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Star-shaped thermosensitive poly-*N*-acyl-1,3-propylenimines with trianglamine core

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Materials and methods

The synthesis of poly-*N*-acyl-1,3-propylenimines by polymerization of 2-alkyl-5,6-dihydro-4*H*-oxazines was carried out in a Discover LabMate single-mode microwave reactor (CEM Corporation, United States) at a magnetron frequency of 2.45 GHz and a maximum generator power of 150 W during 2 h. The reaction temperature (100 °C) was controlled by an IR thermometer on the retort outer surface. The NMR spectra were measured on the Bruker AC400 (400 MHz) spectrometer using chloroform and dimethyl sulfoxide solutions. For the purification of the synthesized polymers, it was used Zellu Trans dialysis tubes (Scienova GmbH, Germany. Material: cellulose, regenerated) with MWCO 3500 Da. Chromatographic analysis was performed on the Shimadzu LC-20AD chromatograph equipped with the refractive detector. Samples were studied with the help of Waters Styragel HT4 column (10 μm, 7.8 × 300 mm) in dimethylformamide solutions at 60 °C. Polyethylene oxide standards were chosen for calibration curve. The absolute values of molar masses are determined by static light scattering methods in dilute solutions in 2-nitropropane. The experiments were performed on a Photocor Complex instrument (Photocor Instruments Inc.), which is equipped with a Photocor DL a diode laser (wavelength λ = 632.8 nm and power 5–30 mW).

Synthetic procedures

Star polymer arms were synthesized using the 'grafting on' approach based on the breaking of polyoxazines 'living chains' on trianglamine **1**. An ampule containing 2-ethyl- or 2-isopropyl-5,6-dihydro-4*H*-oxazine (17.7 mmol), TsOMe (110 mg, 0.59 mmol), and sulfolane (3 mL) was frozen to –196 °C, air was removed under vacuum (0.1 Torr), and the mixture was thawed in argon atmosphere. The cycle was repeated three times, then the ampule was sealed and heated at 70 °C for 48 h. The ampule was opened, and a solution of trianglamine **1** (30 mg, 0.046 mmol) and cesium carbonate (195 mg, 0.6 mmol) in sulfolane (0.5 mL) was added. The ampule was sealed again and heated at 100 °C for 2 h. The reaction mixture was dialyzed against to water and freezing dried.

Arms for block copolymer **2c** were synthesized by polymerization of 2-ethyl-5,6-dihydro-4*H*-oxazine, and thus obtained **3a** was further elongated with 2-isopropyl-5,6-dihydro-4*H*-oxazine. Methyl tosylate (109 mg, 0.6 mmol), 2-ethyl-5,6-dihydrooxazine (1 g, 8.0 mmol) and sulfolane (1 mL) were heated in a sealed ampule at 70 °C for 48 h. The ampule was opened and the second monomer, 2-isopropyl-5,6-dihydrooxazine, (1 g, 8.0 mmol) was added, and the reaction mixture was again heated at 70 °C for 48 h. After completion of polymerization, the process was terminated by addition of trianglamine **1** (21.3 mg, 0.033 mmol) and cesium carbonate (140 mg, 0.43 mmol) in sulfolane (1.0 mL) and heating at 100 °C for 2 h. The reaction mixture was dialyzed against to water and freezing dried.

^{1}H NMR spectrum of **3a** contains multiplets at 1.21 and 2.06 ppm which can be attributed to cyclohexane moieties, doublets at 3.76 and 3.69 ppm relate to benzylic ($ArCH_2$) protons while signals of the acylated poly-*N*-propionyl-1,3-propylenimine chain locate at 3.23 ($CH_2CH_2CH_2N$), 2.28 ($CO–CH_2–CH_3$) 1.71 ($CH_2CH_2CH_2N$) and 0.96 ($CO–CH_2–CH_3$) ppm. In NMR spectra of **3b** and **3c** signals for isopropyl group are observed at 2.65 ($CH(CH_3)_2$) and 1.11 ($CH(CH_3)_2$) ppm.

Job's plot, ^{1}H NMR spectra and thermosensitivity data

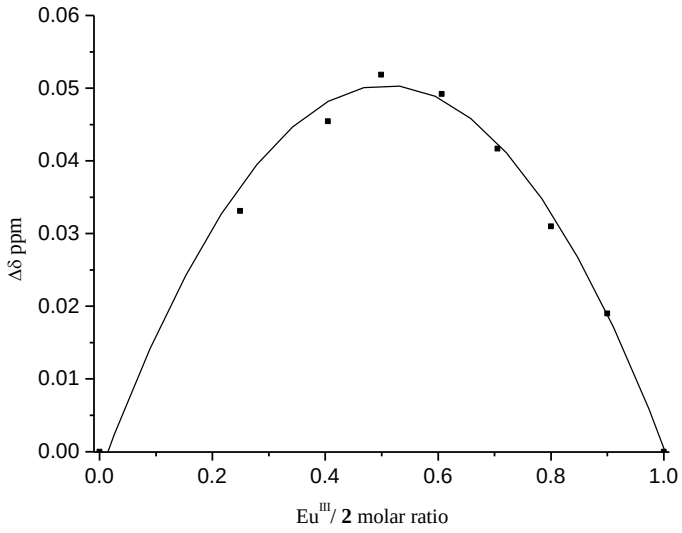

Figure S1 Job's plot analysis in $EuCl_3$ trianglamine mixture (NMR).

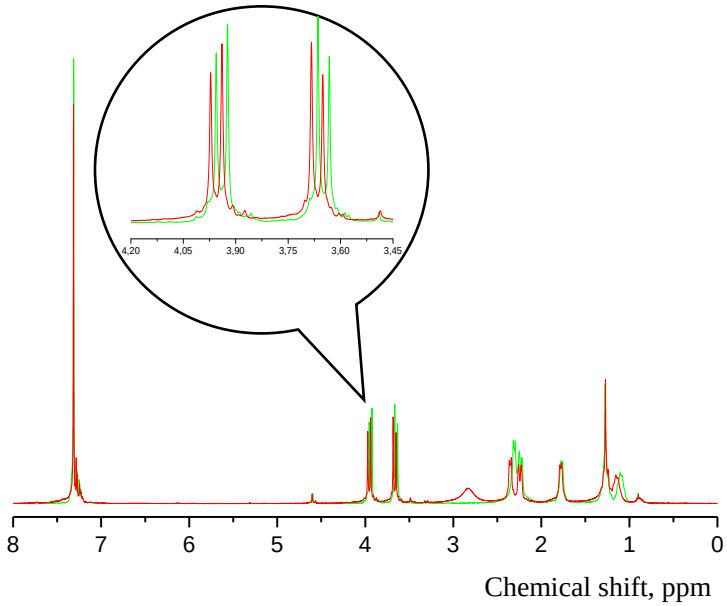

Figure S2 ^{1}H NMR spectrum of trianglamine **1** (green) and its complex **1**·$EuCl_3$ (red).

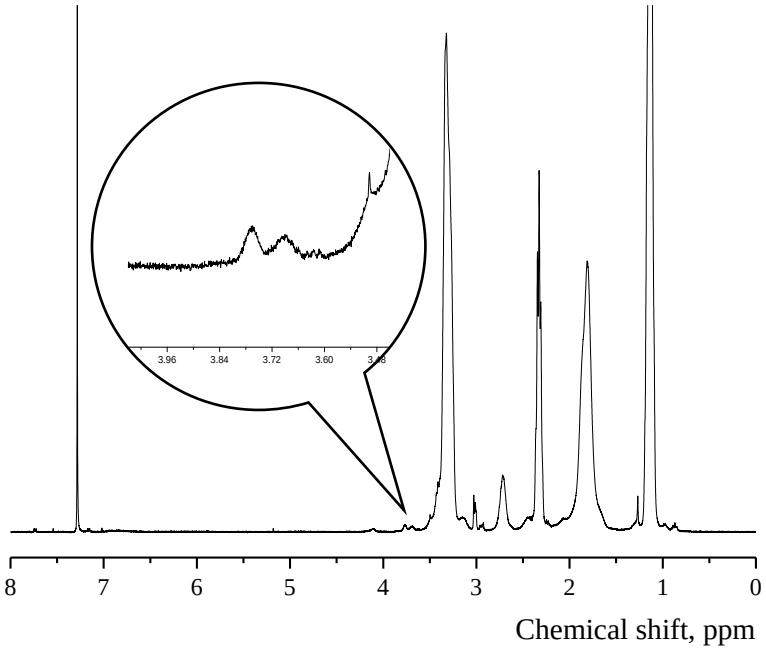

Figure S3 ^{1}H NMR spectrum of **2a**.

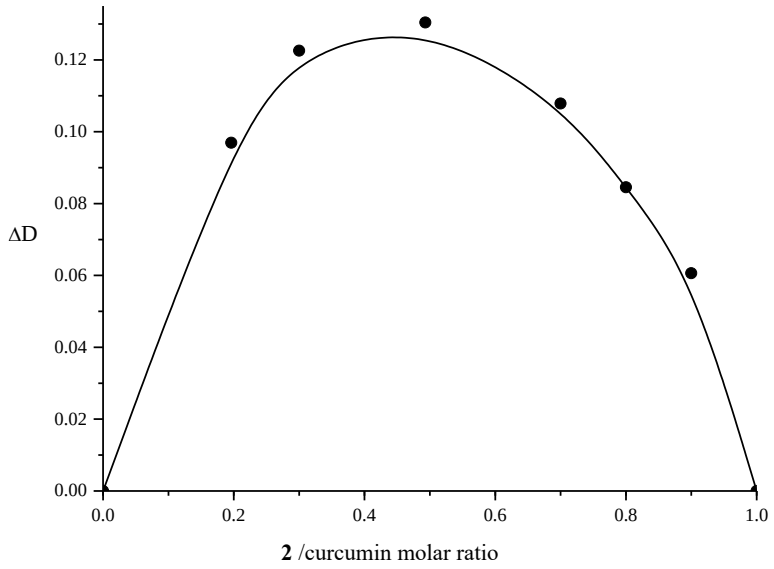

Figure S4 Job's plot analysis of trianglamine (**1**)/curcumin mixture (UV).

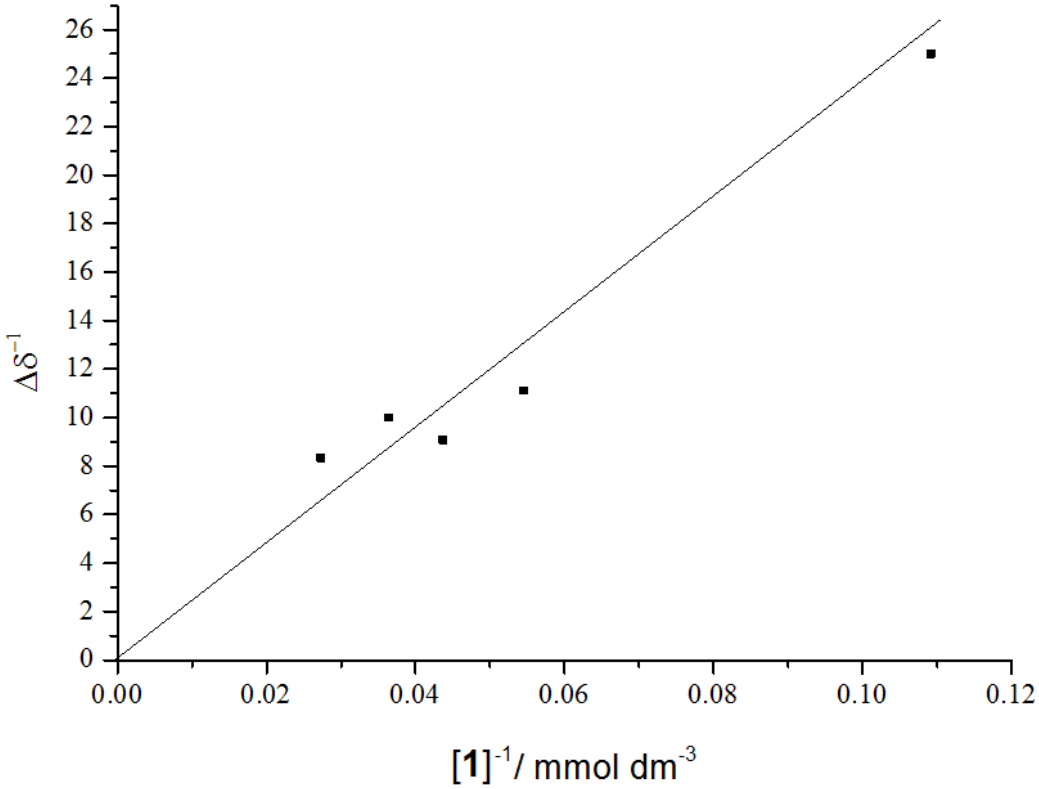

Figure S5 The Benesi–Hildebrand plot for $EuCl_3$/trianglamine (**1**) system.

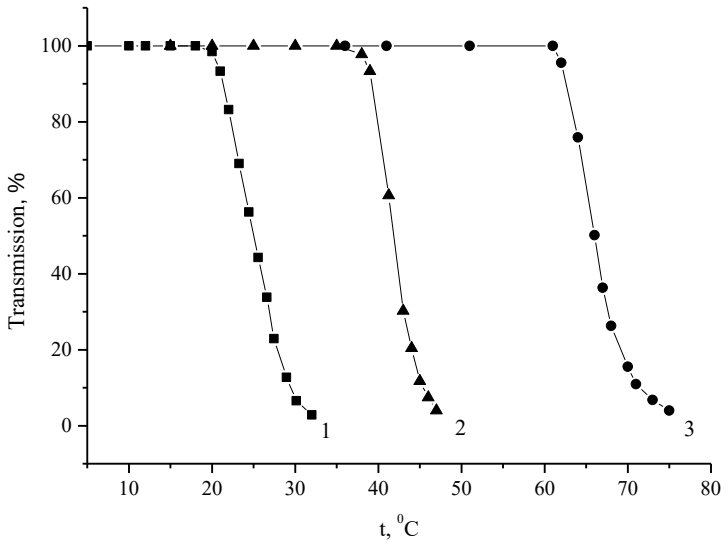

Figure S6 Transmission of 0.5 % aqueous solution of polymers **2b** (*1*), **2c** (*2*) and **2a** (*3*) *vs* temperature.