

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

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**Poly(2-ethyl-2-oxazoline) (PEOX) formed self-assembled fibers in aqueous solutions above the cloud point temperature ( $T_c$ ) through a slow crystallization process. The fiber formation above  $T_c$  happened both in pure water and in the presence of salting-in ( $\text{SCN}^-$ ) and salting-out ( $\text{CH}_3\text{COO}^-$ ) ions. The crystal structure and the melting temperature of the PEOX fibers were determined.**

Polyoxazolines (POX) form an important class of tertiary polyamides which are structural isomers of polyacrylamides and polypeptides.<sup>1</sup> For poly(2-alkyl-2-oxazoline)s (Scheme 1) depending on the nature of the side chain R, the physicochemical properties (hydrophobicity, crystallinity, solubility in water and lower critical solution temperature) of the molecules can be adjusted. The oriented filaments of poly(2-alkyl-2-oxazoline)s were found to be crystalline except for PEOX.<sup>2</sup> The melting temperature increased with decreasing alkyl side chain length from  $\sim 140$  °C for heptadecyl side chains to  $\sim 200$  °C for methyl side chains. In more recent work,<sup>3</sup> POX with short alkyl side chains (methyl, ethyl and propyl) were found to be amorphous in bulk with glass transition temperatures decreasing with alkyl side chain length from  $\sim 80$  °C for methyl side chains to  $\sim 40$  °C for propyl side chains.

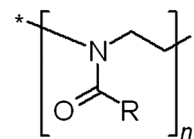
Aqueous solutions of poly(2-alkyl-2-oxazoline)s exhibit thermoresponsive behaviour.<sup>4</sup> The hydrogen bonds formed between the polymer chains and water molecules are broken above the cloud point temperature ( $T_c$ ) resulting in macroscopic phase transition. The mechanism leading to thermoresponsive behaviour has been investigated for POX and some acrylamide based polymers and was related to the transition in the chain conformation from coil to globule as a result of dehydration.<sup>4,5</sup> This transition is reversible with temperature, but with exceptions<sup>6–8</sup> when the solution is kept above  $T_c$  for extended times. The macroscopic phase separation at  $T_c$  brings polymer chains together and allows them to interact closely and self-assemble.

POX with short alkyl side chains (methyl, ethyl and propyl) are soluble in water at room temperature. Long term annealing of poly(2-isopropyl-2-oxazoline)s (PIPOX) above  $T_c$  was shown to cause

irreversible formation of nanofibers that grew into micron sized agglomerates.<sup>6,7</sup> PIPOX nanofibers were formed through a slow directional crystallization process which was not a salting-out effect. The structural isomer of PIPOX, poly(*N*-isopropyl acrylamide), did not form any agglomerates under similar conditions. The proposed mechanism for PIPOX self-assembly was based on hydrophobic and dipolar interactions.<sup>7</sup> Although thermoresponsive behaviour and similar interactions are also present in aqueous PEOX solutions, irreversible formation of fibers and agglomeration could not be observed previously. Here, we report for the first time that water soluble PEOX forms water insoluble crystalline fibers when kept above  $T_c$ . We show that the self-assembly into fibers above  $T_c$  is a slow crystallization process which can be enhanced by the addition of sodium acetate (NaAc,  $\text{CH}_3\text{COONa}$ ).

$T_c$  of PEOX ( $M_w \approx 500\,000$  g mol<sup>-1</sup>) solutions in deionized water ( $c = 1.0$  mg ml<sup>-1</sup>) was determined by dynamic light scattering as 61 °C. When these solutions were kept above  $T_c$  at 70 °C for several weeks, agglomerates were formed in the solution. Fig. 1, top row shows the photograph of the agglomerates in the solution after 45 days at 70 °C, together with the optical micrograph of one such agglomerate in water. The agglomerate is formed of entangled fibers having an average diameter of  $3.8 \pm 0.8$   $\mu\text{m}$ . The formation rate of these agglomerates was rather slow and required weeks to be visible by the naked eye. In the case of aqueous PIPOX solutions, such formation happened within a day.<sup>6,7</sup> The amount of agglomerates obtained after freeze drying was not enough for further thermal and structural analysis. Increasing the concentration of the PEOX solution to 10 mg ml<sup>-1</sup> decreased the cloud point slightly by  $\sim 1$  °C (see ESI, Fig. S1† for the cloud point phase diagram). But in concentrated solutions, the self-assembly into rather well-defined shapes was also hindered because of significant entanglements of the chains and slower relaxations.

At 1.0 mg ml<sup>-1</sup> solution concentration, when NaAc was added into the aqueous solution, the rate of agglomerate formation was significantly enhanced. The agglomerates were visible to the naked eye within days in 0.2 M NaAc solution (Fig. 1, middle row). The



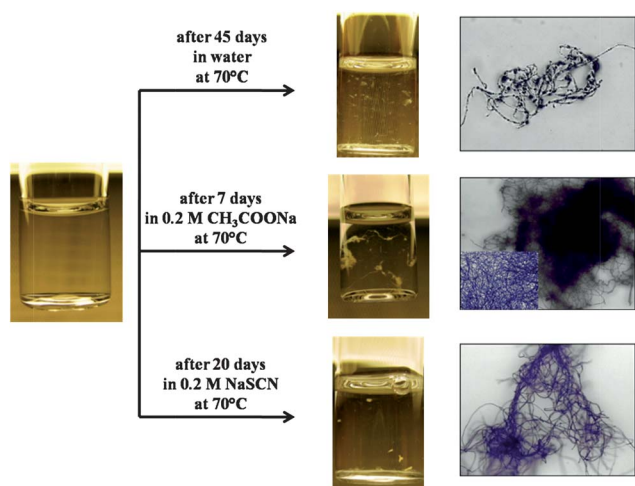
**Scheme 1** Chemical structure of poly(2-alkyl-2-oxazoline)s where R is an alkyl group.

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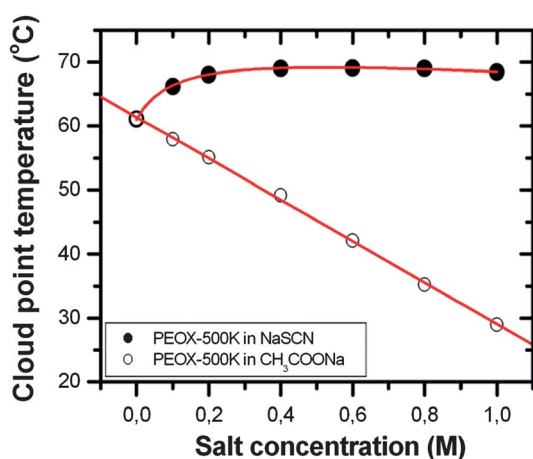
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**Fig. 1** Pictures of the PEOX solutions and the optical micrographs of the agglomerates formed. All solutions were clear at room temperature (left). When the solutions were kept at 70 °C, agglomerates formed in the solution in pure water (top row), in 0.2 M NaAc solution (middle row) and in 0.2 M NaSCN solution (bottom row). The rightmost column shows the optical micrographs of the agglomerates in solution. The inset in the middle row is the optical micrograph of the dry fibers coated on a glass substrate.

agglomerates were denser compared to those in pure water as seen in the optical micrograph (Fig. 1, middle row, right). The less dense regions at the perimeter clearly show entangled micron-sized fibers. The fibers maintained their shape in the dry state when spin coated on solid substrates. The inset in the optical micrograph shows the spin coated fibers on a glass substrate. The fibers had an average diameter of  $2.7 \pm 0.5 \mu\text{m}$  and were stable under ambient conditions for further analysis.

The major effect of NaAc addition on the PEOX solution was to decrease  $T_c$ . Fig. 2 shows the change in the cloud point of  $1.0 \text{ mg ml}^{-1}$  aqueous PEOX solution with the salt concentration. The cloud point decreased linearly with salt concentration. This linear dependence indicates the presence of two different contributions of mostly the  $\text{CH}_3\text{COO}^-$  anion: (i) destabilization of the water molecules



**Fig. 2** The change of the cloud point temperature ( $T_c$ ) of  $1.0 \text{ mg ml}^{-1}$  PEOX solution with NaAc (open circles) and NaSCN (filled circles) salt concentrations. The solid lines were fitted to the data as described in the text.

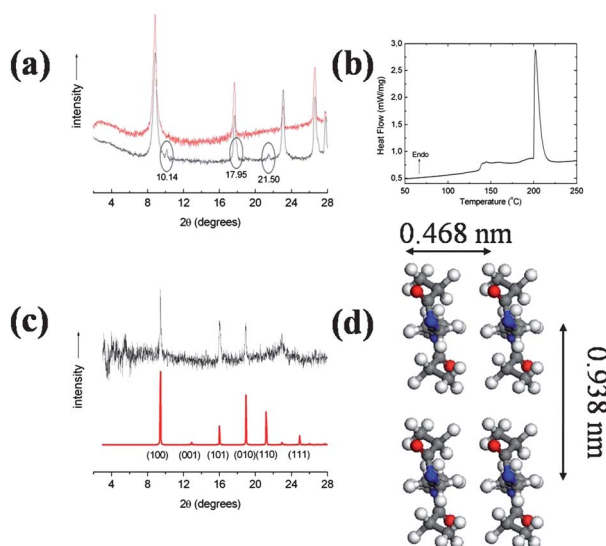
hydrogen-bonded to PEOX and (ii) increase in the interfacial energy of the water/hydrophobic interface.<sup>9</sup> Both of these are salting-out contributions which decrease the solubility of PEOX in water. However, we would like to emphasize that the observed fiber formation and agglomeration were not due to salting-out of the polymer in NaAc solution. The transition between 1-phase and 2-phase states was reversible independent of the amount of salt as long as the solution was not kept for days above  $T_c$ . Fiberlike structures formed both with and without NaAc when the solutions were kept longer above  $T_c$ . The temperature difference  $\Delta T = T - T_c$ , where  $T$  is the temperature at which the solutions were kept, seems to contribute as a driving force to the rate of structure formation. For PEOX solution in 0.2 M NaAc ( $T_c = 55 \text{ }^\circ\text{C}$ ),  $\Delta T$  was  $15 \text{ }^\circ\text{C}$ ; for pure water ( $T_c = 61 \text{ }^\circ\text{C}$ ),  $\Delta T$  was  $9 \text{ }^\circ\text{C}$ .

To check that this self-assembly process also works in the presence of a salting-in anion  $\text{SCN}^-$ , the experiments were repeated in the presence of NaSCN. As shown in Fig. 2,  $T_c$  of  $1.0 \text{ mg ml}^{-1}$  aqueous PEOX solution increased slightly with the concentration of NaSCN. The solid line is a fit to an equation (see ESI† for details) consisting of a linear term (salting-out effect discussed above) and a term for Langmuir adsorption (salting-in effect) corresponding to the binding of the ions to PEOX.<sup>9</sup> Ion binding was the dominant mechanism in PEOX- $\text{SCN}^-$  interaction in the concentration range up to 1.0 M. For PEOX solution in 0.2 M NaSCN ( $T_c = 68 \text{ }^\circ\text{C}$ ),  $\Delta T$  was only  $2 \text{ }^\circ\text{C}$ .

When  $1.0 \text{ mg ml}^{-1}$  PEOX solution in 0.2 M aqueous NaSCN was kept at  $70 \text{ }^\circ\text{C}$ , agglomerates were also formed in the solution and were visible to the naked eye after a few weeks (Fig. 1, bottom row) despite the presence of the salting-in anion  $\text{SCN}^-$ . The rate of agglomeration was slower (the amount of agglomerates was less after a certain time interval) compared to that in  $\text{CH}_3\text{COO}^-$  solution. The optical microscope image of agglomerates in aqueous NaSCN solution is seen in Fig. 1, bottom row, right. The morphology of the agglomerates was similar to those formed in pure water or in the presence of NaAc in that it also consisted of entangled micron-sized fibers. The observation of PEOX fibers both in pure water and in the presence of salting-out or salting-in anions indicates that the ions are not the main driving force in fiber formation above  $T_c$ , but contribute to kinetics of fiber formation either indirectly by changing  $T_c$  or directly by modifying the interactions in a complex way.

The freeze-dried agglomerates from  $1.0 \text{ mg ml}^{-1}$  PEOX solution in 0.2 M aqueous NaAc were further analyzed by X-ray diffraction (XRD) and differential scanning calorimetry (DSC). Fig. 3a shows the XRD data of agglomerates from PEOX-NaAc (lower curve) together with those of NaAc (upper curve). XRD data of PEOX-NaAc were dominated by the NaAc peaks, although the agglomerates were washed several times with water (note that the agglomerates were not soluble in water). In addition, the crystalline peaks of NaAc and PEOX are found to be close to each other. Still, it is possible to identify three peaks corresponding to PEOX crystals at  $2\theta$  values ( $d$  values) of  $10.14^\circ$  (0.871 nm),  $17.95^\circ$  (0.494 nm) and  $21.50^\circ$  (0.413 nm). The DSC analysis of the agglomerates showed an intense endothermic peak at  $201 \text{ }^\circ\text{C}$  in the heating curve (Fig. 3b) which we attribute to the melting of PEOX crystals. DSC of bulk PEOX only showed glass transition at  $T_g \approx 60 \text{ }^\circ\text{C}$ . Annealing bulk PEOX above  $T_g$  at a temperature range of  $100\text{--}140 \text{ }^\circ\text{C}$  did not crystallize PEOX contrary to PIPOX which could be crystallized in the same temperature range.<sup>7</sup>

The agglomerates formed in  $1.0 \text{ mg ml}^{-1}$  PEOX solution in 0.2 M NaSCN were also analyzed by XRD after freeze drying (Fig. 3c,



**Fig. 3** (a) XRD data of the PEOX agglomerates from NaAc containing solution (lower curve) together with those of NaAc (upper curve). (b) The melting peak of PEOX agglomerates from NaAc containing solution as observed by DSC. (c) XRD data of the PEOX agglomerates from NaSCN containing solution (upper curve) together with the calculated XRD data (lower curve) according to the structural model seen in (d).

upper curve). The crystalline peaks of NaSCN are well-separated from the PEOX peaks which made the major PEOX peaks to be individually observed at  $2\theta$  values ( $d$  values) of  $9.44^\circ$  (0.938 nm),  $16.04^\circ$  (0.552 nm) and  $18.94^\circ$  (0.468 nm). Fig. 3d shows the model crystal structure along the PEOX backbone ([001] direction). The ethyl side groups are alternately aligned along the [100] direction to either side of the backbone. The calculated peak positions using this model (Fig. 3c, lower curve) are consistent with the experimentally observed XRD peaks. The observed micron sized PEOX fibers are expected to be formed by fusion of nanofibers, similar to PIPOX.<sup>7</sup>

Both the observed melting temperature ( $T_m$ ) and the lattice constants for PEOX are in agreement with the previously reported values<sup>2</sup> for POX having alkyl side chains (see ESI†, Fig. S3 for  $T_m$  and Fig. S4 for lattice constants). Lattice constant  $d_{100}$  of crystalline POX having alkyl side chains decreases linearly with decreasing alkyl side chain length. This is expected as the side chains open up to either side of the backbone and chains can more closely pack in the case of shorter alkyl side chains.  $T_m$  of crystalline POX having alkyl side chains increases with decreasing alkyl side chain length. This also indicates the difficulty in crystallizing POX with shorter side chains (methyl and ethyl).

Crystallization of PEOX has not been reported before. PEOX was the only polymer which was found to be amorphous in the systematic work of M. Litt *et al.*<sup>2</sup> We could not succeed in crystallizing PEOX either by annealing bulk samples above  $100^\circ\text{C}$ . POX are known to have stiff backbones due to the strong amide dipole whose nitrogen end is on the polymer backbone. In the case of shorter alkyl side chains, amide dipoles can get closer which gives rise to stronger intermolecular interactions. Such strong interactions can hinder the conformational relaxations needed to reach the equilibrium crystalline structure. This is why PEOX agglomeration was much slower in water compared to PIPOX. In the presence of water molecules, the hydration of the amide dipole introduces backbone flexibility which leads to crystallization of PEOX in water above  $T_c$ . Crystalline

PEOX agglomerates form both in pure water, and in the presence of salting-out ( $\text{CH}_3\text{COO}^-$ ) and salting-in ( $\text{SCN}^-$ ) anions above  $T_c$ . The temperature difference  $\Delta T = T - T_c$  between the annealing temperature  $T$  and the cloud point temperature  $T_c$  can be one driving force for enhanced rate of agglomeration. Aqueous PEOX–NaAc solutions having  $\Delta T = 15^\circ\text{C}$  showed the fastest agglomeration compared to pure water ( $\Delta T = 9^\circ\text{C}$ ) and NaSCN containing solutions ( $\Delta T = 2^\circ\text{C}$ ). The differences observed in the lattice constant  $d_{100}$  for PEOX crystallized in the presence of NaAc ( $d_{100} = 0.871$  nm) and NaSCN ( $d_{100} = 0.938$  nm) suggest that electrolytes may influence nucleation of crystals and the resulting structures. This indicates the critical role of different interaction mechanisms of the anions with the PEOX molecules in the self-assembly process.

## Conclusions

Water soluble PEOX formed water insoluble self-assembled fibers in aqueous solutions above the cloud point temperature through a slow crystallization process which could be enhanced by the addition of both salting-out and salting-in ions. In pure water, the agglomerates of entangled fibers were visible to the naked eye within few weeks. The addition of NaAc into the solution significantly increased the rate of agglomerate formation which was not due to the salting-out effect of the  $\text{CH}_3\text{COO}^-$  ions. Agglomerates having similar morphology were also observed in the presence of a salting-in anion  $\text{SCN}^-$ . PEOX crystals were observed for the first time in aqueous solutions. The measured lattice constant and the melting temperature of the PEOX crystals were consistent with previously reported data on POX having longer alkyl side chains. The role of various electrolytes and the temperature on the structure formation is yet to be understood and under investigation.

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