Experimental report

11/11/2015

Proposal: 9-10-1373 **Council:** 4/2014

Title: Contrast variation studies of the micellar structure of poly(N-isopropylacrylamide)-b-poly(dimethylsiloxane)-b-poly(N-isopropylacrylamide)

Research area: Materials

This proposal is a new proposal

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Samples: CHONSi

Instrument	Requested days	Allocated days	From	To
D11	1	1	18/12/2014	19/12/2014

Abstract:

SANS will be used to probe the micellar structure of novel block copolymers of poly(N-isopropylacrylamide)-b-poly(dimethylsiloxane)-b-poly(N-isopropylacrylamide) in aqueous solutions and their transformations upon increase in temperature. These experiments will provide insights into the nature of self-assembly and gelation in solutions of block-copolymers.

The main goal of this proposal was to probe the micellar structure of these triblock copolymers in aqueous solutions and to get detailed information about the distribution of hydrophobic PDMS and thermosensitive PNIPAAM moieties inside polymeric nanoparticles by contrast variation studies.

Two PDMS-PNIPAAM-PDMS copolymers with different block ratios (PDMS 2.5-PNIPAM 7 and PDMS 5-PNIPAM 7) were studied in different mixtures of H_2O/D_2O (Figure 1). Experiments were conducted at two temperatures – 25 and 40 ^oC below and above the cloud point temperature known from DLS experiments.

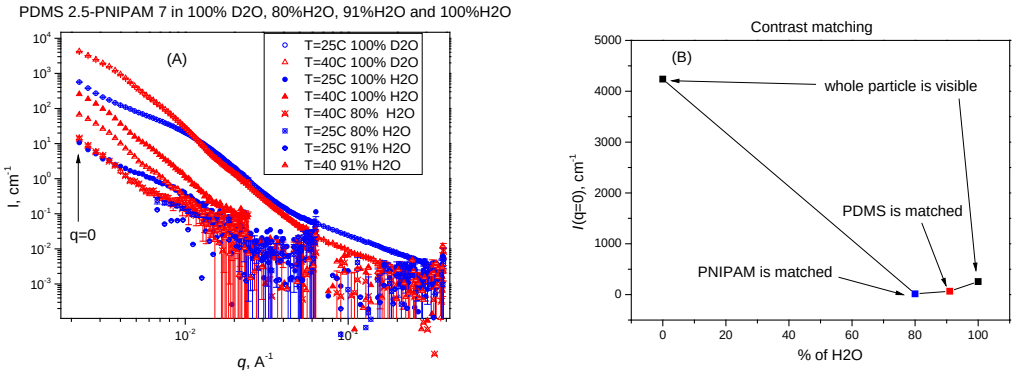

Figure 1. (A) The scattering curves from SANS at two temperatures 25 and 40^{o}C. (B) Stuhrmann plot.

The best fitting in D2O was obtained by the Beucage model (Table 1, Figure 2) . The model describes fractal aggregates consisted of smaller particles. Sizes of whole mass fractal aggregates at 25 and 40 ^oC are consistent with DLS data (data from our proposal) - 36 and 150 nm. The discrepancy could be attributed to different methods (DLS gives R_h, SANS gives R_g).

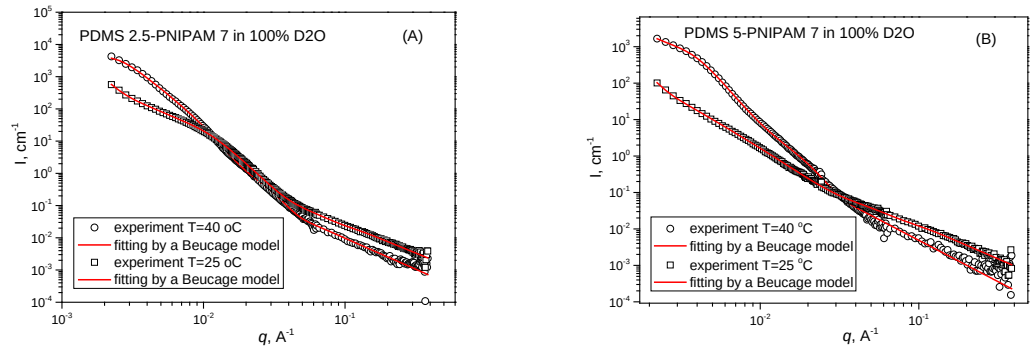

Figure 2. (A) The scattering curves from SANS for PDMS 2.5-PNIPAM 7 system in 100 % D_2O; (B) The scattering curves from SANS for PDMS 5-PNIPAM 7 system in 100 % D_2O.

Table 1. The fitting parameters for SANS data of PDMS 2.5-PNIPAM 7 and PDMS 5-PNIPAM 7 in 100% D_2O fitted by the Beucage model.

	PDMS 2.5-PNIPAM 7		PDMS 5-PNIPAM 7	
Fitting parameter of Beucage model	T=25 ^oC	T=40 ^oC	T=25 ^oC	T=40 ^oC
G	194.4	981±13	2009.8	5974

B	6.0e-6	2.2±0.5 e-5	1.7± 0.3 e-5	8.29e-10 ± 4 e-8
G_s	0.185	2.16	0.10±0.01	3.76±0.01
B_s	4.3 ±0.2 e-4	1.1 ± 0.1 e-4	1.7 ±0.2 e-4	2.6 ± 0.8 e-5
R_g, Å	358±4	1495±8	1479±82	938±2
R_{sub}, Å	58±2	147±1	72±2	85±9
R_s, Å	35±1	85.0±0.3	39±2	126±1
P	3.34±0.02	3.19±0.01	2.51±0.01	5.0±0.1
P_s	1.79±0.01	1.92±0.01	1.87±0.01	2.28±0.01
χ^2	385	6209	240	1877

In D2O the nanoparticle's model could be described as follows:

At 25°C, a nanoparticle of overall radius of 36 nm, consisted of small 3.5-5.8 nm particles, that are arranged inside of a fractal with scaling exponent 3.3 (surface fractal). Inside of small particles, they behave as polymers with some excluded volumes effect (scaling exponent is 1.79)

At 40 °C, nanoparticles are much larger; R_g=150 nm. They consist of smaller particles with 8.5 -14 nm particles, that are arranged inside of a fractal with scaling exponent 3.1 (surface fractal). Inside of small particles, they behave as almost Gaussian polymers (scaling exponent is 1.92)

In 91% of H2O (scattering from PDMS block is masked)

The interesting feature of scattering from PDMS 2.5-PNIPAM 7 solution in 91%H_2O, where PDMS block is masked, is that the scattering curve could be easily scaled with the scattering curve in 100%. That implies that structure of PNIPAM block resembles the structure of whole nanoparticle visible in 100% D_2O.

In 80% of H2O (scattering from PNIPAM block is masked)

Scaling is not working in the case when PNIPAM block is masked (Figure 3A,B). Obviously, the structure of PDMS block is different. We have used a combination of a form factor for aggregate and polydisperse spheres (Figure 3B). The fitting shows the presence of spheres with size 1.2 nm and high polydispersity. Actually, we can say that we have visualize PDMS core.

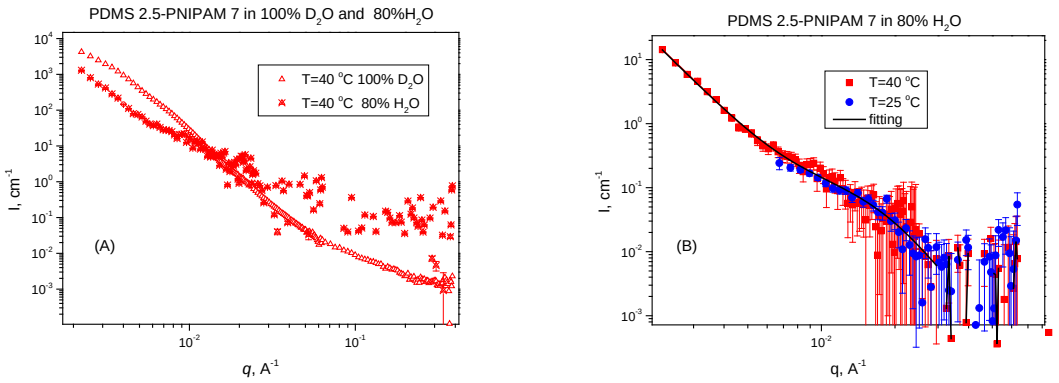

Figure 3. (A) The scattering curves from SANS for PDMS 2.5-PNIPAM 7 system in 80% H2O and 100 % D2O solvents at 40 °C; The data for 80% of H2O solvent were vertically shifted; (B) The scattering curves from SANS for PDMS 2.5-PNIPAM 7 system in 80% H2O solvent at 40 °C.