Dual-Responsive Triblock Terpolymer: Unravelling pH and Temperature Effects on Self-Assembly in Aqueous Solution

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Introduction

Amphiphilic block copolymers self-assemble into micelles of different shapes in aqueous solutions and form hydrogels if the polymer concentration is sufficiently high.[1] Less is known about the micelle and gel formation of triblock terpolymers with pH- and thermoresponsive blocks. The use of functional segments in block copolymers increases the tunability of the nanostructures even further. Here, the effect of temperature and pH values on self-assembly of the dual responsive terpolymer featuring three different blocks is addressed.

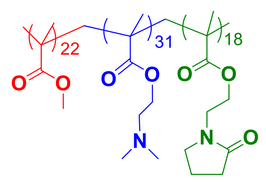
Aim of the work

To investigate the temperature- and pH-dependent micellar structures, charges status

System under investigation

$PMMA_{22}$-*b*-$PDMAEMA_{31}$-*b*-$PNMEP_{18}$

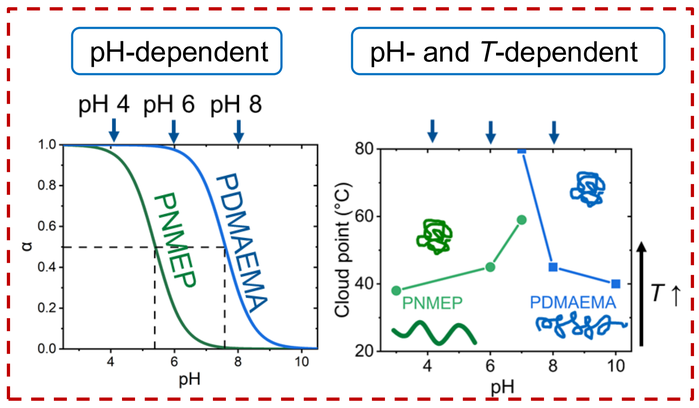
BAC



PMMA: hydrophobic

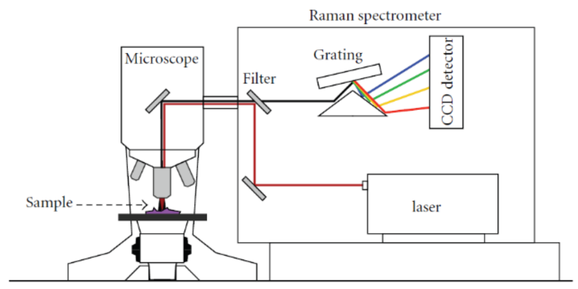
PDMAEMA: pK_a = 7.5
LCST at high pH

PNMEP: pK_a = 5.4 , LCST at low pH



Methods

Raman spectroscopy

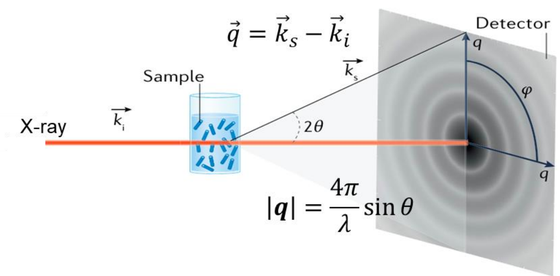


- local intermolecular environment
- BAC solution in D_2O at 1 wt%
- temperature range: 13 - 48 °C
- pH = 4, 6 and 8

→ Gaussian deconvolution of Raman peaks in C-H stretching region

Small-angle x-ray scattering (SAXS)

BioSAXS P12 at EMBL



- the inner structure of micelles
- BAC solution in H_2O at 1 wt%
- $\lambda = 0.124$ nm, SDD = 3 m
- temperature range: 13 - 48 °C
- pH = 4, 6 and 8

→ SAXS curve fitting with structural modes

SAXS fitting model

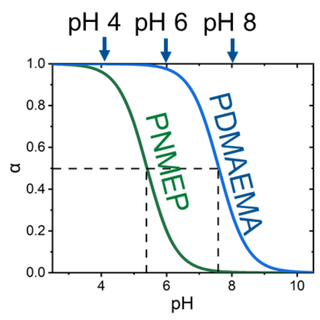
$$I(q) = P_{mic}(q)S(q) + P_{cl}(q) + I_{OZ}(q) + I_{bkg}$$

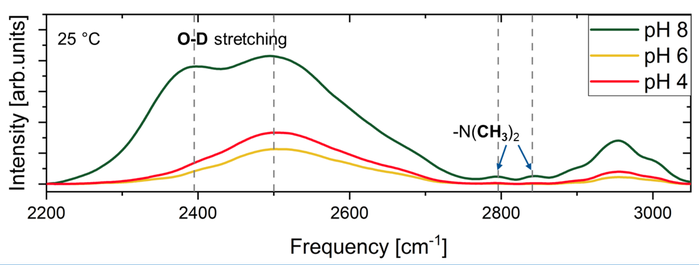
$P_{mic}(q)$	form factor for core-shell spherical or homogeneous cylindrical micelles
$S(q)$	hard-sphere or sticky hard-sphere structure factor
$P_{cl}(q)$	form factor of large clusters, Porod term
$I_{OZ}(q)$	Ornstein-Zernike term for concentration fluctuations, I_{bkg} : background

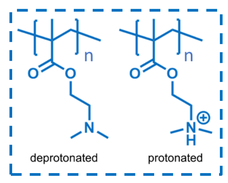
Results

pH-dependent

Raman spectroscopy at 25 °C



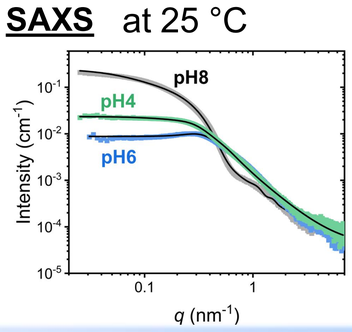


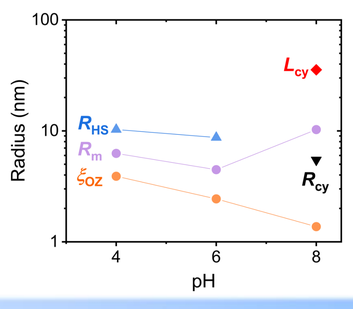


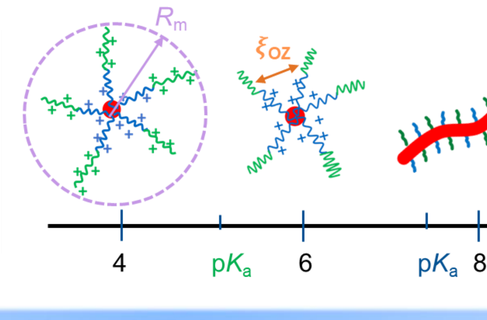
with decreasing pH value

- O-D stretching becomes weaker
  → addition of H_2O to acid solution
- ν(N-$(CH_3)_2$) peaks disappear
  → PDMAEMA block protonated to quaternary ammonium cations in the acidic environment

SAXS at 25 °C





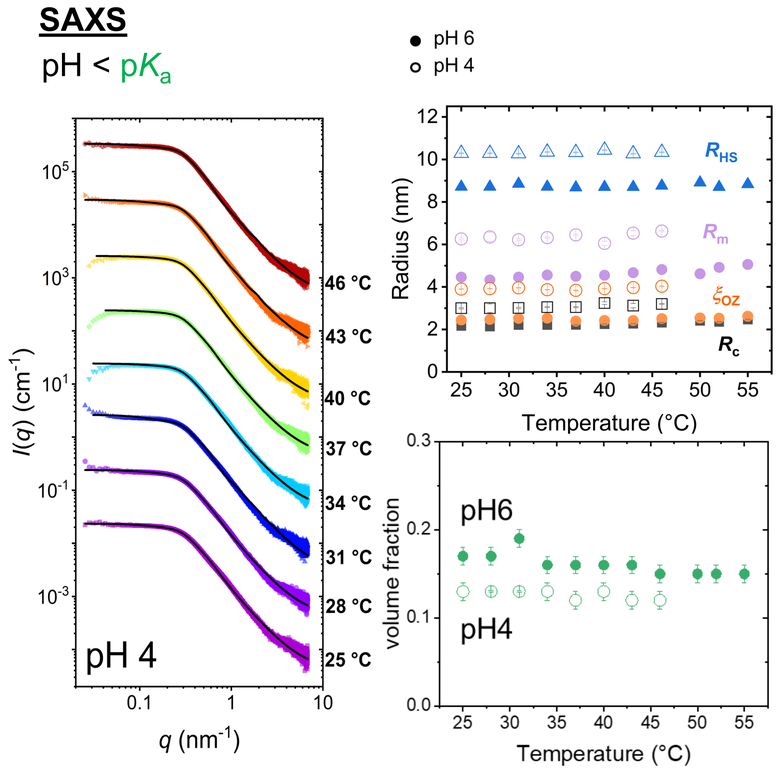


- elongation of polymer chains with increasingly protonated blocks
- charges enhance the concentration fluctuations in the micellar shell
- charges hinder self-assembly

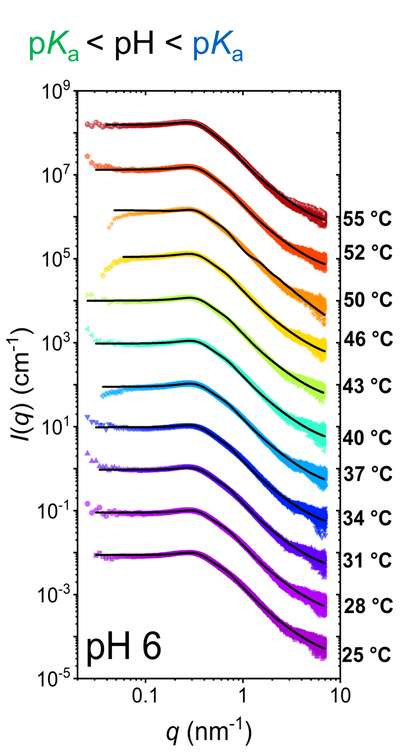
pH- and *T*-dependent

SAXS

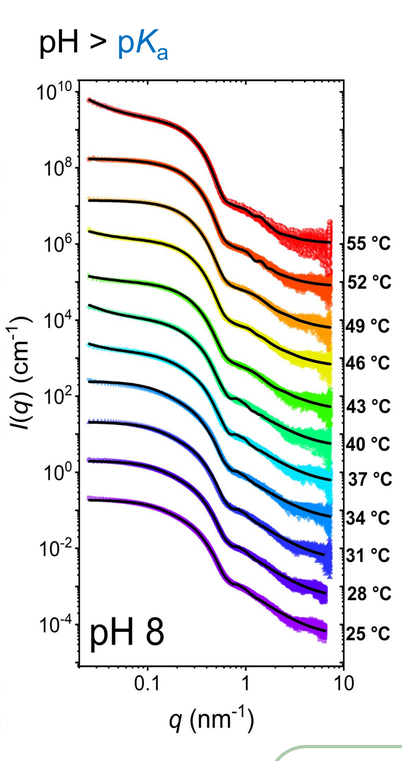
pH < pK_a

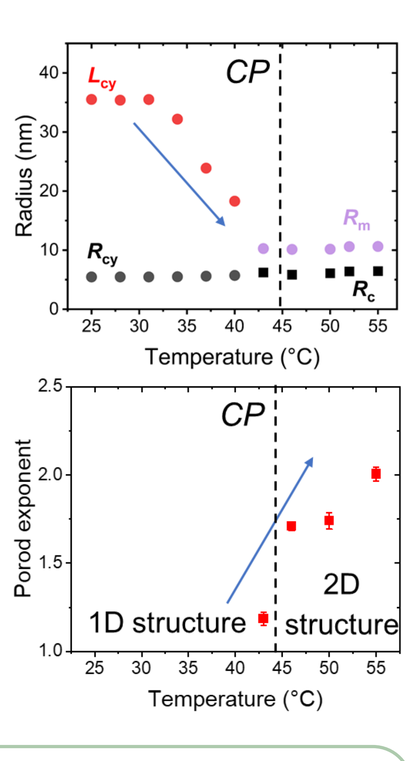


pK_a < pH < pK_a



pH > pK_a





pH < pK_a and pK_a < pH < pK_a

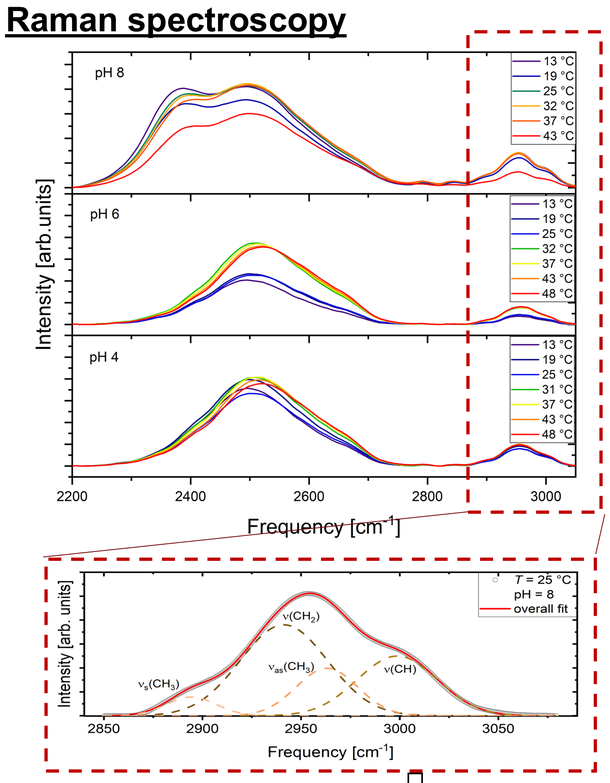
- weak *T*-dependence of structure
- elevated *CP* at pH 6 compared to pH 8
- charges hinder coil-to-globule transition

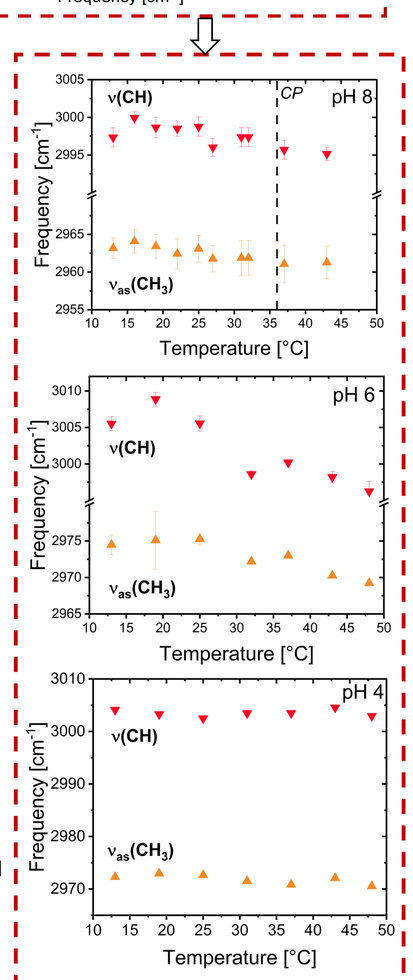
pH > pK_a

- clusters formed at 43 °C and above
- Porod exponent increases
  → cylinders fold to form sheets

- $\nu_{as}(CH_3)$ red shift at pH 8 and 6
  → hydrophobic interactions dominate during phase separation
- temperature-dependency becomes weaker at lower pH

pH- and *T*-dependent





References and Acknowledgement

[1] C. M. Papadakis, C. Tsitsilianis, *Gels*, **2017**, 3, 3.

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Conclusion

- Reduction of hydrogen bonding and formation of hydrophobic domains with increasing temperature
- Increased charge density due to lower pH hinder interaction between micelles due to repulsion of polymer chains, thus hinder the *T*-dependent self-assembly of polymer chains.