Polymer block length and temperature effects on the nanoscale morphology of thermoresponsive double hydrophilic block copolymers

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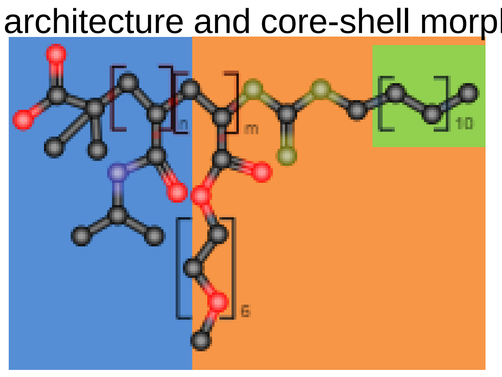
Introduction

Motivation: Elucidating self-assembly of thermoresponsive double hydrophilic block copolymers reinforces the predictive potential for their design as smart scaffolds for encapsulation of hydrophobic pharmaceutics. [1,2]

Aim: We combined small angle neutron scattering (SANS) with Fourier transform infrared (FTIR) spectroscopy to assess the influence of temperature, block length and bond vibrations on nanoscale self-assembled morphologies of novel, thermoresponsive double hydrophilic poly(N-isopropylacrylamide)-*block*-poly(oligo ethylene glycol methyl ether acrylate) (**$PNIPAM_{19k}$-b-$POEGA_{10k}$** and **$PNIPAM_{10k}$-b-$POEGA_{10k}$**) fully protonated block copolymers in 1% wt D_2O solutions (pH=7). The thermoresponsive PNIPAM block leads to self-assembly upon T variation. We identify transformations from spheres to fractal core-shell morphologies in the largest block architecture and core-shell morphologies for the shortest one.



PNIPAM: thermoresponsivity + hydrophilicity

POEGA: hydrophilicity

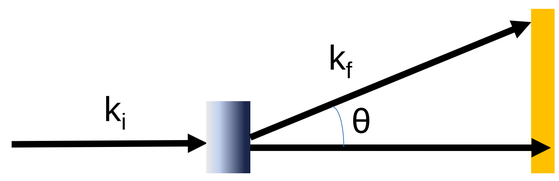
C_{12}: Hydrophobic end group

[1] Maruya Li et al., ACS Omega 2020, 5 (7), 3734–3742

[2] Giaouzi D, Pispas S, J. Pol. Sci., Part A: Polym. Chem (2019), 1; 57(13), 1467

Small angle neutron scattering (SANS)

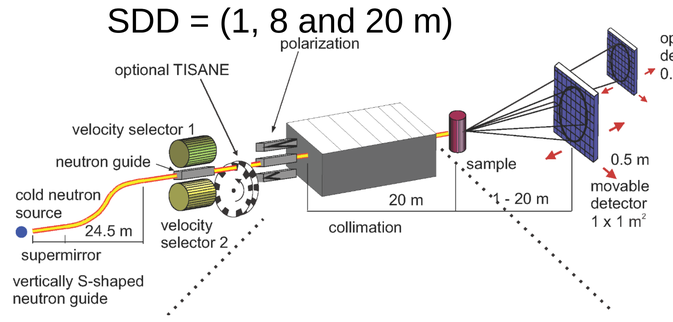
$$q = |k_f - k_i| = 4 \cdot \pi \cdot \sin(\theta) / \lambda$$



$\Delta\lambda/\lambda$ = 10 %

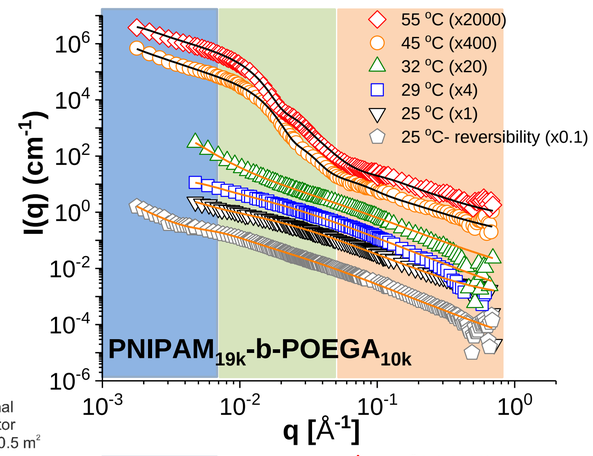
λ = 4.5 Å (and 12 Å for low q's)

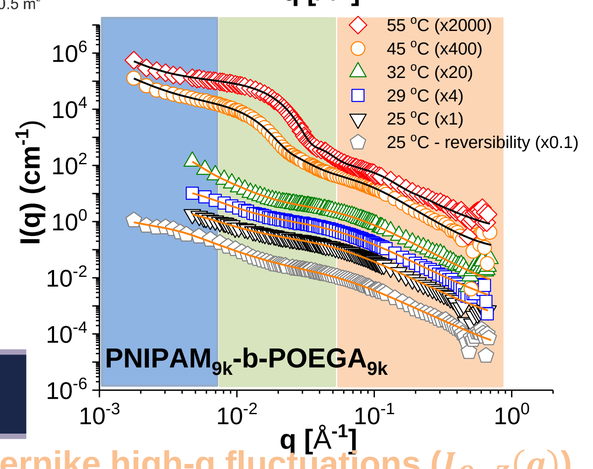
SDD = (1, 8 and 20 m)



SANS-1 instrument (MLZ / FRMII)

S. Mühlbauer et al., NIMA 832, 297-305 (2016).





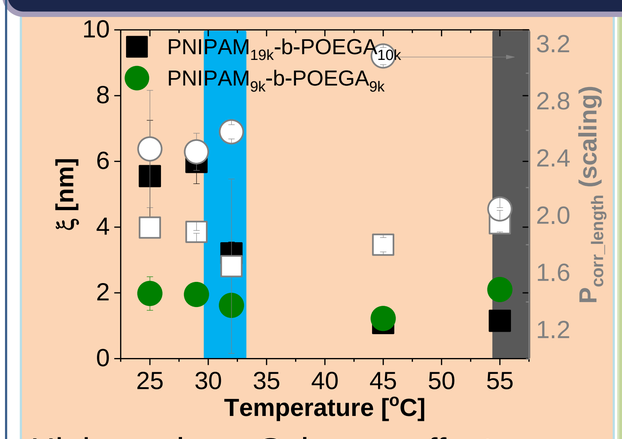
SANS modeling

Large-scale fractals ($I_{cluster}(q)$), Ornstein-Zernike high-q fluctuations ($I_{O-Z}(q)$) and only at elevated temperatures **core-shell micelles, or, fractal micelles** [3]:

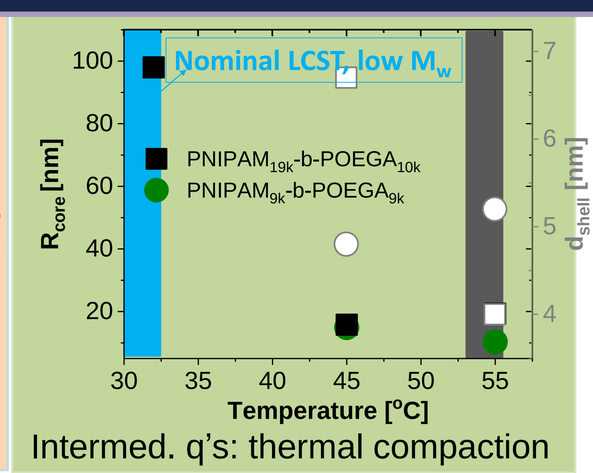
$$I_{tot}(q) = I_{cluster}(q) + I_{fractal,CS}(q) + I_{O-Z}(q) + bkg \quad (PNIPAM_{19k}\text{-b-}POEGA_{10k})$$

$$I_{tot}(q) = I_{cluster}(q) + I_{CS}(q) + I_{O-Z}(q) + bkg \quad (PNIPAM_{9k}\text{-b-}POEGA_{9k})$$

SANS fit results

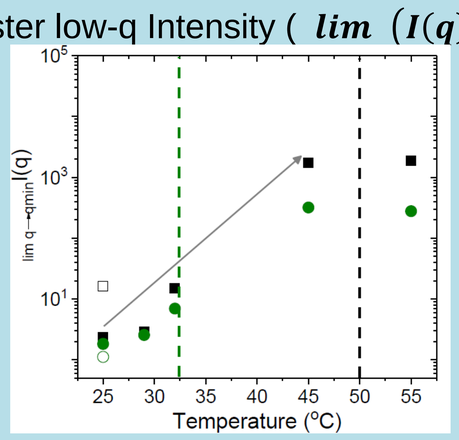


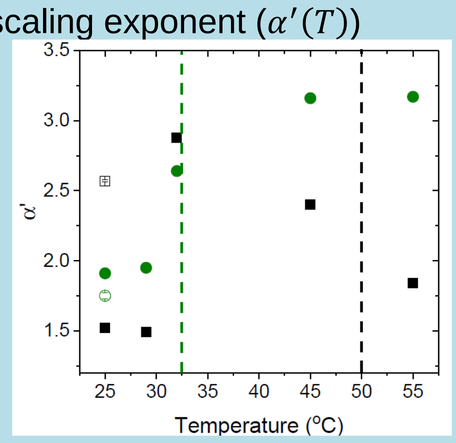
High q values: Solvency effects



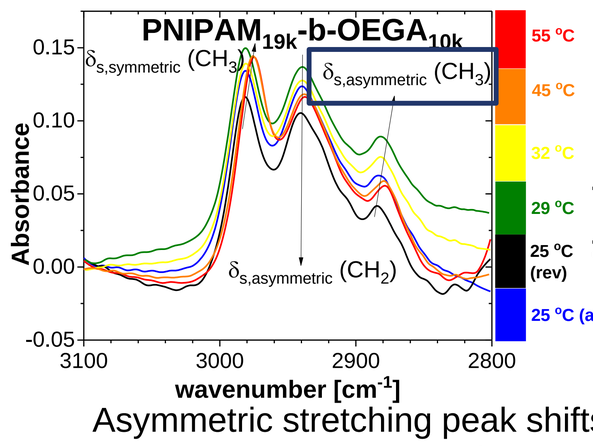
Intermed. q's: thermal compaction

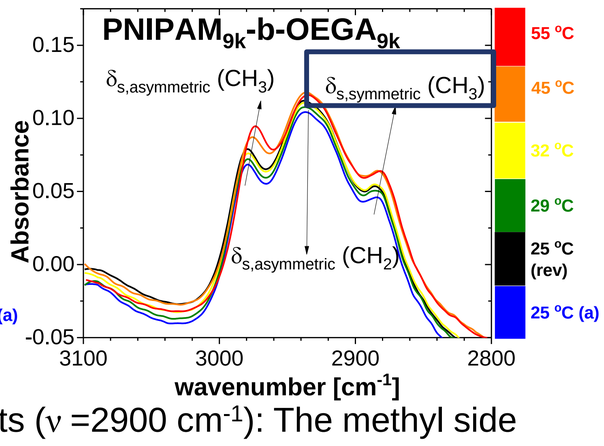
Cluster low-q Intensity ($\lim_{q \to q_{min}} (I(q))$) and scaling exponent ($\alpha'(T)$)



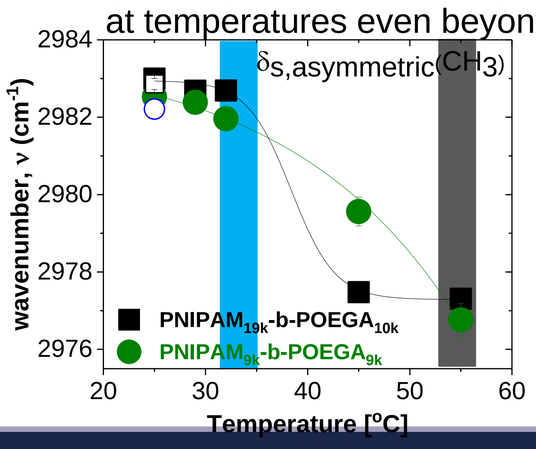


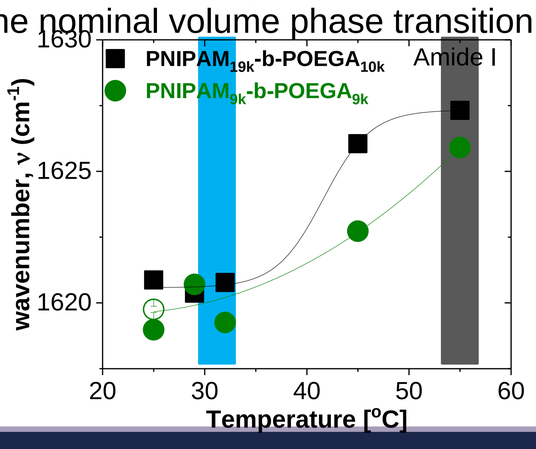
FTIR results

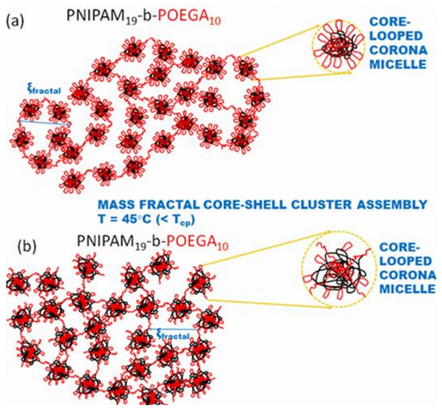


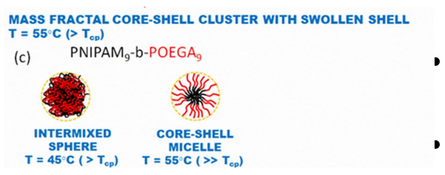


Asymmetric stretching peak shifts (ν =2900 cm^{-1}): The methyl side group hydration sensitively depends on the temperature increase at temperatures even beyond the nominal volume phase transition.









Summary

- FTIR: Δν in asymmetric stretching points to a block-length dependent signaling of side chain dehydration
- SANS: Upon heating, hierarchical assemblies transform into well-defined spherical morphologies (P(q) oscillations)
- The examined block-length differences induce distinct morphologies at low (clusters), intermediate (core-shell) and high (interchain correlation) wavevectors
- ***Vagias A. et al., Macromolecules 2021, 54, 15, 7298–7313***

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