Experimental report

09/10/2017

Proposal: 9-11-1822 **Council:** 10/2016

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

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: 1,2-Dimethoxyethane D10 (CAS number: 107975-86-0)
Sequence-controlled acrylate copolymer solution

Instrument	Requested days	Allocated days	From	To
D22	1	2	16/02/2017	17/02/2017
			02/03/2017	03/03/2017

Abstract:

As part of an ANR (France) / JST (Japan) international project dedicated to "molecular technology," the co-proposers (FG Tournilhac, A. Guimet, ESPCI and Makoto Ouchi, University of Kyoto) are currently studying structures and properties related to the self-assembly of sequence-controlled copolymers. The objective of this proposal is to understand the structure of alternating copolymers that show lower critical solution temperature (LCST) in an organic solvent whereas random copolymers of same composition do not. SANS beamtime is requested to produce reliable structural data with single-chain resolution from radiation-sensitive polymer samples.

Neutron scattering report: experiment 9-11-1822 at the ILL (Grenoble)

Self-association of sequence-controlled polymers in organic solvent.

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This work is a part of an International (France-Japan) ANR/JSP Project devoted to sequence-controlled polymers. It has been previously confirmed, both visually and via UV, that the sequential copolymer **SB** (**a**, **Figure 1**) demonstrates LCST behaviour in solutions of DME.[i] To ascertain changes in the radius of gyration, with respect to temperature, variable temperature SANS was undertaken on samples of **SB** in DME/D_20 (6%) (8 mg/mL) (**b**, **Figure 1**).

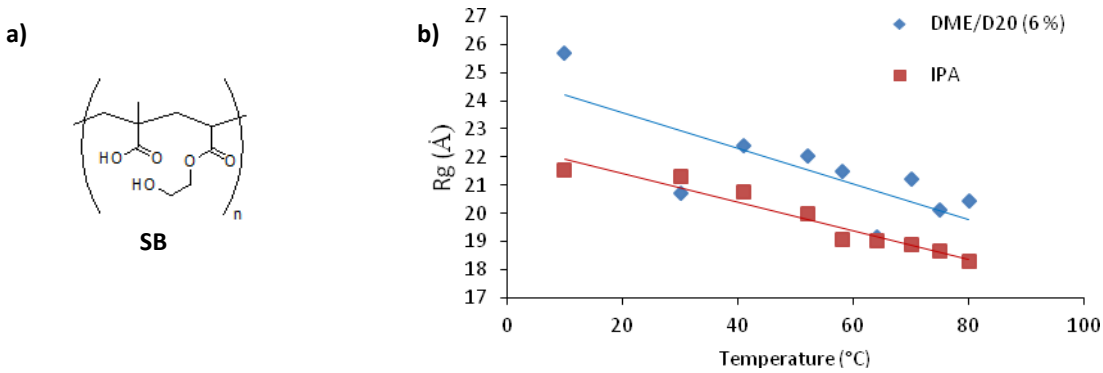

Figure 1. a) sturucture of the sequential copolymer **SB**, **b)** Radius of gyration of copolymers **SB** in DME/D_20 6 %wt and Isopropyl alcohol (8 mg/mL) as a function of temperature, derived from variable temperature SANS at the ILL institute.

During the first beamtime allocation most of the beamtime was unproductive due to a fall of a cadmium trap. Kindly, the beamline contact Dr. Lionel Porcar, proposed extra time for experimentation during 2nd-3rd of March 2017. In both occasions the experiments were performed on line D22 at the Institute Laue Langevin. Chemistry labs at the beamline and in the science building were utilised, and we are grateful for Dr. Ralf Schweins' help in utilising wet chemistry areas and IR spectrometry. Data was obtained directly from the data portal site.

Samples were prepared via dissolution in DME/D_2O 6 %wt, sonication required. The samples were held in a quartz Hellma cell with a 1 mm path, Cell volume = 300 µL. The temperature was imposed by a circulating fluid in the cell's holder rack. Sample-to-detector distances D =17 m, λ = 6 Å, the scattering wave vector q ranged from 0.03 $Å^{-1}$ up to 0.5 $Å^{-1}$.

It was observed that a decrease in radius of gyration with increasing temperature occurs. Interestingly no dramatic rate change was observed in the decrease in R_g (with increasing temperature) as is common among LCST systems.[ii] Furthermore it was observed that solutions of **SB** in deuterated isopropyl alcohol (IPA) also demonstrated similar behaviour, thought again LCST like observations were not recorded visually in the temperature range.

The results have lead to several new investigations including molecular dynamics computations (awarded time for simulation on the mesoPSL computer cluster, see proposal), IR and NMR analysis. The results are currently being prepared for publication.[iii]

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[i] M. Ouchi, M. Nakano, T. Nakanishi, M. Sawamoto, *Ange. Chem.* 2016, **128**, 1-7

[ii] J. Clara-Rahola, A. Fernandez-Nieve, B. Sierra-Martin, A. B. South, L. A. Lyon, J. Kohlbrecher, A. Fernandez Barbero, *J Chem Phys.*, **21**, 2012, 136

[iii] B. Baker, B. Tarus, M. Ouchi, F. Tournilhac, *Paper in preparation*