



Contribution ID: 142

Type: Poster

The structural, thermal and dynamic behavior of the thermoresponsive polymer poly(N-isopropylmethacrylamide)

Tuesday, 18 September 2018 17:15 (15 minutes)

Poly(N-isopropylmethacrylamide) (PNIPMAM) is a thermoresponsive polymer, exhibiting lower critical solution temperature (LCST) behavior in aqueous solution. Compared to the well-investigated poly(N-isopropylacrylamide) (PNIPAM), which has similar chemical structure, PNIPMAM has a higher transition temperature (43 °C [1] instead of 32 °C). This may be due to the presence of the additional methyl groups on the vinyl backbone, which lead to steric hindrance and weaken the intramolecular interactions [2,3]. In order to understand how these effects along with the hydrophobic interactions influence the phase behavior of aqueous solutions of PNIPMAM, we investigate the temperature-dependent phase behavior of PNIPMAM in D₂O using turbidimetry, differential scanning calorimetry (DSC), small-angle neutron scattering (SANS) and dynamic light scattering, covering a large concentration range. We find that the phase transition consists of two steps, namely (i) hydrophobic aggregation at ~39 °C, as evident from turbidimetry, DLS and SANS and (ii) the chain collapse and water release at ~44 °C, as evident from DSC and SANS.

[1] K. Kunota et al., *Polym. J.* **22**, 1051 (1990).

[2] J. Pang et al., *J. Theor. Comput. Chem.* **10**, 359 (2011).

[3] J. Dybal et al., *Vibrat. Spectrosc.* **51**, 44 (2009).

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Session Classification: Poster session 2

Track Classification: P2 Soft matter