Experimental report

14/09/2019

Proposal: DIR-158 **Council:** 4/2018

Title: Self-association of sequence-controlled polymers in organic solvent

Research area: Soft condensed matter

This proposal is a continuation of 9-11-1882

Main proposer: **Francois TOURNILHAC**

Experimental team: Francois TOURNILHAC
ESTHER CAZARES CORTES

Local contacts: Lionel PORCAR

Samples: sequence controlled acrylate copolymer in 1,2-dimethoxyethane D10

Instrument	Requested days	Allocated days	From	To
D22	1	1	26/03/2018	27/03/2018

Abstract:

Neutron scattering report: experiment DIR-158 at the ILL (Grenoble)

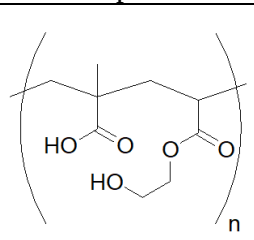
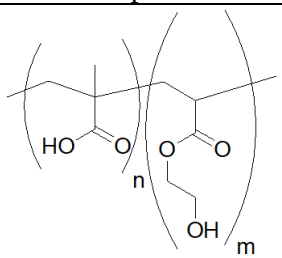
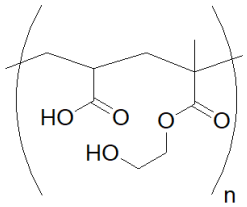
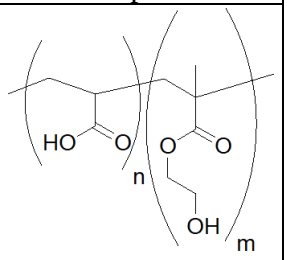
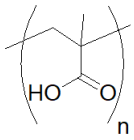
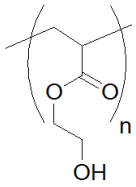
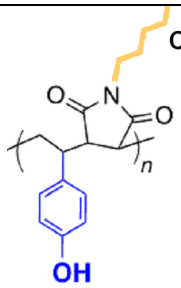
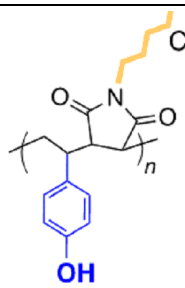
Self-association of sequence-controlled polymers in organic solvent

François Tournilhac,[i] Esther Cazares-Cortes,[i] Bogdan Tarus,[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

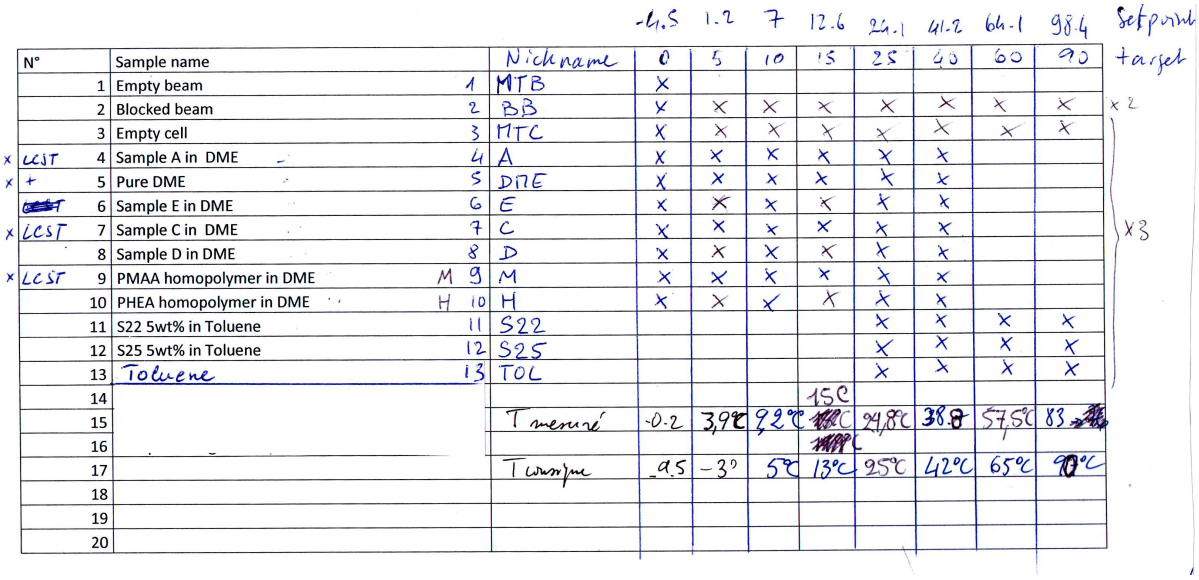
This beamtime was allocated to complement experiments on sequence-controlled copolymers in organic solvents, in continuation of 9-11-1882 experiment.

During this beamtime, eight different polymers samples have been investigated in deuteriated solvents. Samples A, C, S22 and S25 are sequence controlled polymers (alternated) whereas samples D and E are random and pMAA and pHEA are homopolymers. Samples A, C and pMAA show an LCST in dimethoxyethane whereas S22 and S25 form reversible gels in toluene.

Sample A	Sample E	Sample C	Sample D
			
pMAA	pHEA	S22	S25
			

Samples A-E as well as pMAA and pHEA were all investigated at 8 mg/mL concentration in dimethoxyethane d_{10}. The goal was to measure the variations of R_g across the LCST in this solvent. S22 and S25 were investigated at 50 mg/mL concentration in toluene d_8, the goal was to understand the structure of the organogels.

All experiments were performed on line D22 at the Institute Laue Langevin. The radiation was monochromatic λ = 6 Å and sample-to-detector distances D =1.2 m and 5.6 m were used thus covering a momentum transfert range from 0.01 $Å^{-1}$ to 0.68 $Å^{-1}$. Chemistry labs at the beamline and in the science building were utilised. Samples of solutions were prepared via dissolution in DME d_{10}, sonication required. Gels were prepared by dissolution in hot toluene d_8 and heat-transferring the solutions into the cells, where they gelified upon cooling. 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).



	N°	Sample name		Nickname	0	5	10	15	25	40	60	90
	1	Empty beam	1	MTB	X							
	2	Blocked beam	2	BB	X	X	X	X	X	X	X	X
	3	Empty cell	3	MTC	X	X	X	X	X	X	X	X
x	LCST	Sample A in DME	4	A	X	X	X	X	X	X		
x	+	Pure DME	5	DME	X	X	X	X	X	X		
	~~LCST~~	Sample E in DME	6	E	X	X	X	X	X	X		
x	LCST	Sample C in DME	7	C	X	X	X	X	X	X		
	8	Sample D in DME	8	D	X	X	X	X	X	X		
x	LCST	PMMA homopolymer in DME	M 9	M	X	X	X	X	X	X		
	10	PHEA homopolymer in DME	H 10	H	X	X	X	X	X	X		
	11	S22 5wt% in Toluene	11	S22					X	X	X	X
	12	S25 5wt% in Toluene	12	S25					X	X	X	X
	13	Toluene	13	TOL					X	X	X	X
	14							15°C				
	15			T mesuré	-0.2	3,9°C	9,2°C	~~15°C~~	24,8°C	38,8	57,5°C	83 ~~90~~
	16							~~15°C~~				
	17			T consigne	-9,5	-3°	5°C	13°C	25°C	42°C	65°C	90°C
	18											
	19											
	20											

-4.5 1.2 7 12.6 24.1 41.2 64.1 98.4 Setpoint

target

x 2

x 3

Before scans at 60 and 90°C, all solutions in DME were removed from the rack to avoid overpressure or solvent evaporation (boiling point 84°C).

Reduced data were downloaded directly from the ILL data portal site.[1] After applying incoherent scattering corrections, data of solutions were fitted by Debye and Guinier functions, using the Kaleidagraph software in order to produce measurements of Rg as the function of temperature, in the vicinity of phase separation. Data of gels were fitted with different models, using the SASview software. Best results were obtained using the semi-flexible cylinder model.[2]

SANS results about S22 and S25 organogels have been published, together with original chemical synthesis, rheology and other structural studies by solid state NMR, cryoTEM and SAXS.[3]

SANS results about the LCST of pMAA and pHEA have been published, together with chemical synthesis by RAFT, Hansen parameter analysis and other structural studies by IR spectroscopy.[4]

SANS results about the LCST of samples A-E, together with molecular dynamics (MD) simulations and other structural analyses by IR spectroscopy will be the matter of a separate paper.[5]

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

2 J. S. Pedersen, P. Schurtenberger, *Macromolecules*, 1996, **29,** 7602–7612.

3 K. Nishimori, E. Cazares-Cortes, J.-M. Guigner, F. Tournilhac, M. Ouchi. *Polym. Chem.* 2019, **10,** 2327

4 E. Cazares-Cortes, B. C. Baker, K. Nishimori, M. Ouchi, F. Tournilhac, *Macromolecules* 2019, **5215,** 5995-6004.

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