Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Self-assembled poly(2-ethyl-2-oxazoline) fibers in aqueous solutions

Pınar Tatar Güner,[a] Annamaria Miko,[b] Florian Schweinberger,[c] and A. Levent Demirel*[a,b]

Materials & Methods. Poly(2-ethyl-2-oxazoline) (PEOX) (M_w ~ 500,000 g/mol), analytical grade sodium thiocyanate (NaSCN) and sodium acetate (NaAc, CH_3COONa) salts were purchased from Sigma-Aldrich.

1 mg/ml PEOX solutions were prepared in deionized water (18.0 MΩ), in 0.2 M NaAc and 0.2M NaSCN solutions and the solutions were kept in oven at 70°C. Agglomeration was observed above cloud point temperature T_c at all salt concentrations. The agglomerates formed in the solutions were freeze dried for XRD and DSC characterizations. The agglomerates from salt containing solutions were washed several times with deionized water before freeze drying.

DSC measurements were performed by using aluminum hermetic pans and lids on a TGA/DSC Q200 instrument with cooling system (TA Instruments). The heating/cooling rate was kept constant at 10 ºC/min under nitrogen flow of 50 ml/min. Powder XRD measurements of freeze dried coagulates were done in reflection mode by Bruker D8 Discover using CuK_α radiation. Optical micrographs were taken by Leica DMLM microscope. Agglomerate dispersions were spin coated on Si wafers for scanning electron microscopy (SEM) analysis by Zeiss EVO LS-15 microscope. Malvern Zetasizer Nano S DLS instrument was used for the determination of the cloud point temperatures of the solutions.

The structural model for PEOX crystal was created based on the XRD data of the coagulates using Accelrys Materials Studio Modeling software. The lattice constants were adjusted such that the calculated XRD peaks reproduced the experimental XRD data.

Cloud Point Phase Diagram of PEOX.

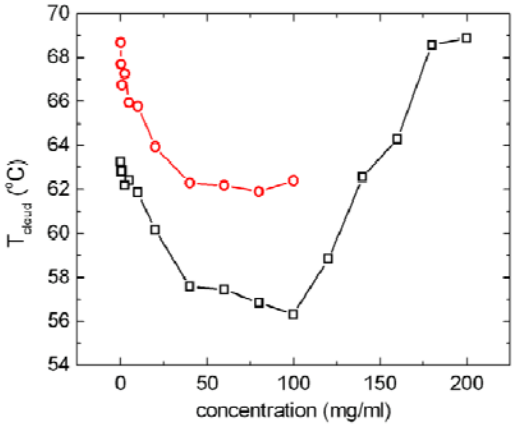

Fig. S1 The dependence of the cloud point temperature (T_{cloud}) on the concentration of the PEOX solution for two different PEOX molecular weights: 50,000 g/mol (circles) and 500,000 g/mol (squares).

Dependence of T_c on the salt concentration. The solid lines in Fig. 2 are fits to the following equation (Ref. 9):

$$T = T_{c\text{-no salt}} + k_1 c + [k_2 k_3 c / (1 + k_3 c)]$$

where c is the salt concentration, k_i are the constants.

The coefficient of the linear term, k_1, is negative and represents the salting-out effect. More specifically, this linear dependence indicates the presence of two different contributions of the anion X^-. i) destabilization of the water molecules hydrogen-bonded to PEOX, ii) increase in the interfacial energy of water/hydrophobic interface. The salting-in effect was represented by the last term (k_2, k_3 > 0). This dependence indicates the Langmuir adsorption of the ions to PEOX.

SEM Analysis.

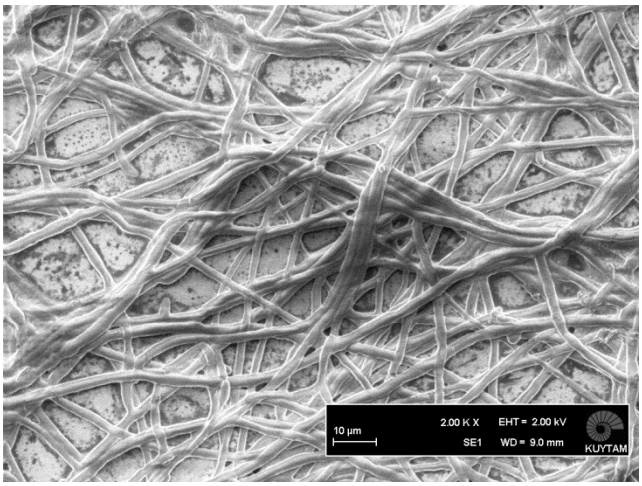

Fig. S2 SEM picture of spin coated PEOX fibers from 0.2 M aqueous NaAc solution. The average fiber diameter was measured as 2.54 ± 0.5 µm which is consistent with the values measured by optical microscopy.

Physical and thermal properties of the fibers.

Table S1 – Thermal and physical properties of the fibers formed in different solutions.

	Duration (days)	Fiber diameters[a] (µm)	T_m (°C)	Lattice constants (nm)
In pure water	45	3.8 ± 0.8	b	b
In 0.2 M NaAc	7	2.7 ± 0.5	201	0.871, 0.494, 0.685
In 0.2 M NaSCN	20	2.9 ± 0.6	220 (broad)	0.938, 0.468, 0.685

a: measured by optical microscopy
b: not enough fibers, could not be measured

Comparison of measured melting temperature and lattice constant of PEOX crystals with poly(oxazoline)s having different alkyl side chain lengths. Both the observed melting temperature (T_m) and the lattice constants (d_{100}) for PEOX are in agreement with the previously reported values (Ref. 2) for POX having alkyl side chains.

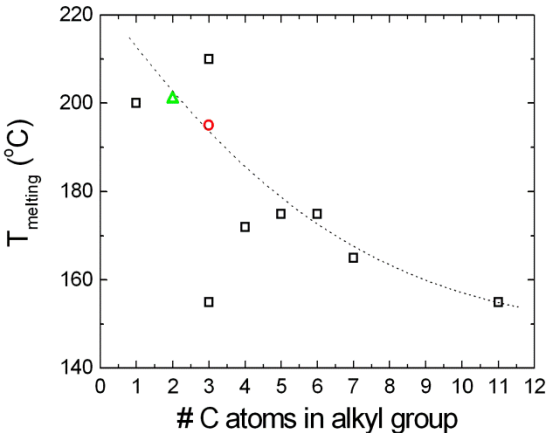

Fig. S3 T_m of crystalline POX having linear alkyl side chains increases with decreasing alkyl side chain length. The replotted data points from Ref. 2 (squares) are seen together with PIPOX melting temperature (circle, from Ref. 6) and the PEOX melting temperature (triangle, measured in this study). The dashed line is to guide the eye.

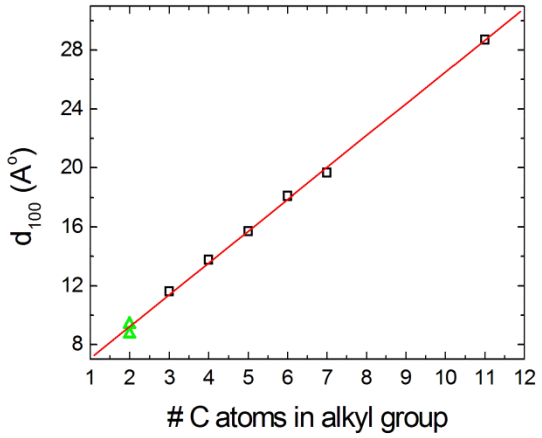

Fig. S4 Lattice constant d_{100} of crystalline POX having linear alkyl side chains decreases with decreasing alkyl side chain length. The replotted data points from Ref. 2 (squares) are seen together with the PEOX lattice constants (triangles, measured in this study. 0.938 nm for agglomerates formed in NaSCN solution and 0.871 nm for agglomerates formed in NaAc solution). The dashed line is a linear fit to the squares.