

Supplementary information for

Tuning solution polymer properties by binary water–ethanol solvent mixtures

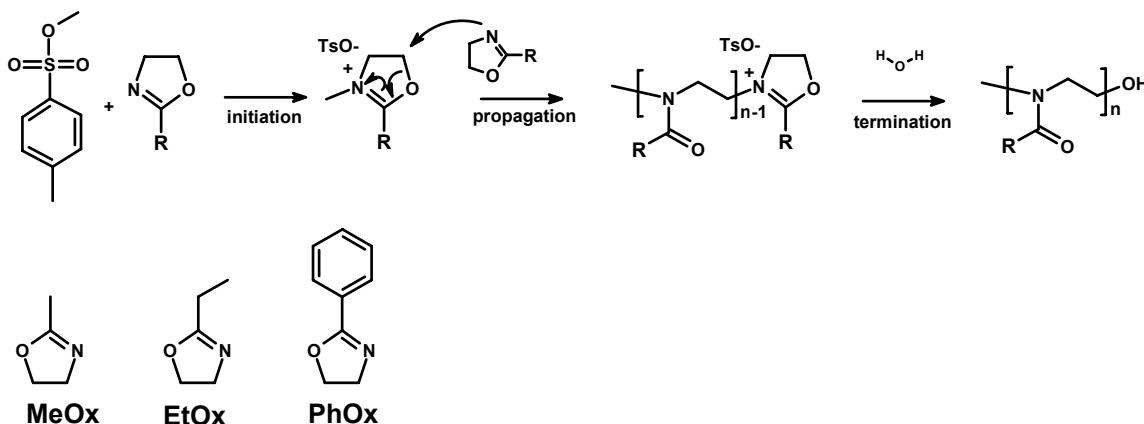
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1. Synthesis and structure of the copolymers

The statistical copolymers consisting of 2-phenyl-2-oxazoline and 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline were synthesized via a cationic ring-opening polymerization mechanism as depicted in Scheme S1. Full details of the synthesis and characterization of the studied copolymers were recently published [R. Hoogenboom, H. M. L. Thijs, M. W. M. Fijten, B. van Lankvelt, U. S. Schubert, One-pot synthesis of 2-phenyl-2-oxazoline containing quasi-diblock copoly(2-oxazoline)s under microwave irradiation. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45*, 416-422]. Detailed investigations on the copolymerization parameters revealed that during these statistical copolymerizations, the MeOx or EtOx is first incorporated followed by incorporation of the PhOx resulting in the formation of quasi-diblock copolymers.



Scheme S1. Schematic representation of the cationic ring-opening polymerization of 2-oxazolines as well as the structure of the used monomer structures.

Polymer synthesis procedure:

Different amounts of methyl tosylate, 2-phenyl-2-oxazoline, 2-methyl-2-oxazoline or 2-ethyl-2-oxazoline and acetonitrile were added into microwave vials resulting in 5.0 mL reaction mixtures containing 4 M total monomer concentration and a total [M]/[I] ratio of 100. For each monomer combination (MeOx-PhOx and EtOx-PhOx), 11 polymerization mixtures were prepared with 0-100 mol% monomer PhOx (steps of 10 mol%). Subsequently, the polymerization mixtures were heated for 45 minutes to 140 °C under microwave irradiation in closed reaction vials to reach full conversion. All polymerization mixtures were quenched after the polymerization by the automated addition of water (50 µL) using the liquid handling system of the microwave synthesizer. The resulting copolymers were dried under vacuum and used without further purification.

2. Details of the solubility screening

The solubility screening was performed for all pMeOx-PhOx and pEtOx-PhOx statistical copolymers at a concentration of 5 mg/mL in water–ethanol mixtures containing 0, 20, 40, 60, 80 and 100 wt.% ethanol resulting in total in 132 experiments, which could be performed within one week. These samples were prepared by adding 5.0 ± 0.2 mg of the polymer and 1.0 mL of the solvent mixture to a 2 mL HPLC vial. The transmission of these copolymer solutions was measured while heating from 20 to 75 °C (1 °C/min) followed by cooling from 75 °C to 20 °C (1 °C/min). This heating and cooling program was repeated and the second cycle was considered for analysis. Wait steps of 10 minutes were programmed in between the heating and cooling runs and 30 minutes in between the cooling and the subsequent heating run.

After this initial screening, detailed investigations were performed to study the solubility, self-assembly, dispersion formation and LCST behavior of selected copolymers. For these investigations, other solvent ratios were used while the concentration of the polymer remained 5.0 ± 0.2 mg in 1.0 mL. For self-assembly and LCST, the same temperature program was used as described above. The detailed solubility studies were performed from -15 °C to 75 °C while the rest of the program was the same. The dispersion stabilities were determined by heating and cooling the sample from 20 °C to 75 °C and back to 20 °C (1 °C/min) with a stirring rate of 700 rpm. Subsequently, the stirring was stopped and the transmission in time was determined. To be able to judge the dispersion stability, the volume of the samples was decreased to 510 μ L so that the liquid was just above the LED and the sensor allowing accurate determination of the 5% transmission point.

The solubility measurements were performed in an automated parallel temperature controlled turbidimeter (Crystal16 from Avantium Technologies BV). This device contains four independent heating blocks that are electrically heated and cooled by peltier elements in combination with a cryostat. Each reactor block contains four different positions for HPLC vials, which are equipped with a LED-source on one side of the vial and a sensor on the other side to measure the transmission through the sample during the temperature program. Each HPLC vial contains a small stirring bar to continuously stir the solution with a stirring speed of 700 rpm during the measurements.

3. Overview of the different observed transmission versus temperature curves and their interpretation

In this section, selected raw measurement data from the Crystal16, that comprise all the different observations, are shown and their interpretation is discussed. In addition, the Figures show pictures of the polymer solution to further illustrate the solubility. The solid line with sharp changes in the graphs shows the temperature profile while the other line with higher roughness shows the simultaneous transmission profile. In general, the transmission slightly decreased upon heating due to a change in sensitivity of the sensor. This was further confirmed by measuring the transmission of solvent samples without polymer. Nonetheless, transmissions of 85% and higher are indicative of clear solutions. Figure S1 depicts the heating and transmission profile that was assigned to completely soluble copolymers (referred to in Figure 1 of the manuscript as soluble at 20 °C) since the transmission never drops below 85%.

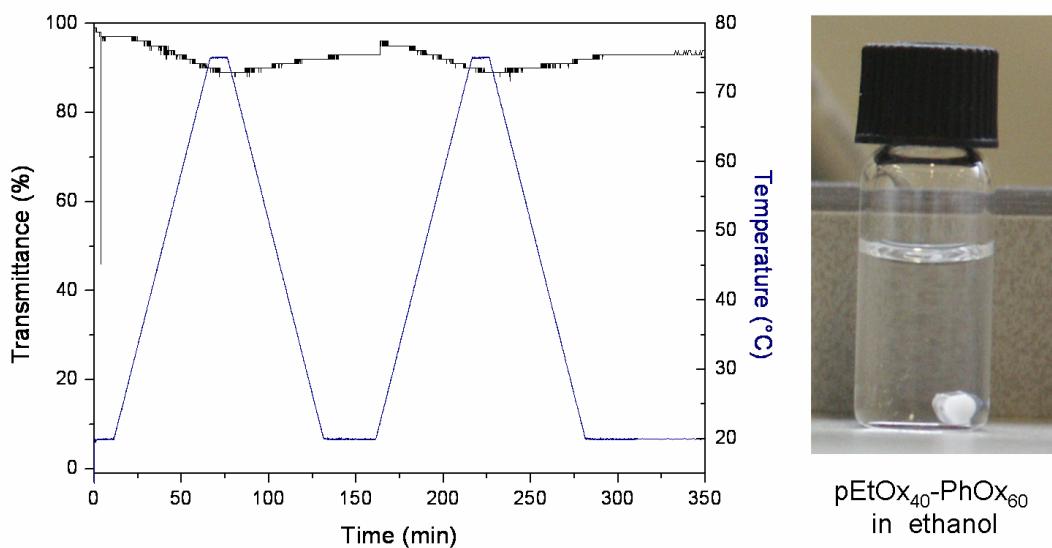


Figure S1. Representative heating and transmission curves for completely soluble polymers.

When the polymer is completely insoluble at the investigated temperature range, small particles will float through the vial due to the stirring. This results in a scattered transmission pattern (Figure S2), because these particles will only be detected when they cross the area in between the LED and the sensor. The presence of particles is further confirmed by the picture of the sample vial.

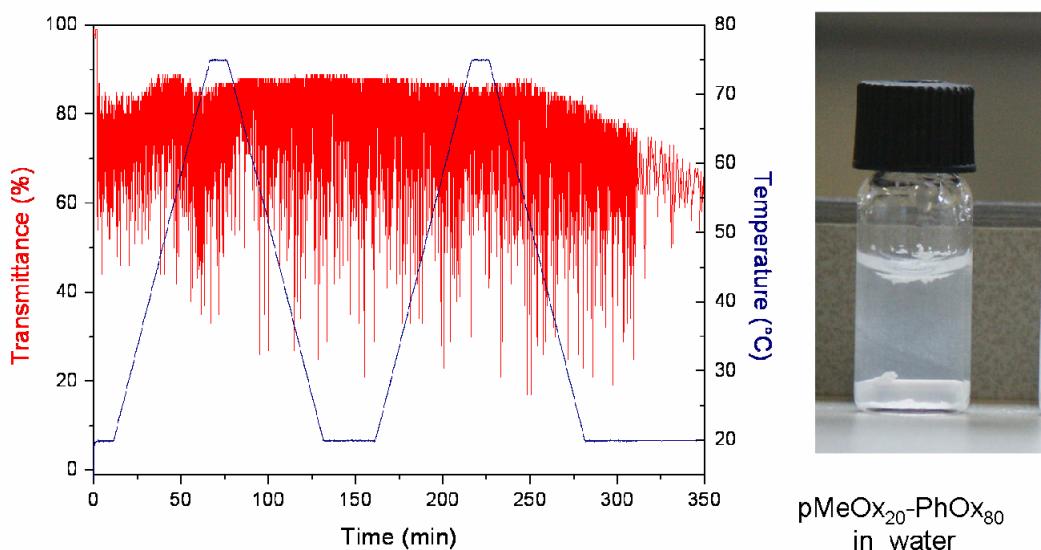


Figure S2. Representative heating and transmission curves for completely insoluble polymers.

Figure S3 also shows a polymer that does not dissolve in the investigated temperature range. However, upon heating the scattered transmission profile changes into zero transmission meaning that the present particles (causing scattering) have changed into a more homogeneous insoluble powder that effectively blocks all the light from the LED before it reaches the detector. This observation together with the picture of the vial demonstrates that this transmission profile is indicative for the formation of a homogeneous polymer dispersion.

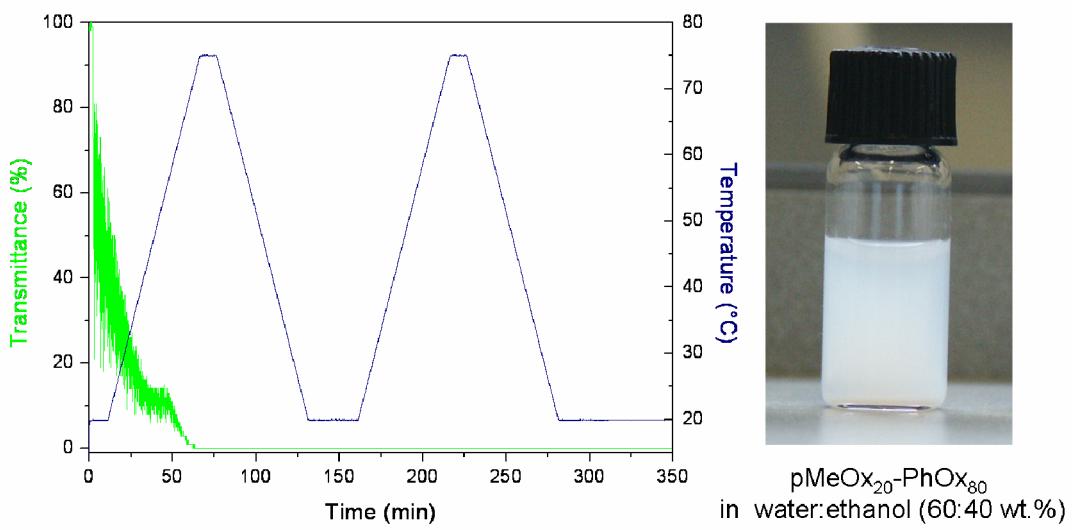


Figure S3. Representative heating and transmission curves for polymers that are dispersed upon heating.

The transmission and heat profiles that are shown in Figure S4 indicate that the polymer is insoluble (low transmission) at low temperatures and becomes soluble (high transmission) at higher temperatures indicating the presence of a upper critical solution temperature (UCST). Although the transmission does not drop completely to zero upon cooling, the picture clearly shows that the polymer precipitates. In this case the amount of precipitate is too little to completely block the sensor. From this solubility plot, the precipitation temperature (T_p) was determined at 50% transmission during the second cooling run. In the final part of the graph the temperature remains constant at 20 °C while the transmission increases again. A visual inspection of the vial revealed that the increased transmission is not due to (partial) solubilization of the polymer, but the precipitated polymer sticks to the wall of the vial resulting in a higher transmission.

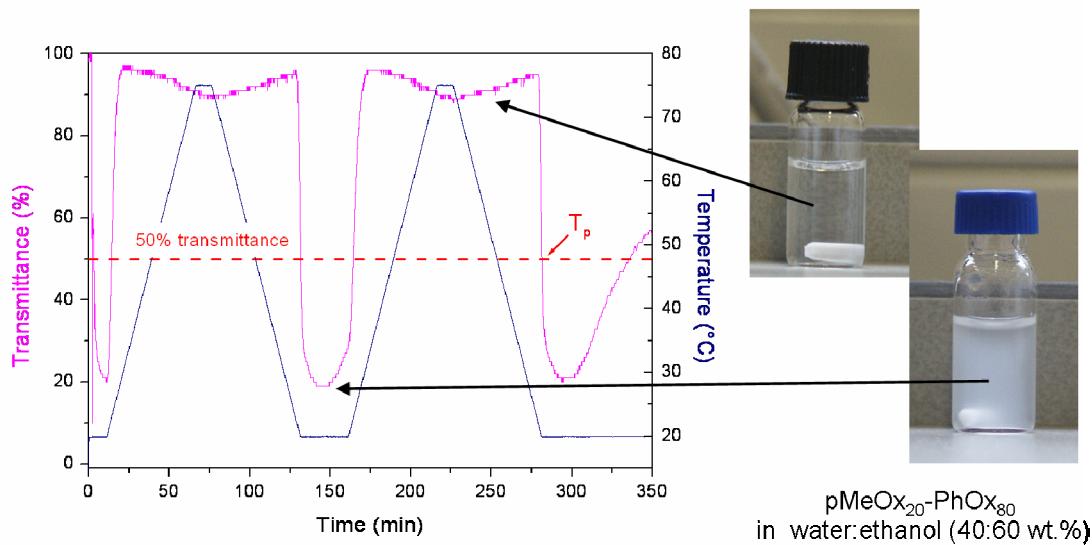


Figure S4. Representative heating and transmission curves for polymers with a UCST.

The transmission profile in Figure S5 shows that the undissolved scattering particles are first dispersed (low transmission) upon heating. Upon further heating, the transmission increases to ~ 70% where it remains constant. The picture of the polymer solution clearly shows a blue color, which is indicative of the presence of micellar structures. Therefore, such transmission profiles were interpreted as the formation of micelles.

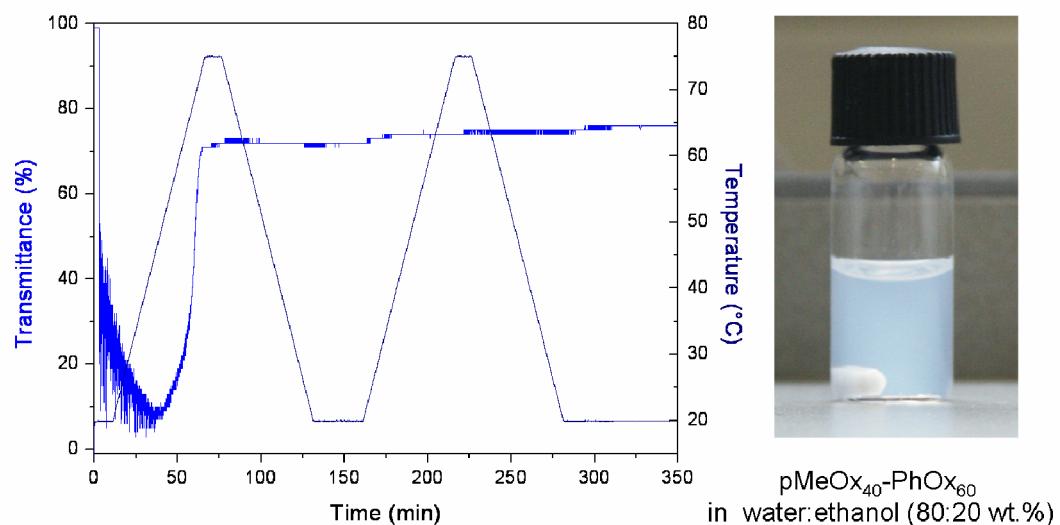


Figure S5. Representative heating and transmission curves for polymers self-assembled into micellar structures upon heating.

The transmission profile in Figure S6 shows the opposite behaviour as Figure S4: High transmission at low temperatures ($> 85\%$) and low transmission at high temperatures. This illustrates that the polymer precipitates upon heating, which means that the polymer has a lower critical solution temperature (LCST). The LCST during both heating and cooling were determined at 50% transmission in the second heating and cooling cycle.

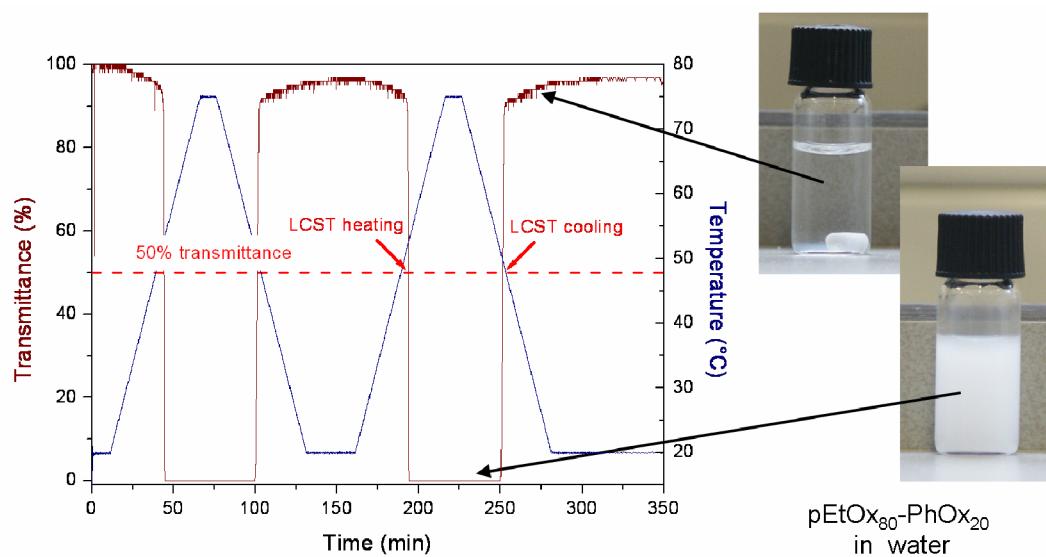


Figure S6. Representative heating and transmission curves for polymers that exhibit LCST behaviour.

Figure S7 show a similar transmission profile as Figure S6. However, when the sample is further heated after the LCTS transition, the transmission increases again indicating that the polymer dissolves. This dissolving upon further heating is also confirmed by the visual inspection of the sample. Therefore, this kind of transmission profile shows a unprecedented observation of polymers having first a LCST transition, which is followed by dissolving upon further heating.

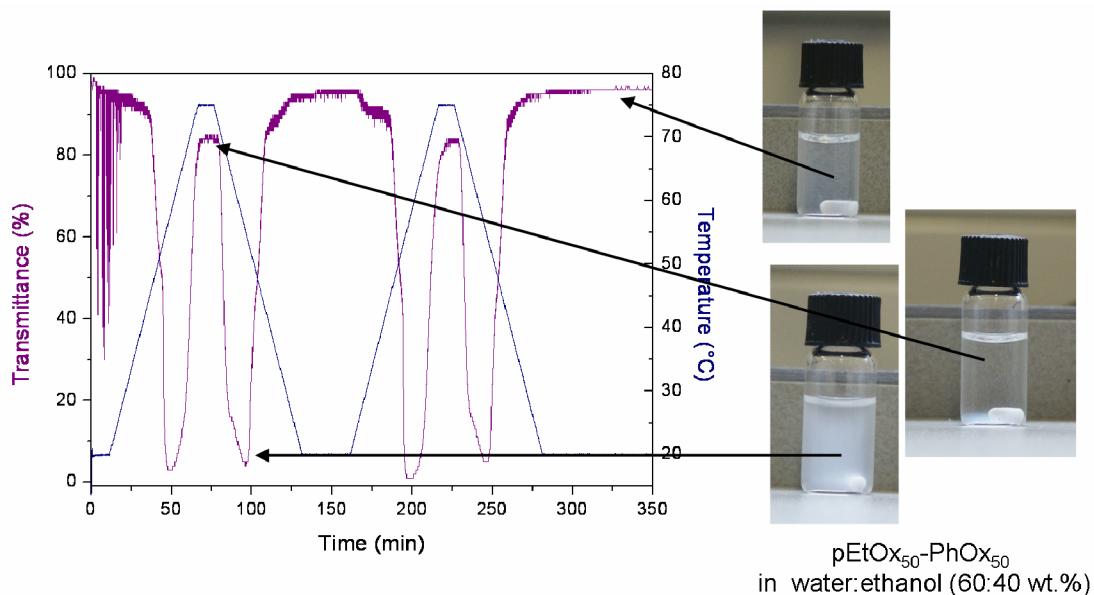


Figure S7. Representative heating and transmission curves for polymers that exhibit LCST behaviour and, subsequently, dissolve upon heating.