	—	0.20±0.06	0.24
1a$_2$	100	1.53	0.28*	0.34	0.28	1.54	0.25	1.46	0.24	0.25±0.03	0.25
1a$_3$	100	1.10	0.15	0.49	0.29	1.32	0.21	1.36	0.22	0.21±0.06	0.20
1b	74	2.92	0.27*	0.69	0.3*	1.63	0.26	—	—	0.26±0.03	0.32
1c	60	—	—	—	—	—	—	0.94	0.15	0.15±0.02	—
2b	72	4.06	0.4*	0.76	0.47*	1.19	0.38	—	—	0.38±0.04	0.34
3b	90	4.74	0.6*	0.87	0.43*	2.7	0.45	—	—	0.45±0.05	0.50

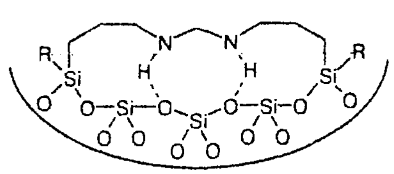
* Calculated using the increment of the content of the element under determination at the second stage of synthesis.

does not change the N molar content in the grafted molecule, the constancy of the N percent content in aminosilicas and CCMS serves as a test for the absence of decomposition of the grafted layer during the reaction proceeding by Scheme 2.

The influence of the reaction conditions on the yield of the grafted acids was studied using Silochromes (due to their macroporous structure no diffusion constraints can be taken into account, see Table 1, samples **1a$_1$**—**1a$_3$**) and nonporous Aerosils (sample **1b**) as examples. In particular, the conversion of the amino groups into the phosphonic groups at the stoichiometric ratio of the reagents on these matrices was shown to be >80% (see Table 2). The multifunctional silica is generated even at a 1.7-fold excess of paraform (sample **1a$_2$**). However, a three-fold excess of formaldehyde already decreases the yield of the grafted aminophosphonic acid (sample **1b**, see Table 2).

The decrease in the conversion of the grafted amino groups to aminophosphonic groups can be caused by a side reaction that is the condensation of two neighboring grafted amines with a formaldehyde molecule (see Scheme 3).

Scheme 3



The excess of paraform in the solution, the cluster character of distribution of the grafted groups on the silica bearing the aminopropyl groups, and the collapsed geometry of the grafted layer favor the stabilization of the material formed.

The primary grafted amines seem to be more reactive than the secondary amines. Thus, for example, **2b** is generated on the surface in a lower yield than **1b$_1$**—**1b$_3$**. Diphosphorylated amine **3b** was obtained from grafted ethylenediamine in a high yield (up to 90%). Mesoporous silicas (silica gels) are essentially less modifiable, as their conversion reaches only 60% at the second stage of the synthesis (see Table 2).

IR spectra of the resulting sorbents contain absorption bands at 2850—2920 and 1580—1600 cm^{-1} that correspond to C—H and C—C oscillations of the grafted hydrocarbon chains. The absorption band of the P=O group (1140—1240 cm^{-1}) is overlapped by the absorption bands of the silica backbone and, thus, is unobserved. The absorption bands of the grafted acid were assigned on the basis of comparison with the spectra of silica bearing aminopropyl groups and its protonated form. Treating the latter with H_3PO_3 solution and paraform results in the disappearance of the intensive band at 1516 cm^{-1} in the silica spectrum that is characteristic for the absorption of the protonated amino group and in the appearance of absorption at 1698 cm^{-1}. The band in the region of stretching oscillations at 3689 cm^{-1}, which can be assigned to the OH group of phosphonic acid, and also the band at 3350 cm^{-1} whose broadening points to the presence of the zwitter-ion form of the grafted ligand are observed for sample **1a$_1$** evacuated at 110 °C over P_2O_5.

NMR spectra were recorded by the high resolution method with magic angle spinning of the sample (MAS) and cross-polarization (CP). Nevertheless, both ^{13}C and ^{31}P spectra of the air-dried samples of grafted aminophosphonic acids are poorly resolved (see Figs. 1 and 2). Broadening of these signals can be due to two reasons: (1) the absence of free rotation of the grafted groups on the SiO_2 surface and (2) the heterogeneity of their microsurroundings. To clarify the reasons for the signal broadening, the ^{13}C NMR spectra of sample **1a$_2$** were recorded at various temperatures. A decrease in the

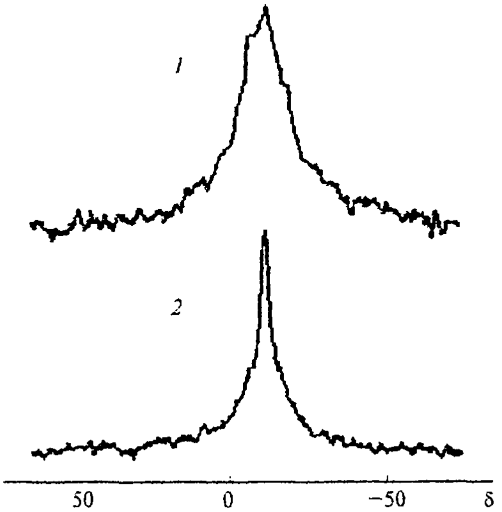


Fig. 1. ^{31}P NMR spectra: (*1*) air-dried **3b** (CP, MAS, ω = 4500 Hz) and (*2*) maximum hydrated **1a**$_2$ (static conditions).

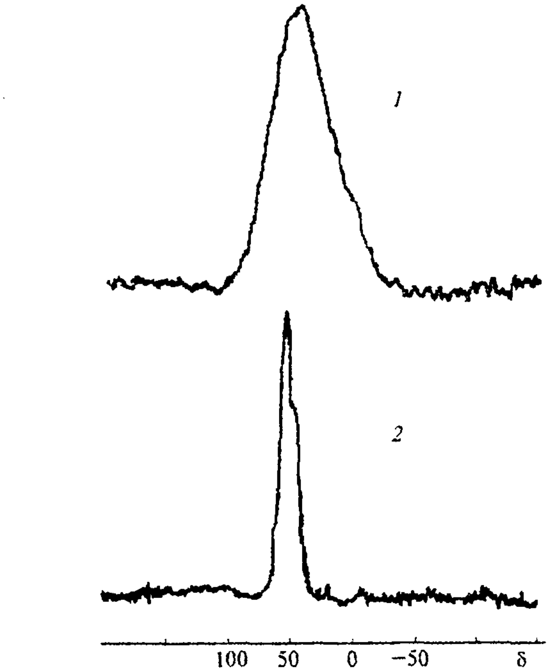
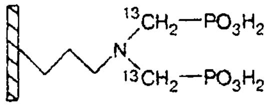


Fig. 2. ^{13}C NMR spectra of air-dried sample **1a**$_2$: (*1*) static conditions and (*2*) CP, MAS, ω = 3000 Hz.

temperature of the spectrum recording from 300 to 180 K appeared not to result in narrowing of the signal. Thus, it is believed that the mobility of the grafted groups does not change with temperature decrease and the absence of free rotation of the grafted groups makes the main contribution to the band width in the spectrum of **1a**$_2$.

All the NMR spectra of air-dried CCMS contain a poorly resolved broadened multiplet. Three components corresponding to the grafted phosphonic groups with various ionization degrees (see Fig. 1) can be distinguished against the background of a broad multiplet at δ −10 in the ^{31}P NMR spectrum of **3b**. According to the method of synthesis, only the methylene groups marked in Scheme 4 were enriched in the ^{13}C isotope, and only the signals of these groups can be found in the ^{13}C NMR spectra (see Fig. 2). In spite of the chemical identity of both methylene fragments in grafted aminodi(methylenephosphonic) acid, its ^{13}C NMR spectrum contains two peaks at δ 44 and 53 instead of one expected peak (see Fig. 2).

Scheme 4



To explain the nature of the signal splitting, we recorded the ^{13}C NMR spectra of sample **3b** at various exciting pulse widths. As seen in Fig. 3, there is no parallelism in the changes in intensities of the split peaks. Therefore, the observed signals are due to the ethylene C atoms with different times of spin-lattice relaxation.

Taking into account the ^{31}P NMR data, we can suppose the spectral differentiation of the methylene units in the grafted molecule to be caused by different types of their interaction with the silica surface. One of two phosphonic groups of the grafted acids is most likely to form a hydrogen bond with a silanol group on the silica, and another group is free (Fig. 4). Such a structure of the grafted layer can be responsible for the difference not only in the periods of the spin-lattice relaxation of various branches of aminodiphosphonic acid but also in the chemical shifts of the C atoms of these methylene groups.

Treating CCMS with water results in a noticeable narrowing of signals in the NMR spectra and in the

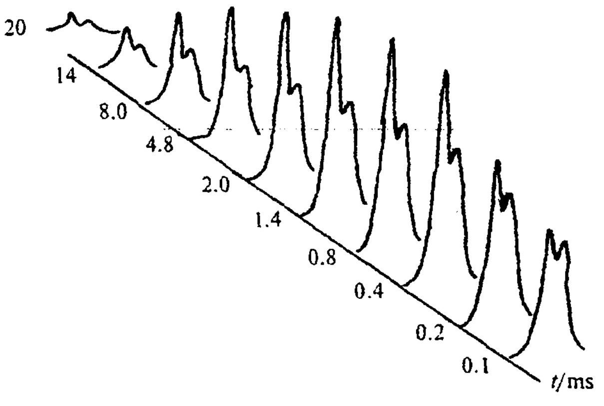


Fig. 3. ^{13}C NMR spectra of sample **3b** recorded with various pulse widths. Recording conditions: CP, MAS, ω = 4000 Hz.

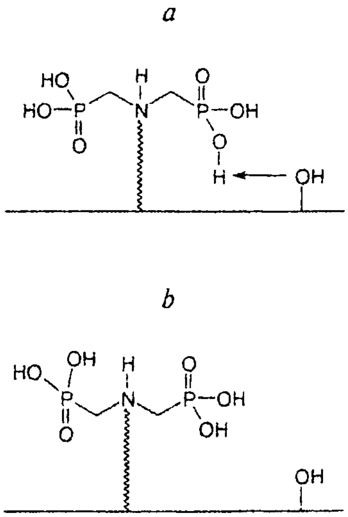


Fig. 4. The structure of the grafted layers of (*a*) air-dried and (*b*) maximally hydrated CCMS.

disappearance of splitting (see Fig. 1). Such changes in spectral characteristics point to essential changes in the structure of the grafted layer upon hydration: free rotation of the grafted groups appears, which eliminates their spectral differentiation. We may conclude that in the case of maximally hydrated silica the grafted aminophosphonic groups do not form hydrogen bonds with the SiO_2 silanol groups, and the grafted layer has an excited (brush) geometry.

Experimental

IR spectra were recorded on a Perkin—Elmer 1700 spectrophotometer. ^{31}P and ^{13}C NMR spectra for air-dried powders were recorded in a temperature range of 180—300 K and for maximally hydrated samples (after precipitation in water at 273 K) on a Durham (200 MHz) spectrometer at 273 K both in the static and MAS modes. The contact time was varied from 0.1 to 20 ms. pH-Titration was performed with an EV-74 ionometer using a silver working electrode and a glass ESL 43-07 auxillary electrode.

The concentration of the groups grafted on the silica surface was determined by elemental analysis and pH-potentiometric titration data. The P content was measured in the London Analytic Laboratory and by the authors according to the method[11] modified for silica analysis. Sorbents (0.1-g samples) were introduced into 50-mL volumetric flasks and 0.6 mL of glacial acetic acid and 0.2 mL of Br_2 were added. The mixture was heated in a sand bath to decolorization of the solution and 5 mL of 25% H_2SO_4, 10 mL of 0.25% potassium vanadate, and 10 mL of 5% ammonium molybdate solutions were added. The resulting solutions were diluted with water up to the marker and stored for 30 min for color development. The optical density of the solutions was measured at 430 nm and l = 1 cm. The calibrating curve was plotted for solutions containing the same components, nonmodified silica, and potassium dihydrophosphate. The interrelation between the optical density of the solution (D) and the concentration of the grafted aminophosphonic acid (C_L) is described by the linear equation $C_L = 1.13D_{430} + 0.052$ with the correlation factor $r = 0.998$.

The protolytic properties of sorbents were studied by pH-metric heterogenous titration. A sorbent specimen (0.2 g) was introduced into a beaker with 25 mL of 0.1 M KCl and titrated by 0.1 M NaOH with continious stirring.

3-Aminopropyl(methyl)diethoxysilane, 3-*N*-(methylaminopropyl)triethoxysilane, and *N*-[3-(diethoxymethylsilyl)propyl]-ethylenediamine (Fluka) for the aminosilica synthesis were purified by vacuum distillation immediately before experiments. Silicas were calcined in a muffle furnace for 8 h at 550±10 °C for activation before modification.

Solvents (toluene, benzene, diglyme, and dioxane) were dried over Na and distilled. Chloroform was shaken with concentrated H_2SO_4 and distilled above P_2O_5. Paraform (Fluka) enriched with ^{13}C atoms was used in some cases. Phosphonic acid (99% purity, Aldrich) was used as received.

Preparation of aminosilicas (general procedure). A solution of 3-(aminopropyl)methyldiethoxysilane in toluene was added on cooling to 15 g of freshly calcinated silica (SCh, SG, and AS) in 200 mL of anhydrous toluene. After mixing, the reaction mass was heated for 10 h at 100 °C. The solid phase was filtered off and washed with toluene from excess modifier in a Soxhlet apparatus. The completeness of washing was tested by the reaction of the washing solution with ninhydrin (the absence of blue color of the solution). Varying the amount of organosilicon modifier, we obtained silicas with concentrations of the grafted amino groups from 0.13 to 0.53 mmol g^{-1} (see Table 1).

Methylamino- and ethylenediaminosilicas were prepared in the same way using [3-(methylamino)propyl]triethoxysilane and *N*-[3-(diethoxymethylsilyl)propyl]ethylenediamine, respectively.

Silicas **1a**$_1$, **1a**$_2$, **1b**, and **3b** were protonated by treating with aqueous HCl. Excess acid was washed out with MeOH, and the samples were dried. Samples **1a**$_3$ and **2b** were protonated just before the synthesis by bubbling HCl through a silica suspension in diglyme. Sample **1c** was protonated in $CHCl_3$.

***N*-Propylaminodi(methylenephosphonic) acid (samples 1a—1c)** grafted covalently to the silica surface was synthesized on the basis of aminosilicas with various concentrations of the grafted groups and various natures of the matrix surface.

Sample 1a$_1$. Protonated Silochrome-NH_2 (10 g) with a concentration of the grafted groups of 0.25 mmol g^{-1} suspended in a mixture of 25 mL of benzene and 75 mL of diglyme was introduced into a three-necked flask supplied with a mechanical stirrer, dropping funnel, and reflux condenser with a calcium chloride tube. Then 0.15 g (5 mmol) of paraform in a paper cartridge was introduced, and 4.1 mL (5 mmol) of 10% H_3PO_3 in diglyme was added. After the addition of the acid the mixture was refluxed and an azeotrope was collected into a trap for azeotropic distillation. After water formation had been completed, the solid phase was filtered off, washed with diglyme and EtOH, and dried in an oven at 100 °C and *in vacuo* (0.15 Torr) at the same temperature.

Sample 1a$_2$ was synthesized in the same way using a 1.7-fold excess of CH_2O (^{13}C) and a 1.2-fold excess of H_3PO_3.

Sample 1a$_3$. This synthesis differed in that the protonation was carried out by bubbling HCl into aminosilica in diglyme till pH = 1. Then a solution of paraform depolymerized in diglyme was added to the suspension. Large excesses of H_3PO_3 (6.6 mol) and of CH_2O (5 mol) were used. The modified silica was washed with dioxane and dried as described above.

Sample 1b was synthesized similarly to **1a**$_2$, but molecular sieves were used for water absorption (instead of azeotropic distillation). We took 4.4 mol of H_3PO_3 and 6.3 mol of CH_2O per mol of grafted amine.

Sample 1c. The synthesis was performed using aminosilica preliminarily protonated in $CHCl_3$ (5.4 mol of H_3PO_3 and 8 mol of CH_2O per mol of amine).

***N*-Methyl-*N*-propylaminomethylenephosphonic acid (2b)** grafted covalently on Aerosil was obtained according to the following procedure. A feeble stream of HCl was bubbled for 30 min into 2 g of Aerosil-NHMe (1 mmol of grafted amino groups) in 50 mL of diglyme. Then 1.2 mL of 10% H_3PO_3 in diglyme (1.4 mmol) and 0.05 g (1.6 mmol) of a suspension of paraform (^{13}C) powder in 15 mL of diglyme were added simultaneously. The mixture was stirred and heated for 2 h. The sorbent was filtered off, washed in a Soxhlet apparatus with diglyme and acetonitrile, air-dried, and evacuated at 110 °C.

Sample 3b. To graft *N*-[2-(propylamino)ethyl]-*N*,*N*-di(methylenephosphonic acid), Aerosil was treated in the same way as in the synthesis of **1a**$_1$ using paraform enriched in ^{13}C.

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