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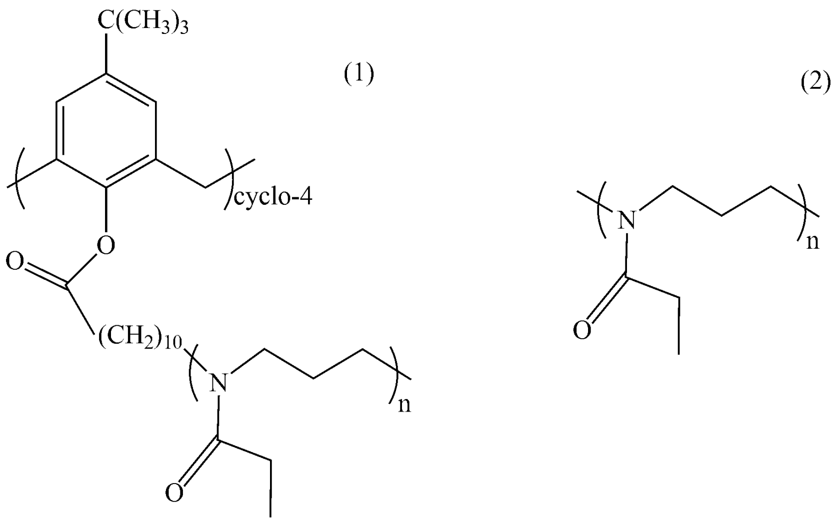
Influence of molecular architecture on behavior of thermoresponsive poly-2-ethyl-2-oxazine in saline media

Anna V. Smirnova, Tatyana Yu. Kirila, Marina M. Dudkina,
Andrey V. Tenkovtsev and Alexander P. Filippov



Scheme S1 The structures of star-shaped C4A–pEtOz (1) and linear pEtOz (2).

Synthesis of linear pEtOz

An ampoule containing the desired amount of initiator (~124 mg), the appropriate amount of 2-ethyl-2-oxazine (feed ratio initiator:monomer = 1:30), and 2 mL of acetonitrile was sealed and heated at 100°C for 12 h. Afterwards 50% aqueous ethanol (1 mL) was added, and the resulting mixture was allowed to stay at room temperature for 24 h. The reaction mixture was dialyzed against water for 24 h, and lyophilized.

Characterization of linear pEtOz

1H NMR (CDCl3): δ ppm. 1.11 (br, CH2CH3), 1.79 (t, NCH2CH2CH2N), 2.27 (q, CH2CH3), 3.29 (m, NCH2CH2CH2N).

NMR spectra were measured on a Bruker AC400 (400 MHz) spectrometer in chloroform solutions. Dialysis was conducted using dialysis bags (CellaSep, Orange Scientific); MWCO, 3500 Da.

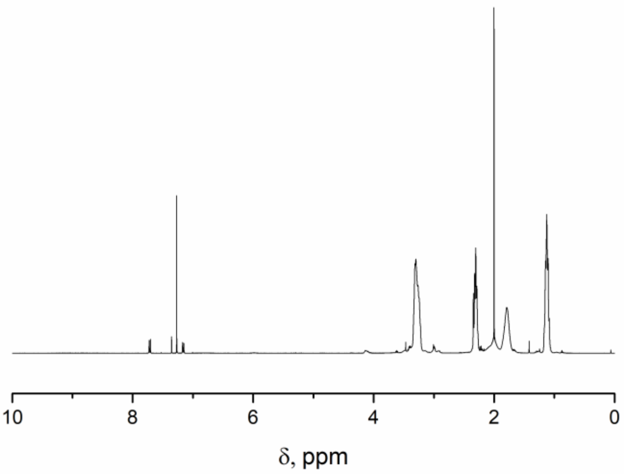


Figure S1 ^{1}H NMR spectrum of linear pEtOz.

^{1}H NMR spectrum of C4A–pEtOz see in [T.U. Kirila, A.V. Smirnova, A.S. Filippov, A.B. Razina, A.V. Tenkovtsev, A.P. Filippov, *Eur. Polym. J.*, 2019, 109215].

Chromatographic analysis was performed on a Shimadzu LC20AD chromatograph equipped with a TSKgel G5000HHR column (5 μm, 7.8 × 300 mm, TosohBioscience). The mobile phase was a solution of LiBr (0.1 mol/L) in DMF at 60°C.

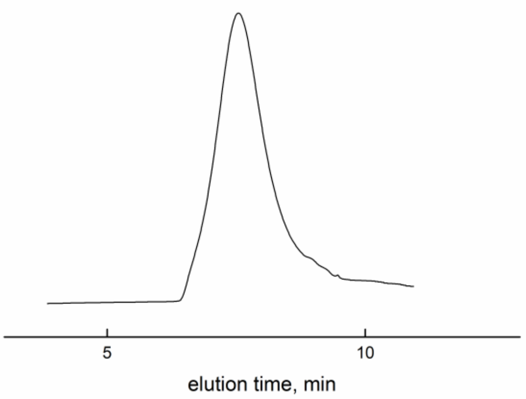


Figure S2 GPC eluogram of linear pEtOz.

Experimental

The self-assembly of pEtOz molecules in aqueous solutions was studied by turbidimetry, static and dynamic light scattering using Photocor Complex instrument (Photocor Instruments Inc., Russia) equipped with a detector for measuring transmitted light intensity. The light source was a diode laser with the wavelength λ = 658.7 nm and power from 5 to 30 mW. The correlation function of the scattered light intensity was obtained using the Photocor-PC2 correlator with the number of channels 288 and processed using the DynalS software. The solution temperature *T* was changed discretely, with the steps ranging from 6 °C at low temperatures to 1 °C near the cloud point. The temperature was regulated with the precision of 0.1 °C.

After the preset temperature was established, the dependences of the intensity of scattered light *I* (at a scattering angle of 90°) and optical transmission *I** on time *t* were recorded (Figure S3). At each temperature, we assumed that *t* = 0 was the moment when the sample reached the required temperature. The equilibrium values of *I* and *I** were reached at time t_{eq}. For linear pEtOz, t_{eq} was smaller than 2000 s, while for star-shaped polymer the t_{eq} value may exceed 8000 s. It is necessary to emphasize that the experiment time was equal to 1400 s at least at each temperature even if the measured characteristics did not depend on time.

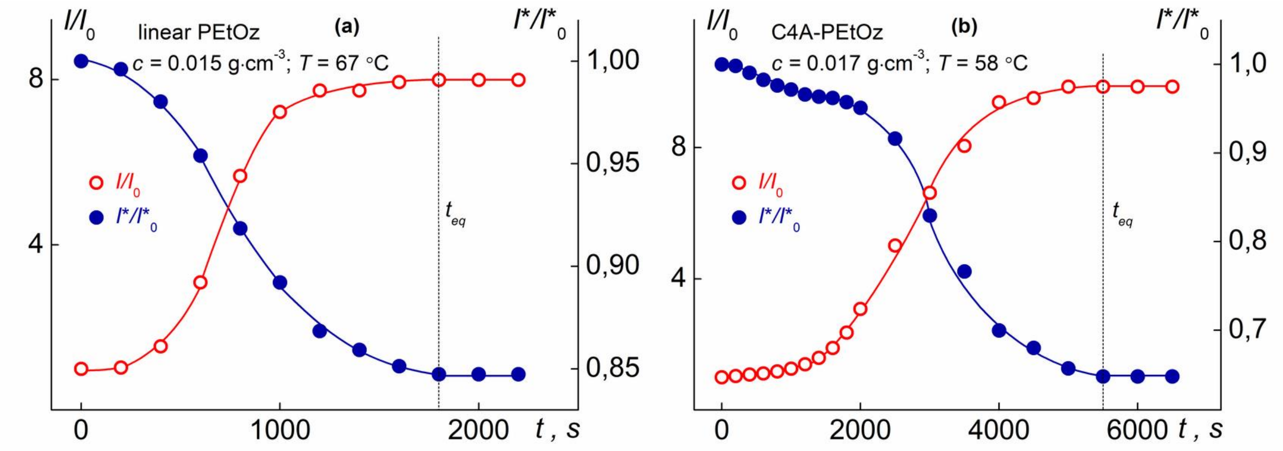


Figure S3 Dependences of light scattering intensity I/I_0 and optical transmission I^*/I_0^* on time *t* for linear pEtOz (a) and C4A–pEtOz (b). I_0 and I_0^* are the values of the intensity of light scattering and optical transmission at *t* = 0.

In equilibrium conditions, when solution characteristics did not change with time, the angle dependences of light scattering intensity *I* and hydrodynamic radii R_h of the scattering particles were analyzed (the scattering angle range was from 45° to 135°). In the cases when different scattering particles were present, the qualitative contribution of each particle type to the summary scattering intensity was estimated using the values of the square under the curved line of the corresponding *I* on R_h distribution peak (Figures S4 and S5).

We have investigated C4A–pEtOz and pEtOz in water-salt solutions at a concentration c = 0.0050 g/cm. The salt concentration variated at 0.00070 to 0.154 M for C4A-PEtOz and at 0, 0.0023 to 0.154 M for PEtOz.

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

NaCl solutions of concentration $c_{NaCl} = 0.70\times10^{-3}$, 9.10×10^{-3} and 36.4×10^{-3} M for C4A–pEtOz and $c_{NaCl} = 2.3\times10^{-3}$, 45.5×10^{-3} и 0.154 M for pEtOz were obtained by a dilution of 0.9 % (0.154 M) NaCl solution for injection, delivered in ampoules. After that, solutions of C4A–pEtOz and pEtOz were prepared separately in each of these saline solvents. Average salt content respect to polymers:

C4A–pEtOz c_{NaCl} = 0.70 mM NaCl: 1 salt molecule per 1 macromolecule;

C4A–pEtOz c_{NaCl} = 9.1 mM NaCl: 4 salt molecules per 1 macromolecule, i.e. 1 salt molecule per 1 arm;

C4A–pEtOz c_{NaCl} = 36.4 mM NaCl: 52 salt molecules per 1 macromolecule, i.e. 13 salt molecule per 1 arm and 1 salt molecule per 1 monomer unit of poly-2-ethyl-2-oxazine;

pEtOz c_{NaCl} = 2.3 mM NaCl: 1 salt molecule per 1 macromolecule;

pEtOz c_{NaCl} = 45.5 mM NaCl: 20 salt molecules per 1 macromolecule, i.e. 1 salt molecule per 1 monomer unit of poly-2-ethyl-2-oxazine.

The relative experimental errors were about 10% for molar mass, from 5% (R_h > 20 nm) to 20% (R_h < 5 nm) for hydrodynamic radii, 1% for light scattering intensity, 3% for optical transmission, and 0.1% polymer and salt concentration. The phase separation temperature was determined with an accuracy of 0.5 degree.

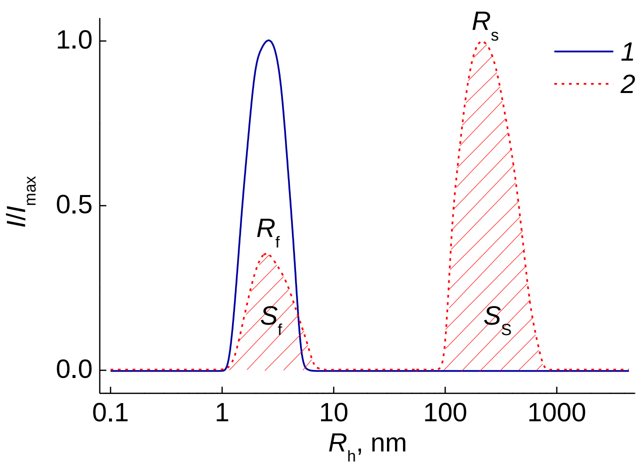


Figure S4 The distribution of light scattering intensity I on hydrodynamic radii R_h of scattering species for pEtOz solution at c_{NaCl} = 0.0455 M and T = 21°C (1) and 60°C (2).
The contributions of fast and slow modes are marked as S_f and S_s, respectively.

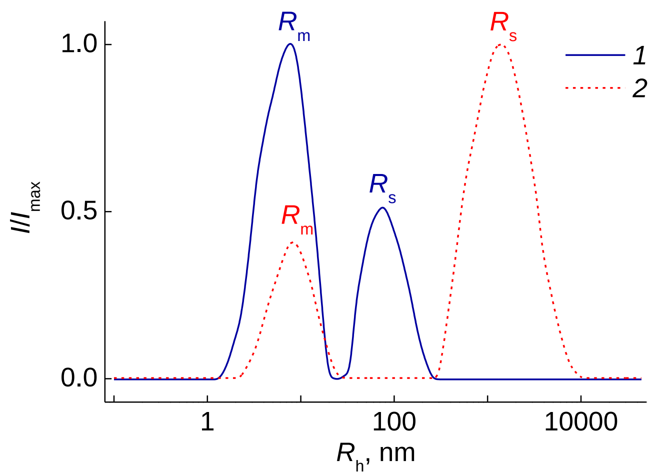


Figure S5 The distribution of light scattering intensity *I* on hydrodynamic radii R_h of scattering species for C4A–pEtOz solution of at c_{NaCl} = 0.0364 M and *T* = 21°C (1) and 33°C (2).

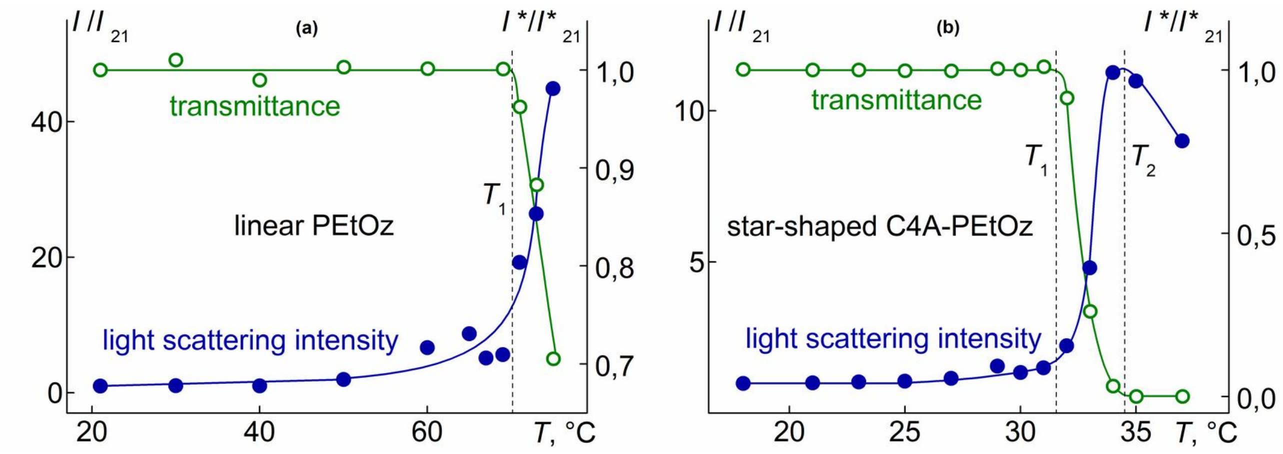


Figure S6 Temperature dependences of light scattering intensity *I* and optical transmittance *I** for solutions of linear pEtOz at c_{NaCl} = 0.0455 M (a) and star-shaped C4A–pEtOz at c_{NaCl} = 0.0364 M (b).