

Experiment Report Form



Experiment title: Water-ion-amide interactions in bio-inspired polyamide structure evolution

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26-01-1034

Beamline:
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Local contact(s): Dipanjan Banerjee

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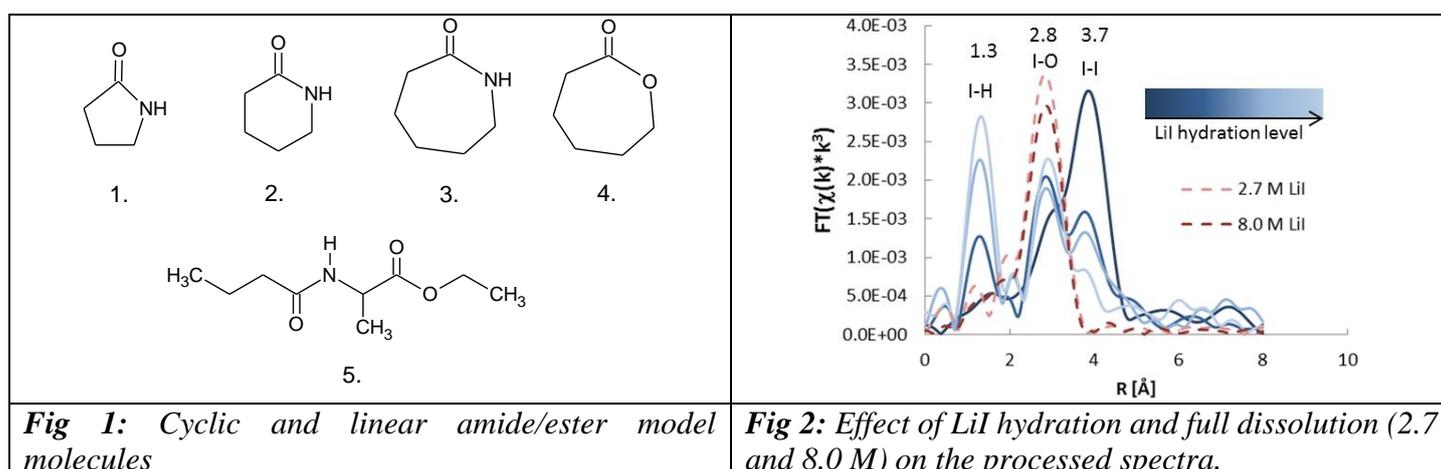
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Report: Inspired by (i) natural silk spinning, (ii) aqueous solubility of polyamides at elevated temperature (200°C, 18 bar) [1] and (iii) successive solubilisation upon cooling by adding a selective combination of ions [2,3], we aim to re-introduce advanced, bio-inspired structural control in industrial polyamides. However, a thorough understanding on the role of the ions is demanded, but hampered by the complexity of polymeric samples. In this study we aim to elucidate the role of halogen anions on amide conformations using low molecular weight linear and cyclic amide-based model molecules, Figure 1. EXAFS is the technique ideally suited for investigating the local environment of bromide and iodide ions.



In order to assign distances in the multicomponent solutions carefully the hydration process of lithium salt pellets was followed in-situ. The spectral changes along the hydration of LiI as well as the spectra of the 2.7 and 8.0 M LiI solutions are presented in Figure 2. It is evident that the I - I coordination number at a distance of 3.7 Å decreases and slightly changes to smaller distance prior to dissolution after which the I-I coordination disappears at that particular distance. Simultaneously the I - H coordination appears and increases in number with the increase in hydration level. Also the I - O coordination becomes more pronounced despite the fact that the coordination number seems less susceptible to the hydration state of the salts. Identical trends are observed along the hydration of LiBr.

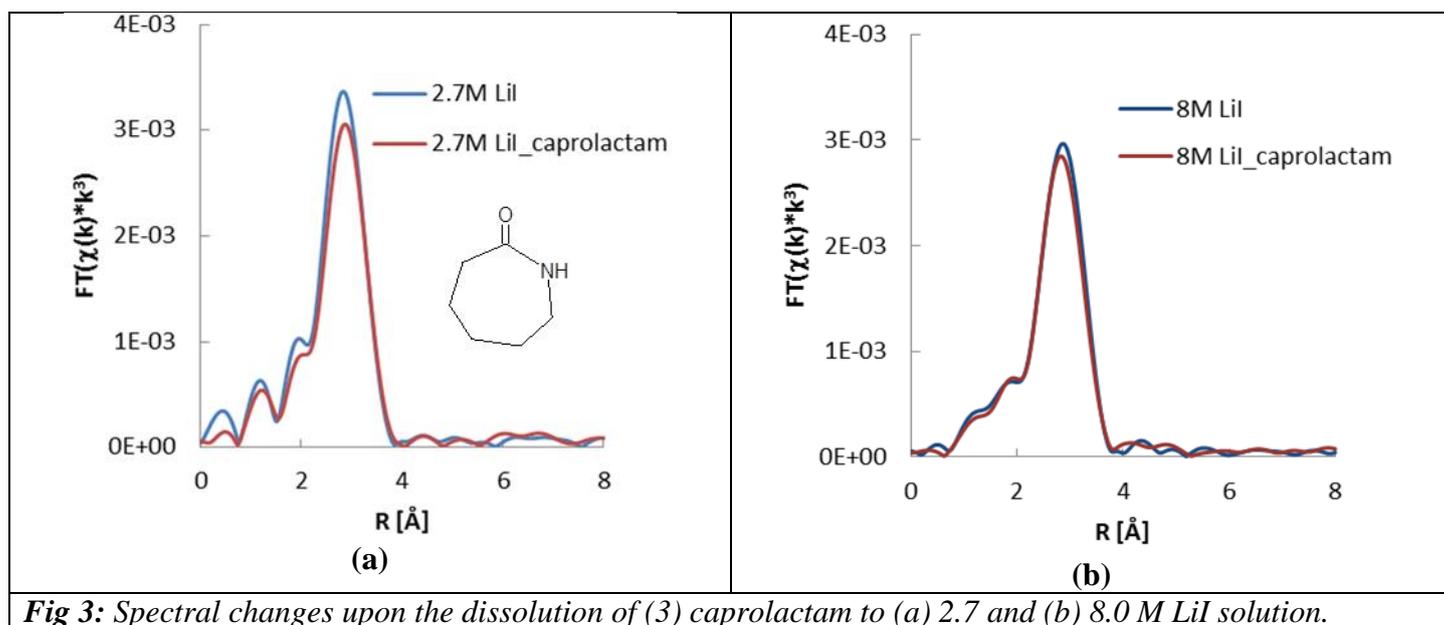


Fig 3: Spectral changes upon the dissolution of (3) caprolactam to (a) 2.7 and (b) 8.0 M LiI solution.

Though only marginal spectral differences between the model molecules upon dissolution were observed, the comparison with the spectra of the 2.7 and 8 M solutions lead to the following observations. The addition of respective amphiphilic model components entails more disorder in the first hydration shell and lower coordination numbers, suggesting competition between the water and organic protons in the first hydration shell for the 2.7 M solutions. In the 8 M solutions the dissolution of the model molecules perturb the I - I and Br - Br interactions, paralleled by an increase in the anion - O coordination number. The spectra of 8 M solutions in the presence of (3) caprolactam and (4) caprolacton are substantially different for which the origin is yet to be verified.

References

1. Vollrath and Knight, Nature 2001, 410.
2. Harings et al., Macromolecules 2012, 45.
3. Deshmukh et al., Macromolecules 2013, 46.