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Synthesis and hydrodynamic properties of star poly(2-alkyl-2-oxazolines) and poly(2-alkyl-2-oxazines) based on sulfochlorinated calix[4]arene initiator

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§1. Materials and methods

Materials and reagents

Sulfolane (Merck) was distilled in vacuum (*BP* = 166 °C, *p* = 1 Torr). Monomers including 2-ethyl-2-oxazoline, 2-isopropyl-2-oxazoline, 2-ethyl-2-oxazine and 2-isopropyl-2-oxazine (Aldrich) were distilled over calcium hydride. *p-tert*-Butylcalix[4]arene (Aldrich), aluminium chloride (Aldrich), phenol (Aldrich) and chlorosulfonic acid (Aldrich) was used as received. The synthesis of the initiator 5,11,17,23-tetrakis(chlorosulfonyl)-25,26,27,28-tetrakis(methoxy-carbonylmethoxy)calix[4]arene was carried out according to the previously published techniques without significant changes. The solvents were dried according to standard methods.

Characterization of chemicals

The ^{1}H NMR spectra were obtained on the Bruker AC400 instrument (400 MHz) for $CDCl_3$ or DMSO-d_6 solutions. Dialysis of polymers was performed using CellaSep dialysis tubes with MWCO 3500 Da. UV–Vis spectra were measured on a LOMO FOTONIKA SF-256 spectrophotometer.

Synthesis of 25,26,27,28-tetrahydroxycalix[4]arene

tert-Butylcalix[4]arene (10 g, 15.4 mmol), phenol (24.5 g, 0.184 mol), aluminum chloride (24.5 g, 0.184 mol) and toluene (150 ml) were loaded into a flask equipped with a stirrer and reflux condenser. The mixture was stirred for 1 h in a stream of argon at room temperature, then it was poured into HCl solution (0.2 M, 170 ml). The organic layer was separated and the remaining solvent was distilled off. The resulting precipitate was washed with methanol (330 ml), then acidified with a few drops of hydrochloric acid, and filtered. The product was purified by extraction into boiling chloroform (150 ml) for 24 hours. Yield: 5.5 g (84%). ^{1}H NMR (400 MHz, DMSO, 20 °C): δ (ppm) 6.0-7.0 (m, 12H), 3.5 (s 8H). Quantitative elemental analysis: C (80.7%), H (8.4%), O (10.9%).

Synthesis of 25,26,27,28-tetrakis(methoxycarbonylmethoxy)calix[4]arene

Potassium carbonate (58 g, 0.42 mol), potassium iodide (22.4 g, 0.134 mol), tetrahydroxycalix[4]arene (3.45 g, 8.2 mmol), and acetonitrile (180 ml) were placed in a flask equipped with a reflux condenser and a dropping funnel. The mixture was heated to 70 °C in a stream of argon, then methyl chloroacetate (36 ml, 0.42 mol) was added dropwise. The mixture was refluxed for 24 h, then poured into water (300 ml). The product was extracted with diethyl

ether (2×100 ml), washed with HCl solution (0.1 M, 100 ml) followed by distilled water. The solvent was removed, and residue was recrystallized from methanol. Yield: 2.1 g (36%). ^{1}H NMR (400 MHz, CDCl3, 20 °C): δ (ppm) 6.9 (m, 12H), 4.27 (m, 8H), 4.10 (s, 8H), 3.7 (s, 12H). Quantitative elemental analysis, %: C, 67.5; H, 6.0; O, 26.5. $C_{40}H_{40}O_{12}$. Calcd., %: C, 67.41, H, 5.66, O, 26.94.

Synthesis of 5,11,17,23-tetrakis(chlorosulfonyl)-25,26,27,28-tetrakis(methoxycarbonyl-methoxy)calix[4]arene **1**

Tetrakis(methoxycarbonylmethoxy)calix[4]arene (2 g, 2.82 mmol) and chloroform (60 ml) were placed in a flask equipped with thermometer, reflux condenser and calcium chloride tube. The solution was cooled to -10 °C, and chlorosulfonic acid (40 ml, 0.6 mol) was then added dropwise. The mixture was stirred at 50 °C for 20 min. After cooling to room temperature, the resulting mixture was poured into a bucket with ice water (400 ml), then petroleum ether (300 ml) was added with vigorous stirring. The precipitate was filtered off, washed with water, petroleum ether, and dried. The product was recrystallized twice in a mixture of CH_2Cl_2 and petroleum ether. Yield: 1.5 g (49%). ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ (ppm) 7.6 (m, 8H), 4.2-4.7 (m, 16H), 3.7 (s, 12H). Quantitative elemental analysis, %: C, 43.8; H, 3.1; Cl, 11.2, O, 31.4; S, 10.5. $C_{40}H_{36}Cl_4O_{20}S_4$. Calcd., %: C, 43.41, H, 3.28, Cl, 12.81; O, 28.91, S, 11.59.

Polymerization kinetic study

A tube was loaded with 2-ethyl-2-oxazoline (0.3 g, 3.03 mmol) of, sulfolane (0.3 g, 2.50 m mol) and initiator **1** (27.8 mg, 0.0252 mmol). The mixture was heated at 100°C, and samples were taken at regular intervals in NMR tubes, cooled to 0°C and then studied by ^{1}H NMR spectroscopy in $CDCl_3$.

Synthesis of star-shaped poly(2-alkyl-2-oxazolines) **2a,b** *and poly(2-alkyl-2-oxazines)* **2c,d**

All samples were synthesized according to the typical procedure. An ampoule was loaded with the initiator **1** and the corresponding monomer at a molar ratio of 1:120, respectively, and equal weight of dry sulfolane was added. The mixture was heated at 100°C until the full conversion of the monomer (24 h for **2a**, 48 h for **2b**, 72 h for **2c**, 96 h for **2d**). In order to terminate the polymerization process, pyrrolidine (1 ml) was added, and the resulting solution was stirred at 50°C for 1 h. The product was dialyzed against water for 24 h and then lyophilized.

Star poly(2-ethyl-2-oxazoline) **2a**

2-Ethyl-2-oxazoline (2 g, 20.1 mmol), initiator **1** (0.1851 g, 0.168 mmol), and sulfolane (2 g, 17 mmol) were taken. The yield of the product was 1.87 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ 3.47 (br, 4H), 2.41+2.32 (br, 2H), 1.14 (m, 3H) ppm.

Star poly(2-isopropyl-2-oxazoline) **2b**

2-Isopropyl-2-oxazoline (2 g, 17.7 mmol), initiator **1** (0.1621 g, 0.147 mmol), and sulfolane (2 g, 17 mmol) were taken. The yield of the product was 1.85 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ 3.44 (br, 4H), 2.87+2.64 (d, 1H), 1.14 (m, 6H) ppm.

Star poly(2-ethyl-2-oxazine) **2c**

2-Ethyl-2-oxazine (2 g, 17.7 mmol), initiator **1** (0.1621 g, 0.147 mmol), and sulfolane (2 g, 17 mmol) were taken. The yield of the product was 1.54 g (71%). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ 3.31 (br, 4H), 2.32 (br, 2H), 1.81 (br, 2H), 1.15 (m, 3H) ppm.

Star poly(2-isopropyl-2-oxazine) **2d**

2-Isopropyl-2-oxazine (2 g, 15.7 mol), initiator **1** (0.1440 g, 0.131 mmol), and sulfolane (2 g, 17 mmol) were taken. The yield of the product was 1.20 g (56%). ^{1}H NMR (400 MHz, $CDCl_3$, 20°C): δ 3.34 (br, 4H), 2.72 (br, 1H), 1.80 (br, 2H), 1.14 (m, 6H) ppm.

§2. ^{1}H NMR spectra

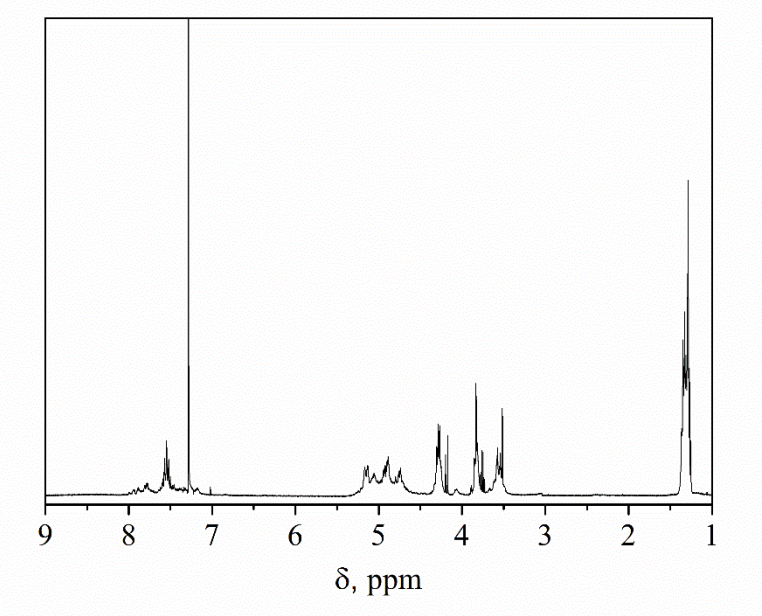

Figure S1. ^{1}H NMR spectrum of initiator **1** based on calix[4]arene functionalized with initiating groups in the upper rim.

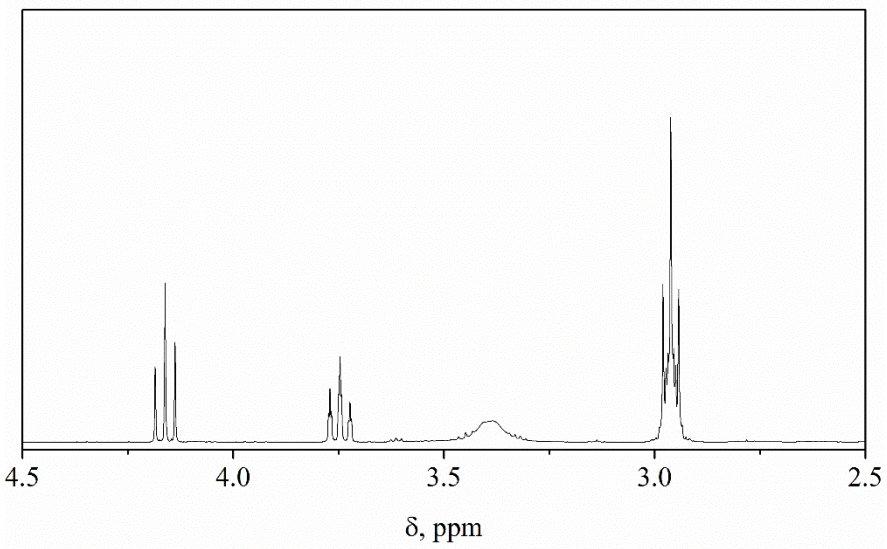

Figure S2. ^{1}H NMR spectrum of the reaction mixture of 2-ethyl-2-oxazoline polymerization in sulfolane at 100°C.

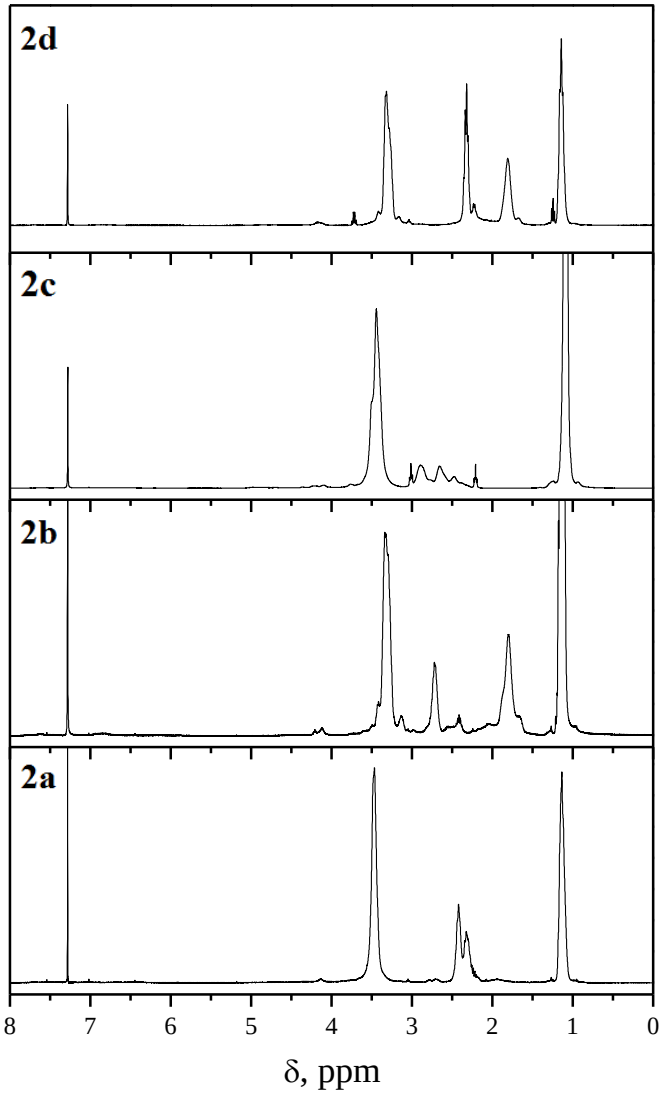

Figure S3 ^{1}H NMR spectra of synthesized star polymers **2a-d**.

§3. Gel permeation chromatography

Chromatographic analysis was performed on the Shimadzu Prominence LC-20 instrument equipped with a RID-10A refractometric detector and a Waters Styragel HT4 column (10 μm, 7.8 × 300 mm). Measurements were carried out in DMF eluent at 60°C with the flow rate of 1.0 ml min^{-1}. The calibration curve was calculated using polystyrene standards.

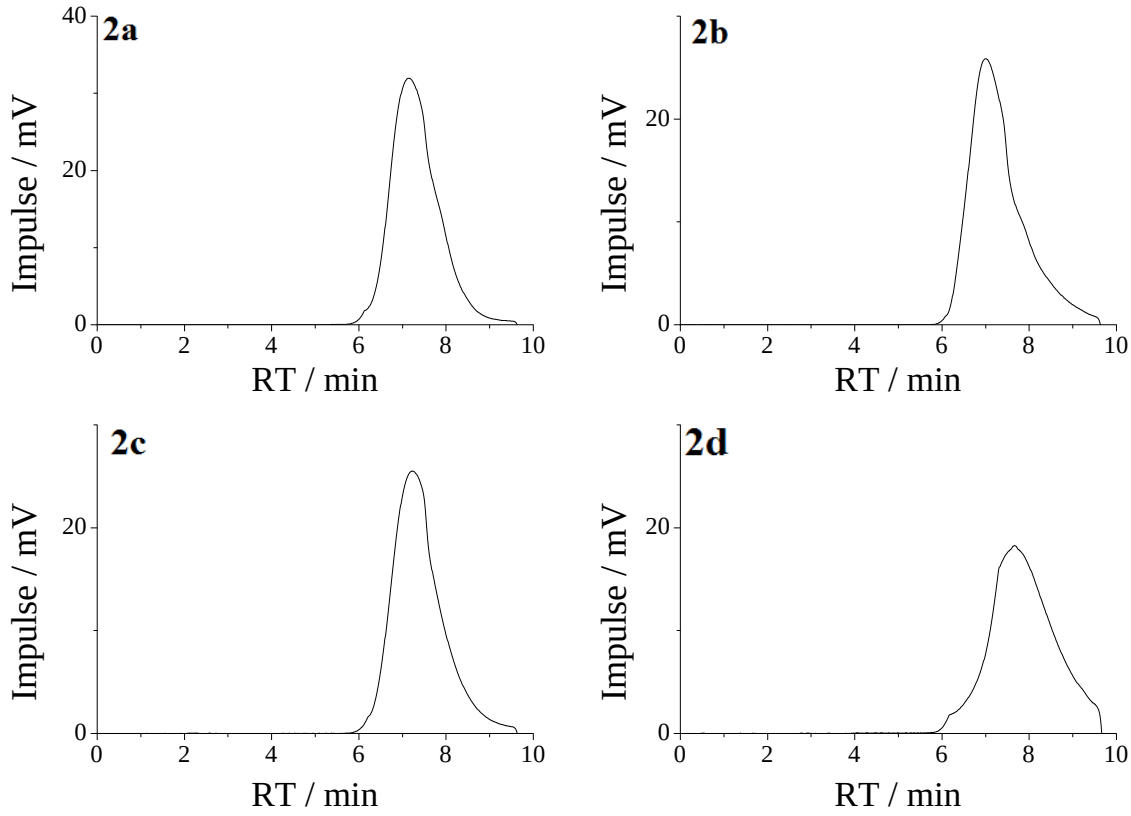

Figure S4. GPC traces of synthesized star polymers **2a-d**.

§4. Molecular hydrodynamic and optic methods

The methods of static and dynamic light scattering were used for the determination of molar mass and hydrodynamic characteristics of star-shaped PAlOx and PAlOz in chloroform (a density of ρ = 1.486 g·cm^{-3}, a dynamic viscosity of η_0 = 0.57 cP, and a refractive index of n_0 = 1.446), in which the aggregates were not formed. The temperature T of the experiments was 21°C. Light scattering experiments were performed using Photocor Complex instrument (Photocor Instruments Inc., Russia) equipped with diode laser Photocor-DL (wavelength λ = 658.7 nm), Photocor-PC2 correlator with 288 channels, and Photocor-PD detection device for measuring the transmitted light intensity. The scattering angle was 90°.

All solutions were filtered into dust-free vials using Millipore filters (Millipore Corporation, USA) with a PTFE membrane with the pore size of 0.20 μm.

The hydrodynamic radii $R_{h\text{-}D}$ of macromolecules were obtained by dynamic light scattering (Figure S5).

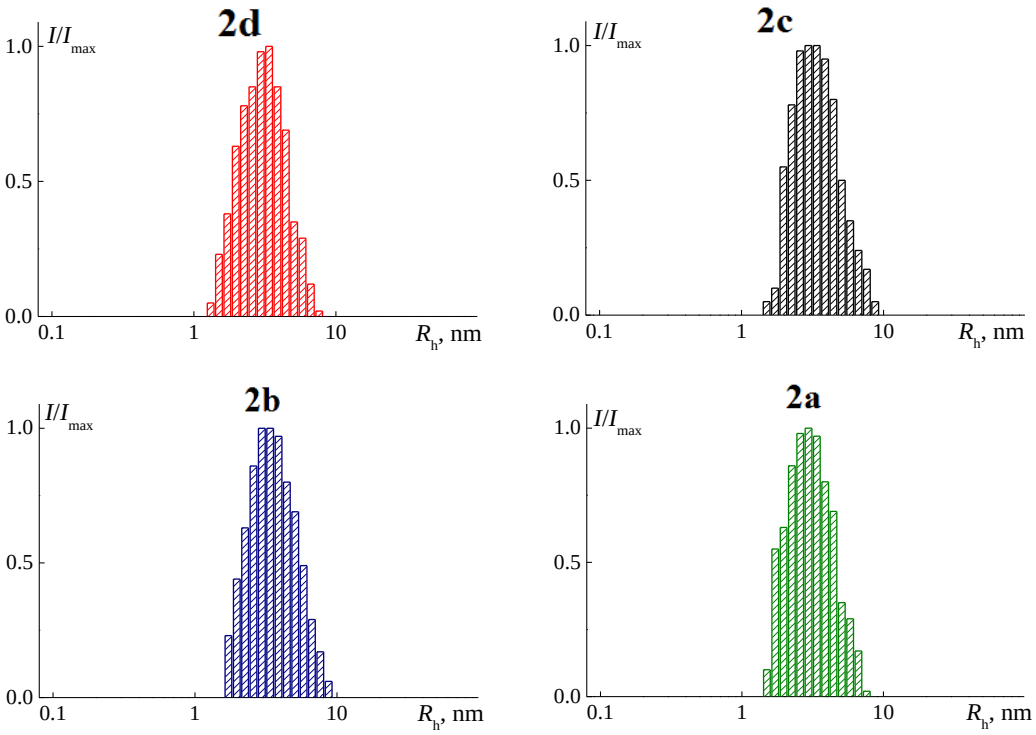

Figure S5 The dependences of relative intensity I/I_{max} of scattered light on the size of scattering species R_h in chloroform solutions of polymer stars **2a-d**.

The weight-average molar masses M_w were obtained by Debye method (Figure S6).

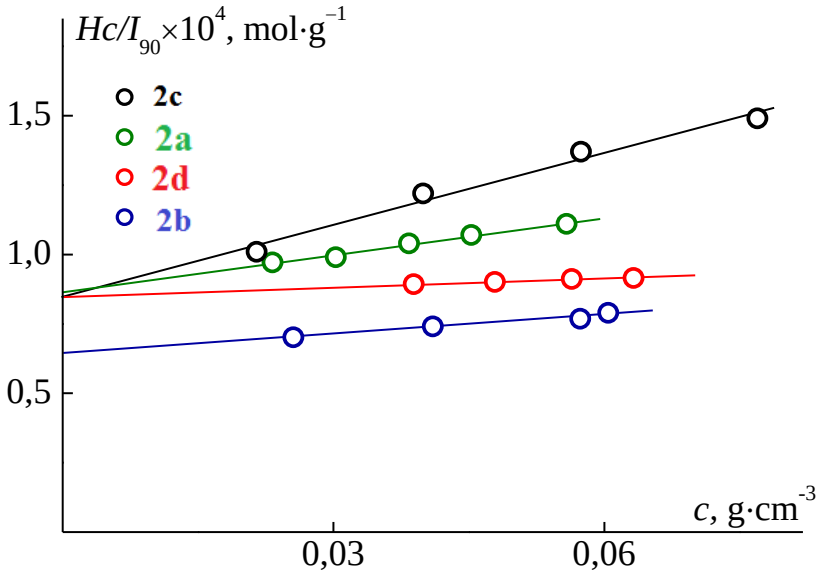

Figure S6 Concentration dependences of Hc/I_{90} for the solutions of polymer stars **2a-d** in chloroform.

The intrinsic viscosity was measured with the Ostwald-type Cannon–Manning capillary viscometer (Cannon Instrument Company Inc., USA) at 21 °C. The solvent efflux time was 78.5 s (Figure S7).

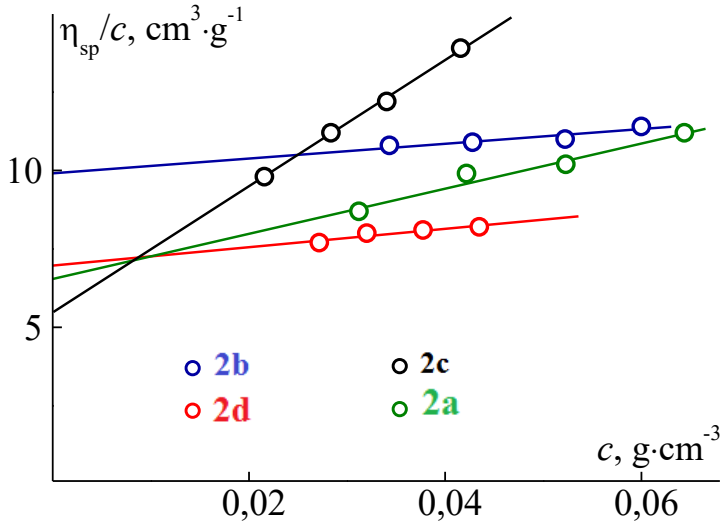

Figure S7 Reduced viscosity η_{sp}/c vs. c for the studied polymer stars **2a** (*1*), **2b** (*2*), **2c** (*3*) and **2d** (*4*). in chloroform.