# Synthesis of siloxane analogs of calixarenes

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First siloxane analogs of calixarenes were synthesized based on the stereoregular *cis*-tetraphenylcyclotetrasiloxanetetrol. Different methods were used to study properties of new compounds in bulk, as well as their behavior at the water—air interface.

Key words: stereoregular organocyclosiloxanes, calixarenes, ethylenoxy groups, Langmuir monolayer.

Calixarenes are cyclic oligomers composed of the phenol fragments bound by the methylene bridges. Molecules of such compounds containing large enough cavities and hydroxy groups play the role of the host in the "guest—host"-type systems. The variation in the structure of such macrocycles changing their size and configuration, as well as their functionalization, make it possible to widely change the selectivity and the efficiency of binding of different substrates. As such, calixarenes are promising components of the sensor devices and supramolecular structures: ionic channels, nanoparticles, and compositional materials with the molecular recognition functions.<sup>1–3</sup>

The complexation properties of such compounds can be considerably improved using Langmuir—Blodgett technology.<sup>4,5</sup> Earlier, calixarenes and their derivatives were studied for the ability to form monolayers at the water—air interface,<sup>6–9</sup> as well as for the influence of the introduction of metal ions in the aqueous subphase on the character of the Langmuir monolayer isotherms.<sup>10–13</sup> The active development of chemistry of calixarenes and their analogs is associated with the high demand for compounds and structures of this type. Because of the serious synthetic limitations, the problem of the preparation of such compounds remains a relevant issue.

In the present work, we describe the synthesis of the first siloxane analogs of calixarene based on the stereoregular *cis*-tetraphenylcyclotetrasiloxanetetrol (1) and the results of the study of their behavior in monolayers at the water—air interface.

## **Results and Discussion**

To synthesize *cis*-tetraphenylcyclotetrasiloxanetetrol (1), we modified a known procedure for its preparation from sodium *cis*-tetraphenylcyclotetrasiloxanolate<sup>14,15</sup> (Scheme 1).

### Scheme 1



i. NaOH, H<sub>2</sub>O, Bu<sup>n</sup>OH; ii. 1) toluene, EtOH, 2) HCl, H<sub>2</sub>O.

The obtained tetrol (1) was used in the synthesis of *cis*-tetra[(phenyl)(dimethylhydride)siloxy]cyclotetrasil-oxane (2) (Scheme 2).

To prepare the first siloxane analogs of calixarenes (3a-c), the methyl allyl ethers of mono-, di-, and triethylene glycol, obtained according to the procedure described

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*i*. Pyridine/toluene, reflux, 1.5 h.

earlier,<sup>16</sup> were silylated in the presence of a Karsted catalyst (Scheme 3).



 $X = -(CH_2 - CH_2 - O)$ Ct is the Karsted catalyst. **3**: n = 1 (**a**), 2 (**b**), 3 (**c**)

The structure and purity of new compounds were confirmed by the GPC data, GLC-MS, <sup>1</sup>H and <sup>29</sup>Si NMR spectroscopy, and elemental analysis.

Thermogravimetric analysis (TGA) showed that the destruction in air (Fig. 1) of compounds 3a-c began at about 200 °C, whereas the destructive processes in argon (Fig. 2) developed at considerably higher temperatures, around 350 °C. It is obvious that such a significant difference in the thermal behavior is related to the presence of the ethylenoxy groups (X) in the chemical structure of the synthesized compounds, which tend to undergo early thermooxidation transformations.<sup>17</sup> This is the reason which leads to the presence of the first decomposition step



**Fig. 1.** The TGA curves for compounds **3a** (1), **3b** (2), and **3c** (3) in air at 10 °C min<sup>-1</sup> heating rate.



**Fig. 2.** The TGA curves for compounds **3a** (1), **3b** (2), and **3c** (3) in the flow of argon at 10 °C min<sup>-1</sup> heating rate.

of compounds 3a-c in air, which is observed in the 200-400 °C temperature range (see Fig. 1). It should be noted that the amount of the mass loss increases in parallel with the length of the ethylenoxy fragment. As a consequence, after the thermooxidation transformations stopped in the region of 700 °C, the decrease in the weight of the solid residue is observed in the following order 3a < 3b < 3c.

Differential scanning calorimetry (DSC) was used to determine glass transition temperature for compounds 3a-c (Fig. 3). We found that the glass transition temperature increases with the length of the ethylenoxy fragment and is equal to -80 (**3a**), -77 (**3b**), and -74 °C (**3c**), approaching the glass transition temperature of high-molecular-weight poly(ethylene oxide), -67 °C.<sup>18</sup>

To characterize the behavior of the molecules at the water—air interface, we studied the surface pressure  $(\pi - A)$  and surface potential  $(\Delta U - A)$  isotherms. The isotherms of compression of Langmuir monolayers  $(\pi - A \text{ and } \Delta U - A)$ 



**Fig. 3.** The DSC curves for compounds **3a** (1), **3b** (2), and **3c** (3) at 10 °C min<sup>-1</sup> heating rate.

of compounds **3a**–**c** are shown in Fig. 4, their principal parameters are given in Table 1. The changes in the morphology of the surface film of compound 3a in the compression-expansion cycle are illustrated in the microphotographs obtained by microscopy at the Brewster angle (Fig. 5). A monotonous growth is observed in the  $\pi - A$ and  $\Delta U - A$  isotherms upon the compression of the Langmuir monolayer of compound 3a. In this case, the growth of the surface potential began long before the surface pressure started to grow. A continuous uniform monolayer is seen on the water surface at the Brewster angle in the early stage (see Fig. 5, a). We assume that in this region the hydrophobic (phenyl) groups in the molecules of compound 3a are oriented toward the air phase, whereas the hydrophilic (siloxane and ethylenoxy) groups lie on the surface of water. The latter suggestion is supported by the fact that poly(ethylene oxide), despite its solubility in water,<sup>19</sup> can form monolayers at the water-air interface. The collapse of the poly(ethylene oxide) monolayer, according to the literature data,<sup>20</sup> is accompanied by a gradual immersion of the ethylenoxy units in water, which is reflected by a plateau in the  $\pi$ -A and  $\Delta U$ -A isotherms.

The further compression of a thin surface film of compound **3a** leads to the appearance of a plateau in the  $\pi$ -A (22 mN m<sup>-1</sup>) and  $\Delta U$ -A isotherms (405 mV) with the



**Fig. 4.**  $\pi - A$  (1-3) and  $\Delta U - A$  (4-6) isotherms upon compression of the Langmuir monolayers of compounds **3a** (1, 4), **3b** (2, 5), and **3c** (3, 6). T = 20 °C.

**Table 1.** Characteristics of  $\pi$ -A and  $\Delta U$ -A isotherms of compounds **3a**-c

Parameters	3a	3b	3c
$A_0/\text{Å}^2$ (molecule) <sup>-1</sup>	185	220	280
$A_1/\text{Å}^2$ (molecule) <sup>-1</sup>	122	130	140
$\pi_1/mN m^{-1}$	22	28.5	32
$\Delta U/mV$	405	445	475
$A_2/\text{Å}^2$ (molecule) <sup>-1</sup>	65	65	_
$\pi_2/mN m^{-1}$	26	31	—

area per one molecule of 122 Å<sup>2</sup>. Supposedly, a conformational rearrangement occurs in this region, when the ethylenoxy groups immerse in water, and the morphology of the surface film becomes irregular (see Fig. 5, *b*). Upon completion of this transition, the growth of the surface pressure resumes to 26 mN m<sup>-1</sup>, and a second plateau is observed in the  $\pi$ -*A* isotherm of the compression of a thin surface film of compound **3a**. The bright round domains are seen on the microphotograph of the surface film shown in Fig. 5, *c*.

The shape of the  $\pi - A$  and  $\Delta U - A$  isotherms of the expansion of a thin surface film of compound **3a** is similar to that of the corresponding compression isotherms. Upon the film expansion, the formed domains undergo destruction and the aggregates can be observed on the surface (see Fig. 5, d), which then spread with the formation of a monolayer. The  $\pi - A$  isotherm completely reproduces upon repeated compression of the monolayer of compound **3a**.

For compounds **3b** and **3c**, the behavior on the water surface in the compression—expansion cycle, as well as the  $\pi$ —A and  $\Delta U$ —A isotherms, are similar to those observed for compound **3a**. From the data in Table 1, it follows that in the order of compounds **3a**, **3b**, and **3c** a growth of the area values per one molecule in both the sparse ( $A_0$ ) and the maximally compressed ( $A_1$ ) monolayers is observed, that indicates that in the initial state the ethylenoxy units lie on the surface of water. It should be noted that in this series the elongation of the ethylenoxy substituent by one ethylenoxy unit results in the increase in the stability of the monolayers ( $\pi_1$ ) by 4—6 mN m<sup>-1</sup> and the maximal value of the surface potential ( $\Delta U$ ) by 30—40 mV.

For the benzyl ether monodendrones with an oligoethylenoxy chain in the focal point, a contribution of the hydrophobic and the hydrophilic moieties to the increase in the stability of monolayers was evaluated, and the increase in the monolayer collapse pressure was found to be 3-4 mN m<sup>-1</sup> with the elongation of the sequence by one ethoxy group.<sup>21</sup> Earlier, such a behavior was observed for the monolayers of carbosilane dendrimers of third and sixth generation with the ethylenoxy units in the shell.<sup>22</sup>



**Fig. 5.** Microphotographs of the thin surface film of compound **3a** at the Brewster angle for compression at the pressure of 10 (*a*), 23 (*b*), and 25 mN m<sup>-1</sup> (*c*) and expansion at the pressure of 23 mN m<sup>-1</sup> (*d*). T = 20 °C.

The second plateau (at  $\pi_2$ ) in the  $\pi$ -A isotherms of compounds **3a**,**b** is observed at practically the same area per one molecule equal to 65 Å<sup>2</sup> (A<sub>2</sub>). Assuming that the ethylenoxy substituents are immersed in water, tetraphenylcyclosiloxane remains on the surface. The area per one siloxane unit is ~17 Å<sup>2</sup>, that correlates with 16 Å<sup>2</sup> per one unit for dimethyl- or methylphenyl-substituted linear<sup>23</sup> and cyclolinear<sup>24</sup> polyorganosiloxanes.

The height of the second step in the surface pressure decreases on going from mono- (see Fig. 4, curve I) to diethylene glycol-substituted cyclotetrasiloxane (see Fig. 4, curve 2). For triethylene glycol-substituted derivative, the second step of the surface pressure is indistinguishable (see Fig. 4, curve 3).

In conclusion, we suggested a convenient method for the synthesis of the siloxane analogs of calixarenes based on *cis*-tetraphenylcyclotetrasiloxanetetrol with mono-, di-, and triethylene glycols. The influence of molecular parameters of compounds obtained on the quantitative characteristics of Langmuir monolayers was demonstrated. The presence of the hydrophilic (ethylenoxy and siloxane) and hydrophobic (arene, methyl, and methylene) fragments in the composition of molecules provides the selforganization on the interphase surfaces and confirms their pronounced amphiphilic nature.

## Experimental

All the organic solvents were dried and distilled over  $CaH_2$ , except dimethylchlorosilane (Aldrich) and pyridine (Aldrich), which were used as purchased. A Karsted catalyst (1,3-divinyl-

1,1,3,3-tetramethyldisiloxane)platinum(0) as a 2% (Pt) solution in xylene (Aldrich) was used for catalysis.

Products were isolated by preparative HPLC using a Shimadzu LC-8A chromatograph, a Smartline RI 2400 refractometric detector (KNAUER, Germany), a Kromasil 300-5Sil, E96811 column (250×30 mm), eluent THF.

GPC analysis was carried out on a chromatographic installation consisting of a STAIER, series 2 high-pressure pump (Akvilon, Russia), a RIDK 102 refractometric detector (Czech Republic), and a JETSTREAM 2 PLUS column termostat (KNAUER, Germany). The thermostatic temperature was 40 °C (±0.1 °C), eluent THF, the flow rate 1.0 mL min<sup>-1</sup>. The column (300×7.8 mm) was filled with Phenogel sorbent (Phenomenex, USA) with particle size 5 µm, pore size 10<sup>3</sup> Å (the passport separation range to 75000 Da). The registration and processing of the measurement results were carried out using the Multi-Khrom 1.6 GPKh program (Ampesand, Russia).

<sup>1</sup>H and <sup>29</sup>Si NMR spectra were recorded on a Bruker Avance<sup>TM</sup> 600 spectrometer (600.22 and 119.26 MHz, respectively). Chemical shifts for <sup>1</sup>H were measured relative to the signal of residual proton CHCl<sub>3</sub> ( $\delta$  7.27). Chemical shifts for <sup>29</sup>Si were measured relative to the external Me<sub>4</sub>Si.

Thermogravimetric studies were carried out on a Derivatograph-C instrument (MOM, Hungary) in air and under argon at  $10 \,^{\circ}\text{C} \min^{-1}$  heating rate.

Studies by DSC were carried out on a DSC-822e (Mettler–Toledo, Switzerland) at  $10 \,^{\circ}$ C min<sup>-1</sup> heating rate.

Formation of Langmuir monolayers and studies of their properties upon compression between two movable barriers at the rate 15 cm<sup>2</sup> min<sup>-1</sup> was carried out using a Minitrough Extended Langmuir trough (KSV, Finland). The subphase was the water with specific resistivity of 18.2 M $\Omega$  cm<sup>-1</sup> (at 25 °C), which was purified and demineralized using a Milli-Q Integral Water Purification System apparatus (Millipore, USA). The subphase was termostated at 20 °C. Twice distilled chloroform was used as a solvent. The surface pressure was determined with the accuracy up to 0.1 mN m<sup>-1</sup> by the Wilhelm method using a roughened platinum plate. The surface potential was measured by the vibrating electrode technique, using a SPOT sensor (KSV, Finland) with the accuracy up to 1 mV. The morphology of the Langmuir films directly on the water surface was visualized using a BAM300 Brewster microscope (KSV, Finland). The microphotographs shown in this work are geometrically corrected with allowance for the observation at the Brewster angle of 53.1° and correspond to the section of the interphase surface of 200×200 um.

**Sodium** *cis*-tetraphenylcyclotetrasiloxanolate. The preparation of sodium *cis*-tetraphenylcyclotetrasiloxanolate was carried out according to the modified procedure, <sup>14</sup> by the mixing of tributoxyphenylsilane (23.04 g, 0.071 mol) in *n*-butanol (80 mL) and NaOH (3.00 g, 0.075 mol) (with allowance for the substance purity) in water (1.28 mL, 0.071 mol). The crystals formed over time after the cooling were filtered and washed with hexane on a Schott funnel. To remove excessive solvents (hexane and *n*-butanol), the crystals were dried *in vacuo* of a water-jet pump for 1 h to obtain a white crystalline compound (10.25 g) containing solvent molecules of butanol. Found (%): C, 54.93; H, 9.15; Na, 6.05; Si, 7.09. [PhSi(O)ONa]<sub>4</sub> · 12(*h*-C<sub>4</sub>H<sub>9</sub>OH), C<sub>72</sub>H<sub>140</sub>Na<sub>4</sub>O<sub>24</sub>Si<sub>4</sub>. Calculated (%): C, 54.24; H, 8.85; Na, 5.77; Si, 5.77.

*cis*-**Tetraphenylcyclotetrasiloxanetetrol (1).** The sodium *cis*-tetraphenylcyclotetrasiloxanolate (10.25 g, 6.4 mmol) was dis-

solved in a mixture of toluene (66 mL) and ethanol (2.5 mL), then, the solution was added dropwise to a solution of concentrated HCl (10 mL) in water (653 mL) with vigorous stirring. The reaction mixture was stirred for 2–3 min. The crystals formed were separated on a Schott funnel, washed with water, until the test on the presence of Cl<sup>-</sup> ions was negative, and toluene. The product **1** was dried *in vacuo* in the presence of CaCl<sub>2</sub> for 24 h. The yield was 3.3 g (93.2%). Found (%): C, 52.25; H, 4.19; Si, 20.24.  $C_{24}H_{24}Si_4O_8$ . Calculated (%): C, 52.14; H, 4.38; Si, 20.33. <sup>1</sup>H NMR ((CD<sub>3</sub>)<sub>2</sub>O), & 7.36 (d, 8 H, o-C<sub>6</sub>H<sub>5</sub>, J = 6 Hz); 7.26 (t, 4 H, p-C<sub>6</sub>H<sub>5</sub>, J = 12 Hz); 7.18 (t, 8 H, m-C<sub>6</sub>H<sub>5</sub>, J = 18 Hz); 6.25 (s, 4 H, OH). <sup>29</sup>Si NMR ((CD<sub>3</sub>)<sub>2</sub>O), & -69.9.

cis-Tetra[(phenyl)(dimethylhydride)siloxy]cyclotetrasiloxane (2). A mixture of compound 1 (1.7 g, 3.08 mmol) and pyridine (1.08 g, 12.3 mmol) in toluene (40 mL) was added to a solution of chlorodimethylsilane (1.74 g, 12.3 mmol) in toluene (10 mL) with vigorous stirring. The reaction mixture was refluxed for 1.5 h, then filtered from the precipitate of pyridine hydrochloride. The resulting solution was washed with distilled water until the test on the presence of Cl- ions was negative and dried with sodium sulfate. After evaporation of the solvent on a rotary evaporator, the product 2 was concentrated *in vacuo* of an oil pump with heating in a water bath (60-70 °C). The yield was 1.64 g (68%). Found (%): C, 49.18; H, 6.15; Si, 28.35. C<sub>32</sub>H<sub>48</sub>O<sub>8</sub>Si<sub>8</sub>. Calculated (%): C, 48.94; H, 6.16; Si, 28.61. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 7.38 (d, 8 H, o-C<sub>6</sub>H<sub>5</sub>, J = 6 Hz); 7.33 (t, 4 H, p-C<sub>6</sub>H<sub>5</sub>, J = 12 Hz); 7.18 (t, 8 H, m-C<sub>6</sub> $\underline{H}_5$ , J = 18 Hz,); 4.92–4.90 (m, 4 H, Si– $\underline{H}$ ); 0.32-0.31 (d, 24 H, CH<sub>3</sub>, J = 6 Hz). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ: -17.3 (4 Si, O-<u>Si</u>-(CH<sub>3</sub>)<sub>2</sub>), -78.1 (4 Si, <u>Si</u>-O-Si).

cis-Tetra{(phenyl)[(dimethyl)(methylpropylmonoethylene glycol)siloxy]}cyclotetrasiloxane (3a). A Karsted catalyst (3 µL, 0.1 µL per 1 mL of the reaction mixture) was added to a solution of monoethylene glycol methyl allyl ether (1.95 g, 16.68 mmol) in benzene (10 mL). Then, a solution of compound 2 (2.88 g, 3.67 mmol) in benzene (15 mL) was added slowly dropwise with vigorous stirring, and the reaction mixture was stirred for 2 days at 65 °C. After evaporation of the solvent the product 3a was isolated by preparative HPLC. The yield was 1.56 g (34%). Found (%): C, 53.60; H, 7.69; Si, 17.78. C<sub>56</sub>H<sub>96</sub>O<sub>16</sub>Si<sub>8</sub>. Calculated (%): C, 53.81; H, 7.74; Si, 17.96. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ: 7.32 (d, 4 H,  $o-C_6H_5$ , J = 6 Hz); 7.28 (t, 8 H,  $p-C_6H_5$ , J = 18 Hz); 7.11 (t, 8 H, m-C<sub>6</sub> $\underline{H}_5$ , J = 18 Hz); 3.53 (t, 10 H, O-CH<sub>2</sub>-C $\underline{H}_2$ , J = 6 Hz); 3.41 (t, 6 H, O-C<u>H</u><sub>2</sub>-CH<sub>2</sub>, J = 12 Hz,); 3.38 (s, 12 H, O-CH<sub>3</sub>); 3.37-3.34 (m, 8 H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 1.68-1.63 (m, 8 H, CH<sub>2</sub>-C<u>H</u><sub>2</sub>-CH<sub>2</sub>); 0.65-0.63 (m, 8 H, Si-C<u>H</u><sub>2</sub>); 0.24 (s, 24 H, Si-(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ: 11.1 (4 Si, O-<u>Si</u>-CH<sub>2</sub>); -79.5 (4 Si, <u>Si</u>-O-Si).

*cis*-Tetra {phenyl[(dimethyl)(methylpropyldiethylene glycol)siloxy]}cyclotetrasiloxane (3b). The reaction and the work-up were carried out similarly to the preparation of compound 3a. Compound 2 (2 g, 3.25 mmol) in benzene (10 mL) was added to a mixture of diethylene glycol methyl allyl ether (2.39 g, 14.9 mol) in benzene (8 mL) and a Karsted catalyst (2 µL, 0.1 µL per 1 mL of the reaction mixture), and the mixture was stirred at 65 °C for 2 days. After evaporation of the solvent, the product 3b was isolated by preparative HPLC. The yield was 1.49 g (41%). Found (%): C, 53.68; H, 7.75; Si, 15.46.  $C_{64}H_{112}O_{20}Si_8$ . Calculated (%): C, 53.90; H, 7.92; Si, 15.75. <sup>1</sup>H NMR (CDCl<sub>3</sub>), &: 7.32–7.26 (m, 12 H, o-C $H_2$ ); 7.11–7.07 (m, 8 H, p-C $_6H_5$ ); 3.66–3.61 (m, 18 H, O–CH<sub>2</sub>–CH<sub>2</sub>); 3.57 (t, 14 H, O–CH<sub>2</sub>– CH<sub>2</sub>, J = 12 Hz); 3.40 (s, 12 H, O–CH<sub>3</sub>); 3.38–3.37 (m, 8 H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 1.62–1.57 (m, 8 H, CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>); 0.60–0.57 (m, 8 H, Si-CH<sub>2</sub>); 0.20 (s, 24 H, Si-(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), δ: 11.1 (4 Si, O-<u>Si</u>-CH<sub>2</sub>); -79.6 (4 Si, <u>Si</u>-O-Si).

*cis*-Tetra{phenyl[(dimethyl)(methylpropyltriethylene glycol)siloxy]}cyclotetrasiloxane (3c) was obtained similarly from compound 2 (2.5 g, 3.18 mmol) in benzene (14 mL), triethylene glycol methyl allyl ether (3 g, 14.6 mmol) in benzene (12 mL), and a Karsted catalyst (3  $\mu$ L, 0.1  $\mu$ L per 1 mL of the reaction mixture), the yield was 2.14 g (42%). Found (%): C, 52.54; H, 7.69; Si, 14.32. C<sub>72</sub>H<sub>128</sub>O<sub>24</sub>Si<sub>8</sub>. Calculated (%): C, 53.97; H, 8.05; Si, 14.02. <sup>1</sup>H NMR (CDCl<sub>3</sub>), &: 7.28-7.05 (m, 12 H, C<sub>6</sub>H<sub>5</sub>); 7.09-7.06 (m, 8 H, 4-m-C<sub>6</sub>H<sub>5</sub>); 3.66-3.61 (m, 26 H, OCH<sub>2</sub>CH<sub>2</sub>); 3.56-3.55 (m, 22 H, OCH<sub>2</sub>CH<sub>2</sub>); 3.38 (s, 12 H, OCH<sub>3</sub>); 3.36-3.34 (m, 8 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 1.61-1.56 (m, 8 H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>); 0.59-0.56 (m, 8 H, Si-CH<sub>2</sub>); 0.19 (s, 24 H, Si(CH<sub>3</sub>)<sub>2</sub>). <sup>29</sup>Si NMR (CDCl<sub>3</sub>), &: 11.1 (4 Si, O-<u>Si</u>-CH<sub>2</sub>); -79.6 (4 Si, Si-O-Si).

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#### References

- 1. R. Ludwig, J. Fresenius, Anal. Chem., 2000, 367, 103-128.
- V. Torgov, G. Kostin, V. Mashukov, T. Korda, A. Drapaillo, V. Kalchenko, *Solv. Extr. Ion Exch.*, 2005, 23, 171–187.
- G. A. Evtyugin, E. E. Stoikova, R. V. Shamagsumova, *Russ. Chem. Rev. (Engl. Transl.)*, 2010, **79**, 1071–1097.
- 4. L. M. Blinov, Russ. Chem. Rev. (Engl. Transl.), 1983, 52, 713-735.
- 5. Y. Matsuzawa, Colloids Surf., A, 2004, 247, 47-53.
- J. C. Tyson, J. L. Moore, K. D. Hughes, D. M. Collardet, Langmuir, 1997, 13, 2068–2073.
- A. K. Hassan, A. V. Nabok, A. K. Ray, F. Davis, C. J. Stirling, *Thin Solid Films*, 1998, 327–329, 686–689.
- F. Liu, G. Lu, W. He, M. Liu, L. Zhu, *Thin Solid Films*, 2002, **414**, 72–77.
- 9. J. H. Kim, Y. G. Kim, K. H. Li, S. W. Kang, Synth. Met., 2001, 117, 145–148.

- 10. L. Dei, A. Casnati, P. Lonostro, *Langmuir*, 1995, **11**, 1268–1272.
- Y. Zhifeng, S. Pang, W. He, X. Shi, Z. Guo, L. Zhu, Spectrochim. Acta, Part A, 2001, 57, 1443–1447.
- H. Weijiang, L. Fang, Y. Zhifeng, Y. Zhang, Z. Guo, L. Zhu, Langmuir, 2001, 17, 1143–1149.
- D. Vollhardt, J. Gloede, G. Weidemann, R. Rudert, *Lang-muir*, 2003, **19**, 4228–4234.
- O. Shchegolikhina, Yu. Pozdniakova, M. Antipin, D. Katsoulis, N. Auner, H. Herrshaft, *Organometallics*, 2000, 19, 1077–1082.
- O. Shchegolikhina, Y. Pozdnyakova, Y. Molodtsova, S. Korkin, S. Bukalov, L. Leites, K. Lyssenko, A. Peregudov, N. Auner, D. Katsoulis, *Inorg Chem.*, 2002, 41, 6892–6904.
- 16. J. Light, R. Breslow, Org. Synth., 1995, 72, 199-208.
- R. S. Goglev, M. B. Neiman, Vysokomolekulyarnye soedineniya. Khimicheskie svoistva i modifikatsiya polimerov [High-molecular-weight Compounds. Chemical Properties and Modification of Polymers], Nauka, Moscow, 1964, 156 pp. (in Russian).
- D. W. Van Krevelen, Properties of Polymers: Their Estimation and Correlation with Chemical Structure, Elsevier, Amsterdam, 1972, p. 439.
- 19. D. J. Kuzmenka, S. Granick, *Macromolecules*, 1988, **21**, 779–782.
- M. Winterhalter, H. Burner, S. Marzinka, R. Benz, J. Kasianowicz, *Biophys. J.*, 1995, 69, 1372–1381.
- 21. J. P. Kampf, C. W. Frank, E. E. Malmstrom, C. J. Hawker, *Langmuir*, 1999, **15**, 227–233.
- 22. N. A. Novozhilova, Yu. N. Malakhova, A. I. Buzin, M. I. Buzin, E. A. Tatarinova, N. G. Vasilenko, A. M. Muzafarov, *Russ. Chem. Bull. (Int. Ed.)*, 2013, **62**, 2514–2526 [*Izv. Akad. Nauk, Ser. Khim.*, 2013, 2514].
- 23. H. W. Fox, P. W. Taylor, W. A. Zisman, *Ind. Eng. Chem*, 1947, **39**, 1401–1409.
- 24. S. I. Belousov, A. I. Buzin, Y. K. Godovskii, *Polym. Sci., Ser. B* (*Engl. Transl.*), 1999, **41**, 303–324 [*Vysokomolekulyar. Soedin., Ser. B*, 1999, **41**, 1687–1711].

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