Experimental report

01/10/2019

Proposal: 9-11-1878 **Council:** 4/2018

Title: Self-association of sequence-controlled copolymers in water

Research area: Chemistry

This proposal is a new proposal

Main proposer: Francois TOURNILHAC

Experimental team: Francois TOURNILHAC
ESTHER CAZARES CORTES

Local contacts: Lionel PORCAR

Samples: NaCl
KCl
AgNO3
CuSO4
poly(methacrylic acid-alt-hydroxyethyl acrylate)
poly(methacrylic acid-co-hydroxyethyl acrylate)
poly(acrylic acid-alt-hydroxyethyl methacrylate)
Li2SO4
poly(acrylic acid-co-hydroxyethyl methacrylate)

Instrument	Requested days	Allocated days	From	To
D22	2	0		
D33	0	2	15/09/2018	17/09/2018

Abstract:

As part of an international ANR France / JST Japan project dedicated to "molecular technology," the applicants are currently studying structures and properties related to the self-assembly of sequence-controlled copolymers. The objective of this proposal is to elucidate the mechanisms behind the lower critical solution temperature (LCST) behavior recently observed in water. SANS beamtime is requested to produce reliable structural data with single-chain resolution from radiation-sensitive polymer samples within the LCST regions.

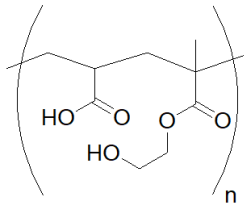
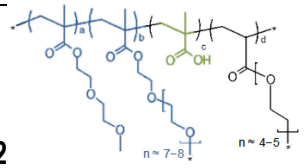
Neutron scattering report: experiment 9-11-1878 at the ILL (Grenoble)

Self-association of sequence-controlled copolymers in water

François Tournilhac,[i] Benjamin Baker,[i] Esther Cazares-Cortes,[i] Makoto Ouchi.[ii]

[i] Matière Molle et Chimie. ESPCI 10 rue Vauquelin 75005 Paris, France
[ii] Department of Polymer Chemistry, Kyoto University 615-8510, Japan

During this beamtime, two different polymers samples have been investigated. Sample 1, is a sequence controlled polymer; samples 2 is of microgel type. Compounds 1 and 2 show an LCST in water. Compound 1 also shows an LCST in dimethoxyethane (DME).

Compound	Solvent	Conc.	Sample	pH
D_2O			4	6.64
 **1**	D_2O	8 mg/mL	8	1.14
			3	3.52
			10	4.20
			9	4.67
			5	5.07
			6	5.72
			7	10.72
	DME/D_2O		22	-
DME/D_2O			21	-
 **2**	D_2O	8.35 wt%	O	5.32
		÷10	X	7.31
		÷100	Y	7.96
		÷1000	Z	8.07

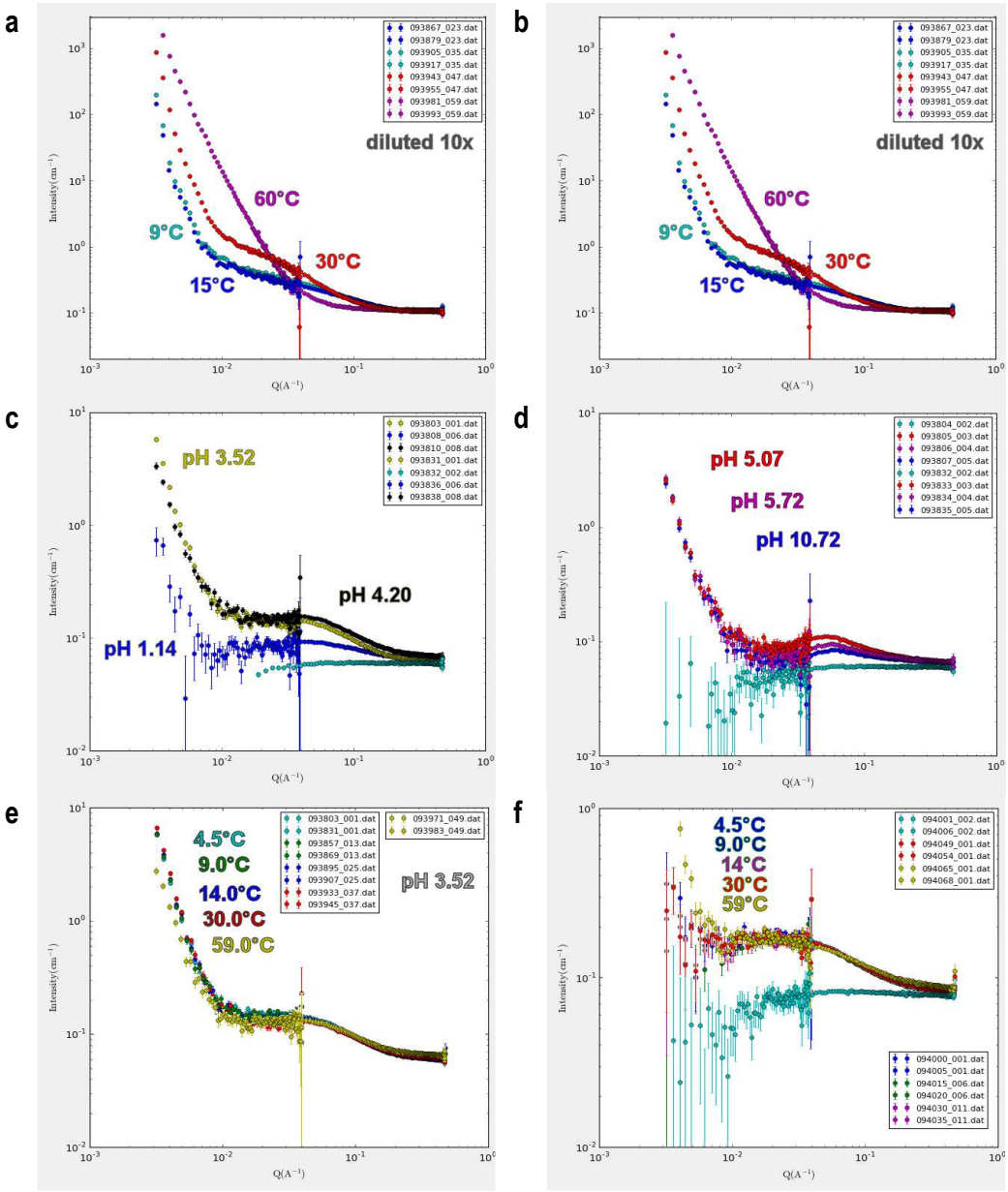
Target T	Actual T
0°C	4.5°C
6°C	9°C
13°C	14°C
31°C	30°C
65°C	59°C

Compound 1 was investigated at 8 mg/mL concentration in D_2O at different pH values and in dimethoxyethane d_{10} + 6 vol% D_2O. The goal was to measure the variations of R_g across the LCST in these solvents. Compound 2 was investigated at 8.35 wt% concentration, as well as 10×, 100× and 1000× diluted in D_2O. the goal was to investigate the structure of the microgels as a function of temperature and concentration.

All experiments were performed on line D33 at the Institute Laue Langevin. The radiation was monochromatic λ = 6 Å and sample-to-detector distances D = 2 m and 12 m were used thus covering a momentum transfert range from 0.003 $Å^{-1}$ to 0.47 $Å^{-1}$. Chemistry labs at the beamline and in the science building were utilised.

Samples of solutions were prepared via dissolution in D_2O or DME d_{10}/D_2O mixtures, sonication required. For compound 1, we observed that the solubility range in D_2O starts at pH > 4, whereas it starts at pH > 3 in water. The pH value was adjusted to different values by addition of NaOH.
The samples were held in quartz Hellma cells with a 1 mm path; cell volume = 300 µL. The temperature was imposed by a circulating fluid in the cell's holder rack. SANS data were collected at eight different temperatures, the actual temperature was measured close to the samples at any time (see table).

Reduced data were downloaded directly from the ILL data portal site.[1] **a:** Compound 2, data at 30°C for different dilutions; **b:** Compound 2, data at different temperatures for one dilution. **c:** Compound 1, data at low pH. **d:** Compound 1, data at high pH. **e:** Compound 1 at pH 3.52, data at different temperatures, **f:** Compound 1 in DME d_{10}/D_2O, data at different temperatures.



SANS results in D_2O will be fitted with different models to elucidate the structure of solutions and microgels. SANS results in DME d_{10}/D_2O will be combined with existing data with different labelling combinations,[2,3] molecular dynamics (MD) simulations and other structural analyses by IR spectroscopy to elucidate the structural origin of the LCST.[4]

1 F. Tournilhac, B. Baker, E. Cazares-Cortes, M. Ouchi, L. Porcar, L. Porcar, DOI: 10.5291/ILL-DATA.9-11-1878.

2 F. Tournilhac, B. Baker, T. Derouineau; A. Guimet; M. Ouchi and L. Porcar, DOI: 10.5291/ILL-DATA.9-11-1822

3 F. Tournilhac, E. Cazares-Cortes, M. Ouchi, L. Porcar, B. Tarus, DOI: 10.5291/ILL-DATA.DIR-158.

4 B. Tarus, E. Cazares-Cortes, B. Baker, M. Ouchi, F. Tournilhac *in preparation.*