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The synthesis of phosphorylated silsesquioxanes and the investigation of the ability to aggregation and interaction with aromatic dicarboxylic acids

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ABSTRACT

For the first time, silsesquioxanes containing aminophosphonate fragments were synthesized by condensation of the aminophosphonate derivatives with trialkoxysilane moieties under acid catalysis conditions. According to 29Si NMR, IR-spectroscopies, the silsesquioxane obtained have ladder-like structure with T_4 and T_6 silicon atoms. Information obtained from the MALDI-TOF mass spectra was used to deduce the structure of both oligomeric derivatives and the silsesquioxane framework. The morphology of the polysilsesquioxanes formed was investigated by transmission electron microscopy. The T_6-silsesquioxanes bearing aminophosphonate moieties contrary to T_4-silsesquioxanes tend to form aggregates of prolate shape. Their aggregation behavior was analyzed by the dynamic light scattering method. T_6-silsesquioxane tends to form submicron-sized aggregates in aqueous solutions. The ability of these silsesquioxanes to recognize aromatic dicarboxylic acids was studied by the UV-spectroscopy.

Introduction

The synthesis of macromolecules and materials able to molecular recognition of various substrates is one of the main recent research tendencies. For realization of the ability to bind and recognize molecules, polyfunctional moieties containing both acceptor and donor groups are usually introduced in the synthetic receptor structure. Thus, aminophosphonate derivatives provide significant interest due to presence of proton acceptor (phosphoryl and) proton donor (amino groups) [1], from which the acid is an analog of natural compounds used in medicine [2]. It was shown that aminophosphonates exert high antiviral [3], antibacterial [4], antifungal [5], antimicrobial [6], and antitumor activity [7].

Meanwhile the development of low-cost materials becomes relevant. The silicon derivatives are excellent from this point of view. Concerning silsesquioxanes with empirical formulas $SiO_{3/2}$, it should be noted that even though silsesquioxane chemistry spans over a half of the century, the interest continues to increase [8]. Synthesis of silsesquioxanes with the specified structure has been studied previously [9–13]. Nevertheless the study of the conditions for polycondensation of the organosilicon derivatives and their products calls for more careful investigation. Due to the low toxicity and high thermomechanical stability the appropriate materials based on silsesquioxanes are quite competitive and demanded.

Therefore, we have proposed the hypothesis that the combination of silsesquioxane as a core of hybrid materials containing simultaneously proton donor and acceptor groups can lead to selective receptor function toward biological substrates. Nano-sized building blocks and their capability to effectively recognition of biologically relevant substrates [14,15], combined with low toxicity and availability make it promising to study the condensation products of the organosilicon derivatives.

Thus, the synthesis silsesquioxanes containing aminophosphonate fragments by polycondensation of the aminophosphonate derivatives with trialkoxysilane moieties under acid catalysis conditions and investigating their ability to recognize aromatic dicarboxylic acids is the main goal of this work.

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Experimental

The ^{1}H, ^{13}C, ^{29}Si and ^{31}P NMR spectra were recorded on Bruker Avance-400 spectrometer. Chemical shifts were determined relatively to the signals of residual protons of the deuterated solvent ($CDCl_3$). The concentration of the sample solutions was 3–5%. Most of the chemicals were purchased from Aldrich and used as received without additional purification. Organic solvents were purified by standard procedures. IR spectra were recorded with Spectrum 400 IR spectrometer (Perkin Elmer). Elemental analysis was performed with Perkin Elmer 2400 Series II instrument. Mass spectra were recorded with the MALDI-TOF Dynamo Finnigan. The mass spectra were obtained on Bruker Ultraflex III MALDI-TOF instrument. First grade Millipore® water was prepared from distilled water on Simplicity 185.

Synthesis

*General method for synthesis of compounds **1**–**3***

In the presence of 3Å molecular sieves, the mixture of 1.00 g (4.5 mmol) of 3-aminopropyltriethoxysilane in 4.5 mmol dry ketone (acetone, cyclopentanone or cyclohexanone) and catalytic amount of *p*-toluenesulfonic acid was stirred during 30 min. Acetone (in the case of compound **1**) and THF (in the case of compound **2** and **3**) were used as solvents. 0.58 g (4.5 mmol) of diethylphosphite were added to this mixture followed by stirring for 4 h at r.t. The progress of reaction was controlled by ^{31}P NMR spectroscopy. Molecular sieves were filtered off and the acetone was evaporated. The residue was dissolved in diethyl ester.

*(O,O′-Diethyl)-2-(3-(triethoxysilyl)propyl-amino)propane-2-yl-phosphonate (**1**).* Product yield 1.60 g (89%). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 0.58 (2H, m, CH_2Si), 1.23 (6H, t, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.27 (6H, s, $(CH_3)_2C$), 1.33 (9H, t, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.55 (2H, m, $CH_2\underline{CH_2}CH_2$), 2.60 (2H, t, $NH\underline{CH_2}CH_2$), 3.70 (4H, q, $^{3}J_{HH} = 7.0$, $SiO\underline{CH_2}CH_3$). ^{31}P NMR ($CDCl_3$, δ, ppm): 31.32. ^{13}C NMR ($CDCl_3$, δ, ppm): 8.00, 16.56, 18.29, 23.02, 24.41, 45.81, 53.41, 58.33, 61.30. ^{29}Si NMR ($CDCl_3$, δ, ppm): −45.79. IR (ν/cm^{-1}): 949 (P═O); 1050, 1076, 1100 (Si–O); 1023 (P–O–C); 3415 (NH). El. Anal. Calcd. (%): C, 48.22; H, 9.36; N, 3.51; P, 7.77; Si, 7.05. Found (%): C, 48.10; H, 9.30; N, 3.50; P, 7.89; Si, 7.15. MALDI-TOF MS: calculated $[M^+]$ $m/z = 398.53$, found $[M + Na]^+$ $m/z = 419.9$.

*(O,O′-Diethyl)-1-(3-(triethoxysilyl)propyl-amino) cyclobutane-2-yl-phosphonate (**2**).* Product yield 1.72 g (90%). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 0.58 (2H, m, CH_2Si), 1.23 (6H, t, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.59–2.08 (8H, m, $-(CH_2)_4-$), 1.33 (9H, t, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.55 (2H, m, $CH_2\underline{CH_2}CH_2$), 2.60 (2H, t, $NH\underline{CH_2}CH_2$), 3.70 (9H, q, $^{3}J_{HH} = 7.0$, $SiO\underline{CH_2}CH_3$). ^{31}P NMR ($CDCl_3$, δ, ppm): 31.77. ^{13}C NMR ($CDCl_3$, δ, ppm): 7.90, 16.60, 18.28, 24.54, 36.38, 46.78, 58.31, 61.69, 63.62. ^{29}Si NMR ($CDCl_3$, δ, ppm): −47.50. IR (ν/cm^{-1}): 948 (P═O); 1100 (Si–O); 1074 (P–O–C); 2973 (NH). El. Anal. Calcd. (%): C, 45.25; H, 8.66; N, 3.51; P, 7.77; Si, 7.05. Found (%): C, 45.12; H, 8.44; N, 3.39; P, 7.78; Si, 7.11. MALDI-TOF MS: calculated $[M^+]$ $m/z = 424.2$, found $[M + Na]^+$ $m/z = 448.0$.

*(O,O′-Diethyl)-2-(3-(triethoxysilyl)propyl-amino)cyclopentane-2-yl-phosphonate (**3**).* Product yield 1.78 g (90%). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*/Hz): 0.7 (2H, m, CH_2Si), 1.22 (6H, t, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.59–2.08 (10H, m, $-(CH_2)_5-$), 1.31 (9H, t, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.56 (2H, m, $CH_2\underline{CH_2}CH_2$), 2.71 (2H, t, $NH\underline{CH_2}CH_2$), 3.70 (9H, q, $^{3}J_{HH} = 7.0$, $SiO\underline{CH_2}CH_3$). ^{31}P NMR ($CDCl_3$, δ, ppm): 30.73. ^{13}C NMR ($CDCl_3$, δ, ppm): 7.90, 16.60, 18.28, 24.54, 36.38, 46.78, 58.31, 61.69, 63.62. ^{29}Si NMR ($CDCl_3$, δ, ppm): −44.96. IR (ν/cm^{-1}): 946 (P═O); 1100 (Si–O); 1062 (P–O–C); 2929 (NH). El. Anal. Calcd. (%): C, 47.83; H, 9.15; N, 3.30; P, 6.84; Si, 6.24. Found (%): C, 47.70; H, 9.21; N, 3.41; P, 6.89; Si, 6.15. MALDI-TOF MS: calculated $[M^+]$ $m/z = 438.24$, found $[M + Na]^+$ $m/z = 461.9$.

*Polycondensation of the compounds **1**–**3** in hydrochloric acid*

1.00 g (0.25 mmol) of the compounds **1**–**3** were dissolved in 5 ml of methanol and 2.5 mmol (0.76 ml) hydrochloric acid were added dropwise. The mixture was refluxed for 20 days at r.t. or 6 days at 35 °C. The reaction mixture was then passed through the ion exchange resin Amberlit IRA-400.

*Dodecaethyl 2,2′,2″,2‴,2⁗,2⁗′-(3,3′,3″,3‴,3⁗,3⁗′-(3,5,9,11-tetrahydroxy-2,4,6,8,10,12,13-heptaoxa-1,3,5,7,9,11-hexasila-bicyclo[5.5.1]tridecane-1,3,5,7,9,11-hexayl)hexakis(propane-3,1-diyl))hexakis(azanediyl)hexakis(propane-2,2-diyl)hexaphosphonate (**4**).* Product yield 0.92 g (85%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.58 (2H, bs, CH_2Si), 1.35 (6H, bs, $(CH_3)_2C$), 1.68 (6H, bs, $CH_2\underline{CH_3}$), 2.043 (2H, bs, $CH_2\underline{CH_2}CH_2$), 2.6 (2H, bs, $NH\underline{CH_2}CH_2$), 4.02 (4H, m, $O\underline{CH_2}CH_3$). ^{31}P NMR ($CDCl_3$, δ, ppm): 31.13. ^{13}C NMR ($CDCl_3$, δ, ppm): 8.00, 16.56, 24.41, 45.81, 53.41, 58.33, 61.30. ^{29}Si NMR ($CDCl_3$, δ, ppm): −69.03. IR (ν/cm^{-1}): 950 (P═O); 1046 (Si–O); 1022 (P–O–C); 3389 (NH). El. Anal. Calcd. (%): C, 40.80; H, 8.10; N, 4.76; P, 10.52; Si, 9.54. Found (%): C, 40.42; H, 8.24; N, 4.79; P, 10.78; Si, 8.31.

*Dodecaethyl 1,1′,1″,1‴,1⁗,1⁗′-(3,3′,3″,3‴,3⁗,3⁗′-(3,5,9,11-tetrahydroxy-2,4,6,8,10,12,13-heptaoxa-1,3,5,7,9,11-hexasila-bicyclo[5.5.1]tridecane-1,3,5,7,9,11-hexayl)hexakis(propane-3,1-diyl))hexakis(azanediyl)hexakis(cyclopentane-1,1-diyl)hexaphosphonate (**5**).* Product yield 1.15 g (88%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.58 (2H, bs, CH_2Si), 1.23 (6H, bs, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.59–2.08 (8H, m, $-(CH_2)_4-$), 1.55 (2H, bs, $CH_2\underline{CH_2}CH_2$), 2.6 (2H, bs, $NH\underline{CH_2}CH_2$), 3.7 (4H, m, $O\underline{CH_2}CH_3$). ^{31}P NMR ($CDCl_3$, δ, ppm): 31.77. ^{13}C NMR ($CDCl_3$, δ, ppm): 7.90, 16.60, 36.38, 46.78, 58.31, 61.69, 63.62. ^{29}Si NMR ($CDCl_3$, δ, ppm): −66.83. IR (ν/cm^{-1}): 950 (P═O); 1046 (Si–O); 1022 (P–O–C); 3306 (NH). El. Anal. Calcd. (%): C, 44.99; H, 8.07; N, 4.37; P, 8.01; Si, 8.77. Found (%): C, 44.69; H, 8.12; N, 4.23; P, 8.13; Si, 8.57.

*Dodecaethyl (3,3′,3″,3‴,3⁗,3⁗′-(3,5,9,11-tetrahydroxy-2,4,6,8,10,12,13-heptaoxa-1,3,5,7,9,11-hexasila-bicyclo[5.5.1]tridecane-1,3,5,7,9,11-hexayl)hexakis(propane-3,1-diyl))hexakis(azanediyl)hexakis(-methylene)hexaphosphonate (**6**).* Product yield 1.11 g (82%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.70 (2H, bs, CH_2Si), 1.22 (6H, t, $^{3}J_{HH} = 7.0$, $CH_2\underline{CH_3}$), 1.59–2.08 (10H, m, $-(CH_2)_5-$), 1.56 (2H, bs, $CH_2\underline{CH_2}CH_2$), 2.71 (2H, bs, $NH\underline{CH_2}CH_2$), 4.10 (4H, m, $O\underline{CH_2}CH_3$). ^{31}P NMR ($CDCl_3$, δ, ppm): 30.73. ^{13}C NMR ($CDCl_3$, δ, ppm): 7.90, 16.60, 36.38, 46.78, 58.31, 61.69, 63.62. ^{29}Si NMR ($CDCl_3$, δ, ppm): −66.91. IR (ν/cm^{-1}): 951 (P═O); 1045, 1095 (Si–O); 1020 (P–O–C); 3309 (NH). El. Anal. Calcd. (%): C, 46.69; H, 8.34; N, 4.19; P, 9.26; Si, 8.40. Found (%): C, 46.42; H, 8.24; N, 4.39; P, 9.48; Si, 8.31.

*Polycondensation of the compounds **1**–**3** in acetic acid*

A solution of 0.01 mmol of the compounds **1**–**3** was prepared by dropwise addition of 5 ml of acetic acid followed by refluxing for 20 days at r.t. or 6 days at 35 °C. The reaction mixture was dissolved in methanol and passed through the ion exchange resin Amberlit IRA-400.

*Octaethyl 2,2′,2″,2‴-(3,3′,3″,3‴-(2,4,6,8-tetrahydroxy-1,3,5,7,2,4,6,8-tetraoxatetrasilocane-2,4,6,8-tetrayl)tetrakis(propane-3,1-diyl))tetrakis(azanediyl)tetrakis(propane-2,2-diyl)tetraphosphonate (**7**).* Product yield 1.41 g (79%). ^{1}H NMR ($CDCl_3$, δ, ppm): 0.58 (2H, bs, CH_2Si), 1.35 (6H, bs, $(CH_3)_2C$), 1.68 (6H, bs, $CH_2\underline{CH_3}$), 2.04 (2H, bs, $CH_2\underline{CH_2}CH_2$), 2.60(2H, bs, $NH\underline{CH_2}CH_2$), 4.02 (4H, m, $O\underline{CH_2}CH_3$). ^{31}P NMR spectrum ($CDCl_3$, δ, ppm): 31.13. ^{13}C NMR ($CDCl_3$, δ, ppm): 8.00, 16.56, 24.41, 45.81, 53.41, 58.33, 61.30. ^{29}Si NMR ($CDCl_3$, δ,