Experimental Report

Proposal: **9-11-1650** **Council:** 10/2012

Title: Partially deuterated gradient poly(2-oxazolines): contrast variation studies

This proposal is a new proposal

Researh Area: Soft condensed matter

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Samples:
poly(2-d3-methyl-2-oxazoline)75-stat-poly(2-phenyl-2-oxazoline)25 /(NC4D3OH4) 75-stat-(NC9OH9)25
poly(2-d3-methyl-2-oxazoline)25-block-poly(2-phenyl-2-oxazoline)75 /(NC4D3OH4) 25-block-(NC9OH9)75
poly(2-d3-methyl-2-oxazoline)50-block-poly(2-phenyl-2-oxazoline)50 /(NC4D3OH4) 50-block-(NC9OH9)50
poly(2-d3-methyl-2-oxazoline)75-block-poly(2-phenyl-2-oxazoline)25 /(NC4D3OH4) 75-block-(NC9OH9)25
poly(2-d3-methyl-2-oxazoline)25-stat-poly(2-phenyl-2-oxazoline)75 /(NC4D3OH4) 25-stat-(NC9OH9)75
poly(2-d3-methyl-2-oxazoline)50-stat-poly(2-phenyl-2-oxazoline)50 /(NC4D3OH4) 50-stat-(NC9OH9)50

Instrument	Req. Days	All. Days	From	To
D11	2	1	03/05/2013	04/05/2013

Abstract:

Recently, new copolymers were developed that are more complex than conventional block copolymer amphiphiles. These gradient copolymers are based on poly(2-methyl-2-oxazoline) and hydrophobic poly(2-phenyl-2-oxazoline), whereby the structure gradually changes along the polymer chain. It was demonstrated that the self-assembly of these gradient copolymers can be easily tuned although the detailed information e.g. distribution of two blocks inside the nanostructure is still missing. The main goal of this proposal is to obtain the detailed information about the distribution of hydrophilic, and hydrophobic moieties inside polymeric nanoparticles by contrast variation studies. To fulfill the aim, partially deuterated gradient copolymers with different composition will be studied. Using different composition of H2O/D2O we will try to mask the scattering from the selected blocks to make them invisible for neutrons.

The main goal of the proposal was to examine new amphiphilic gradient copolymers were developed that are more complex than conventional block copolymer amphiphiles. These gradient copolymers are based on poly(2-methyl-2-oxazoline) and hydrophobic poly(2-phenyl-2-oxazoline), whereby the structure gradually changes along the polymer chain (Figure 1a).

In our studies, series of amphiphilic poly(2-methyl-2-oxazoline)$_{75}$-block-poly(2-phenyl-2-oxazoline)$_{25}$ block copolymer and gradient poly(2-methyl-2-oxazoline)$_{75}$-stat-poly(2-phenyl-2-oxazoline)$_{25}$ (pMeOx50-stat-PhOx50) were synthesized (Figure 1a). We were able to fit the scattered SANS data by the model of an ellipsoid block copolymer micelle (Table 1). Calculated aggregation numbers are in agreement with DLS, SLS data measured previously. It was established that block copolymers have higher N_{aggr} values than gradient ones. Our results show that block copolymers have a much more solvent in a core in comparison with gradient copolymers that have almost no solvent inside (Table 1).

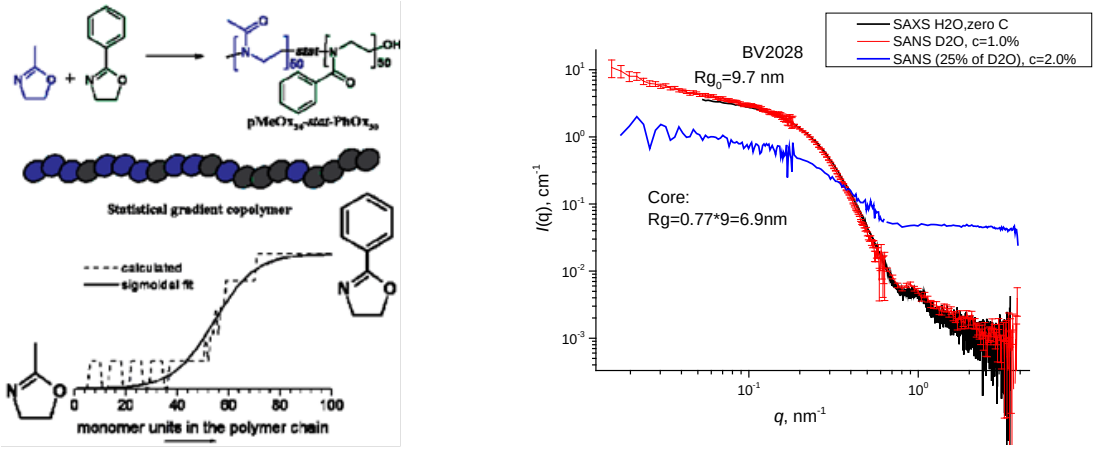

Figure 2. **A**: Chemical structure of amphiphilic gradient copolymers together with the gradual change in monomer structure along the the polymer chain. **B**. Combined SAXS and SANS data for block copolymer BV2028, including contrast matching by SANS

Table 1. Fitting parameters by the model of elliptical block copolymer micelles

Fitting parameter	BV2024 - grad	BV2028- block
Nagg	47.8	85
V_core, nm3	10	9
V_brush, nm3	27	23
Scat length_core	0.0022	0.0022
Scat length_core	0.0015	0.0014
Xsolv_core	0.00005	0.21
Rg, nm	2.3	2.3
eccentricity	1.9	2.23

Detailed inspection of scattered intensity at high q-range clearly revealed the difference in chain conformation of MeOx, that is presumably forms a shell around PheOx block (Figure 2).

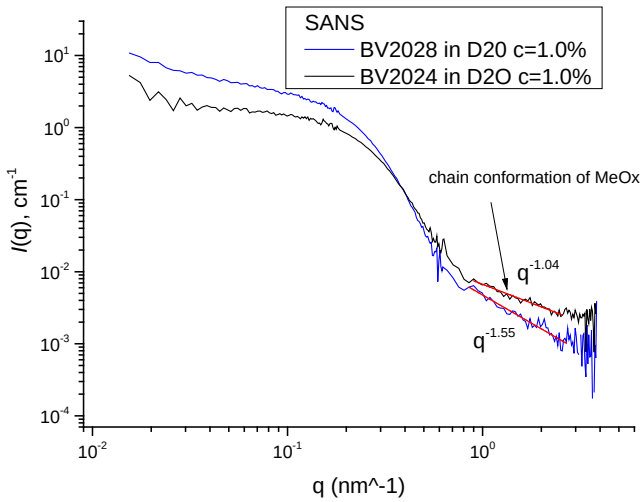

Figure 2. SANS data for gradient (BV2024) and block (BV2028) copolymers. At high q-range chain conformation is different.