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Influence of hydrophilic and hydrophobic low-molecular-weight additives on the thermoresponsiveness of star-shaped poly-2-isopropyl-2-oxazoline in solution

Alina I. Amirova, Tatyana U. Kirila, Alexey N. Blokhin, Alla B. Razina, Anna E. Bursian, Andrey V. Tenkovtsev and Alexander P. Filippov

Solutions preparation

All molar polymer concentrations of solutions with N-PTS were calculated using M_w value. Volume concentration 0.005 g ml^{-1} of polyPr^{i}Ox solutions was recalculated to molar concentration using eight-average molecular weight M_w = 16300 g mol^{-1}:

0.005 g ml^{-1} = 0.005/16300 mol ml^{-1} = 3.07×10^{-7} mol ml^{-1} = 3.07×10^{-4} mol L^{-1} (i.e. 0.307×10^{-3} M).

Firstly, the relation of 1 N-PTS molecule per 1 monomer unit polyPr^{i}Ox is preserved. The molarity of N-PTS was calculated from target polymer concentration; the N-PTS solution was prepared in bidistilled water. After that, solutions of polyPr^{i}Ox of target concentrations were prepared separately in each of saline solvents.

Secondly, the effect of N-PTS content on the characteristics of the solutions was analyzed at polyPr^{i}Ox concentrations c = 0.005 and 0.0002 g ml^{-1}. The N-PTS solutions in bidistilled water were prepared in a wide concentration interval (0.33×10^{-3} – 39.3×10^{-3} M). At a concentration polyPr^{i}Ox of c = 0.005 g ml^{-1} average salt content respect to polymers:

polyPr^{i}Ox in 0.33 mM N-PTS: 1 salt molecule per 1 macromolecule;

polyPr^{i}Ox in 2.47 mM N-PTS: 8.0 salt molecule per 1 macromolecule, i.e. 1.0 salt molecule per 1 arm;

polyPr^{i}Ox in 39.3 mM N-PTS: 128 salt molecule per 1 macromolecule, i.e. 16 salt molecule per 1 arm and 1 salt molecule per 1 monomer unit of isopropyl-2-oxazoline.

A similar calculation was carried out for c = 0.0002 g ml^{-1}.

Tetraphenylporphyrin (TPhP) was purchased from Sigma-Aldrich and used without further purification. A certain amount of polyPr^{i}Ox (0.1 g) was carefully ground in a mortar with two times the molar excess of TPhP (0.0077g). The resulting fine brown powder was mixed with 10 mL of distilled water. The resulting mixture was sonicated for 15 min and shaken by the magnetic stirrer for 4 hours. After centrifugation at 4000 rpm, 15 min, the supernatant was twice filtered through Chromafil syringe filters with a pore size of 0.2 μm. For further research, the solution was diluted twice with either distilled water or an aqueous NaCl solution so that the final salt concentration equals 0.15 M (isotonic saline), resulting polymer concentration was 0.2 g ml^{-1} in both solvents. To determine the final resulting amount of TPhP in the solution, 5 ml of the aqueous polyPr^{i}Ox–TPhP complex solution was subjected to evaporation at room temperature and then dried in vacuum to a constant weight. The solid residue was re-dissolved in 5 ml of chloroform. The absorption of the solution at $\lambda = 419$ nm (so-called Soret band), where there is no measurable absorption of the polymer, was compared with the calibration curve.

Instruments

The Photocor Complex instrument equipped with a diode laser (wavelength $\lambda = 659.1$ nm) and a detector for measuring the transmitted light intensity I^* was used in experiments. Temperature T was ranged discretely from 21 to 76 °C. Scattering intensity I, I^*, hydrodynamic dimensions $R_{h\text{-}i}$ of the *i*-type scattering objects (one of two or three modes) and the contribution S_i of each particle type to the summary scattering intensity (as the square under the curved line of the corresponding peak of the distribution of I on R_h, Figure S1) were measured when equilibrium state was achieved at each T value, i.e. I, I^*, $R_{h\text{-}i}$ and S_i did not vary in time. The detailed measurement procedure was described previously [J. Polym. Res., 2016, 23, 221]. Temperature T_1 of the phase separation was determined as points of onset of the transparency decrease (Figure 2).

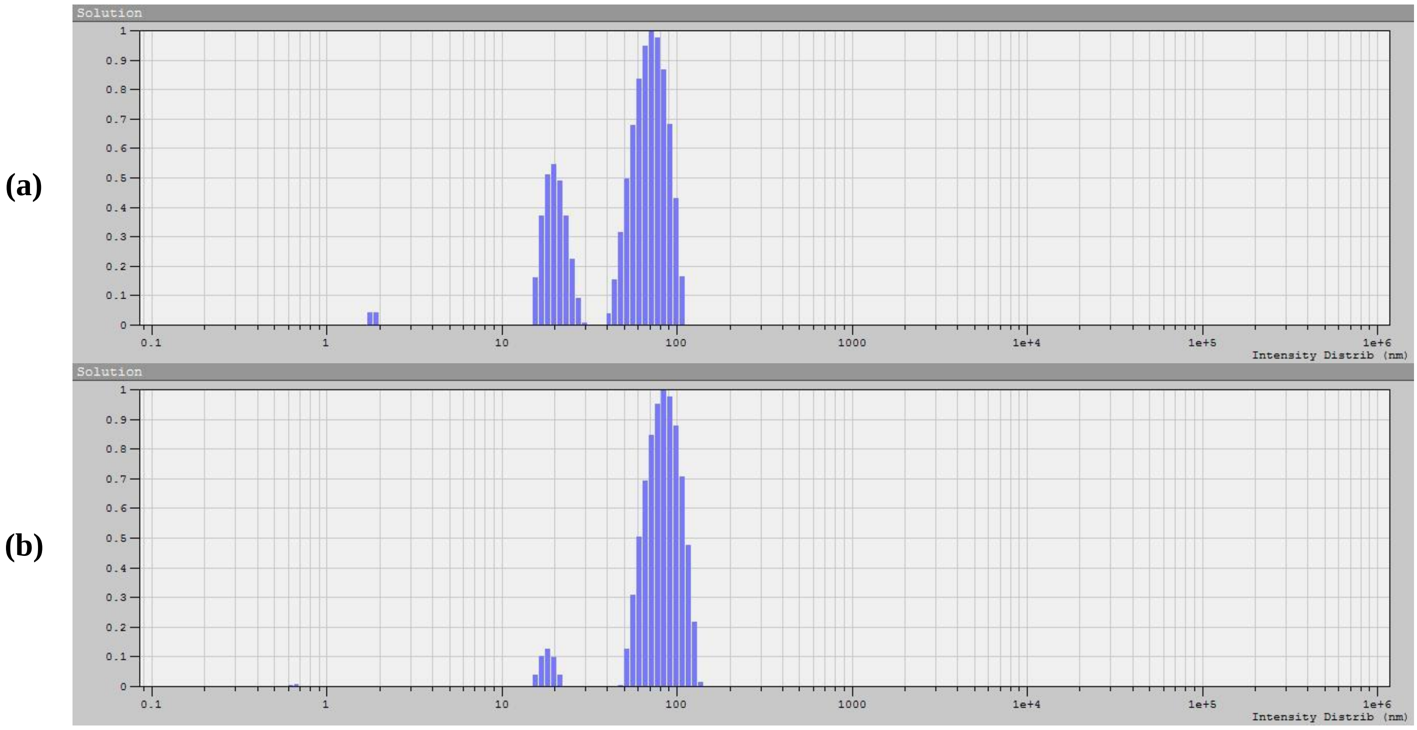

Figure S1 Distribution of light scattering intensity on hydrodynamic radii of scattering species in solution of **(a)** polyPr^{i}Ox at N-PTS content 1 molecule per 1 macromolecule, polymer concentration *c* = 0.005 g ml^{-1} and *T* = 21 °C. **(b)** polyPr^{i}Ox–TPhP complex at polymer concentration *c* = 0.002 g ml^{-1} and *T* = 21 °C.