Experimental report

15/06/2016

Proposal:	**9-11-1734**	**Council:**	10/2014

Title: Ampholytic triblock terpolymer in dependence on pH value and solvent nature - hydrophobic association and electrostatic interactions

Research area: Soft condensed matter

This proposal is a new proposal

Main proposer: **Christine PAPADAKIS**

Experimental team:
Bart-Jan NIEBUUR
Margarita DYAKONOVA
Natalya VISHNEVETSKAYA
Konstantinos RAFTOPOULOS

Local contacts: Isabelle GRILLO

Samples: poly(methyl methacrylateâb-(diethylamino)ethyl methacrylate-co-methacrylic acid)-b-methyl methacrylate)

Instrument	Requested days	Allocated days	From	To
D33	3	3	16/05/2015	18/05/2015
			24/06/2015	25/06/2015
D22	3	0		

Abstract:

PMMA86-b-P(DEA190-co-MAA96)-b-PMMA86, poly(methyl methacrylate–b-(diethylamino)ethyl methacrylate-co-methacrylic acid)-b-methyl methacrylate), is a telechelic polymer composed of a hydrophilic ampholytic middle block and hydrophobic end blocks. Depending on pH value, the polymer can adopt different conformations as a result of the protonation/deprotonation equilibrium in the middle block upon pH variation. We aim to investigate the network formation mechanism in presence of two opposite effects: aggregation tendency of the hydrophobic outer blocks and electrostatic repulsion along the middle block. The latter will also be varied by changing the solvent nature. Addition of acetone alters the dielectric permittivity of the solvent and additionally enhances the solubility of the PMMA blocks, which has an impact on the structural characteristics of the obtained network. Static and kinetic experiments will be carried out.

The aim of the beamtime was to investigate the influence of the solvent nature on the structure of a pH-responsive, self-assembled hydrogel. The hydrogel is formed by the triblock copolymer $PMMA_{86}$-*b*-P(DEA_{190}-*co*-MAA_{96})-*b*-$PMMA_{86}$ where PMMA stands for poly(methyl methacrylate), PDEA for poy(2-(diethylamino)ethyl methacrylate) and PMAA for poly(methacrylic acid). In pure water, they system is strongly pH responsive, which allows tuning of its structural and rheological properties for various applications [1]. The responsiveness is caused by the weak ampholytic nature of the middle block P(DEA_{190}-*co*-MAA_{96}) whose degree of ionization depends on pH. At the pD value of 3.0, which was investigated in the present study, PDEA is protonated, resulting in a positive net charge of the block, whereas the degree of deprotonation of PMAA is very low [2]. The PMMA end blocks are hydrophobic and form dense micellar cores, which form the physical cross-links of the network. Repulsive electrostatic interactions between equally charged PDEA sequences lead to stretching of the middle block, which, at high concentrations and above a certain degree of ionization, is sufficient to bridge neighboring micelles, leading to the formation of a gel network. The addition of acetone is expected to have two effects: Firstly, it is expected to decrease the dielectric permittivity of the solvent, and, hence, to screen the repulsive electrostatic interactions along and between the polyampholytic P(DEA-*co*-MAA) blocks and thus to reduce the charge density in the system. Secondly, being a good solvent for PMMA, acetone is expected to enhance the mobility of the hydrophobic PMMA moieties and to facilitate their exchange between different physical cross-links in the network.

Using SANS at D33, we investigated the structures of gels formed at a concentration of 0.5 wt% of $PMMA_{86}$-*b*-P(DEA_{190}-*co*-MAA_{96})-*b*-$PMMA_{86}$ in mixtures of D_2O and $(CD_3)_2CO$ (named D-acetone hereafter) at pD 3.0. The polymers were dissolved in D-acetone at room temperature. Solution homogenization was achieved by centrifugation and subsequent stirring. When gels had been obtained, the desired amount of D-acetone in the solution was achieved by letting superfluous acetone evaporate. Afterwards, a pre-calculated amount of D_2O was added to install the desired concentration of polymer of 0.5 wt%. The pD value of 3.0 was fixed by adding 0.1 M hydrochloric acid (HCl) in D_2O. The gels were again homogenized by stirring and centrifuging. The samples without D-acetone and with D-acetone content up to 10 wt% were mounted in 1 mm quartz cuvettes (Hellma), whereas the samples with D-acetone contents of 15-30 wt% were mounted in 2 mm quartz cuvettes (Hellma). All samples were measured at room temperature. The scattering signal was collected by a 128 × 128 ^{3}He tube detector with a pixel size of 0.5 × 0.5 cm^2. The neutron wavelength was chosen at $\lambda = 0.5$ nm with a spread $\Delta\lambda/\lambda = 10\%$. Using sample-detector distances (SDDs) of 2.0 m and 12.5 m, a range of momentum transfers $q = 0.036$ to 5.7 nm^{-1} was covered. The exposure times were 15 min and 30 min at SDD = 2.0 m and 12.5 m, respectively. The scattering of boron carbide was used for correcting the intensities for the dark current. H_2O was used to measure the detector sensitivity and to calibrate the intensity. The scattering of the cell containing solvent was subtracted from the sample scattering, taking the transmissions into account. The data were azimuthally averaged. All data reductions were performed using the software LAMP provided by ILL.

The scattering curves of solutions of $PMMA_{86}$-*b*-P(DEA_{190}-*co*-MAA_{96})-*b*-$PMMA_{86}$ at 0.5 wt% in D_2O/D-acetone mixtures in dependence on the content of D-acetone are presented in Figure 1.

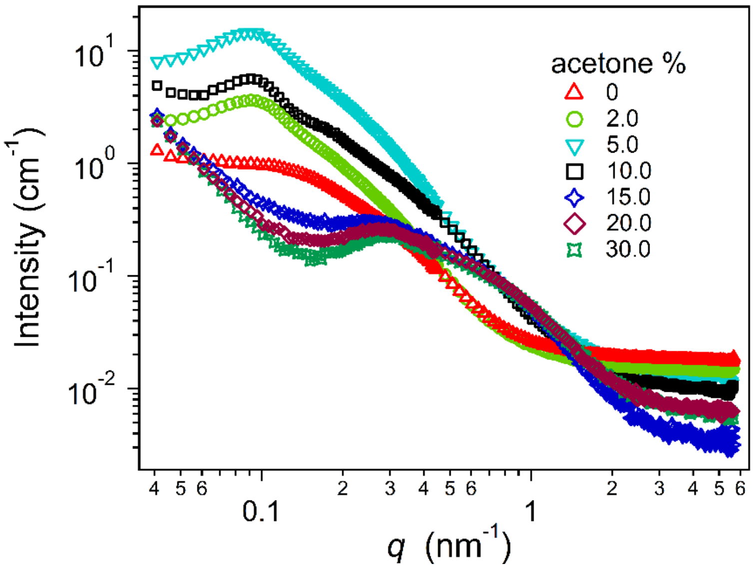

Figure 1. SANS curves of 0.5 wt% aqueous solutions of PMMA$_{86}$-*b*-P(DEA$_{190}$-*co*-MAA$_{96}$)-*b*-PMMA$_{86}$ at pD 3.0 in D$_2$O/D-acetone mixtures, measured at room temperature. The curves are shifted vertically for clarity. The content of D-acetone is indicated in the graph.

The curve of the solution without D-acetone shows a weak maximum at $q \sim 0.15$ nm^{-1} and a rather broad shoulder at higher q values. The peak is attributed to a structure factor, describing the interactions between the particles in solution. Although the shoulder is not so pronounced, we suppose that it contains information about the structural characteristics of the particles. We assume that these are formed by a compact core from hydrophobic PMMA, with the ionized ampholytic blocks forming a shell around the core.

In presence of 2, 5 and 10 wt% of D-acetone, both, the structure factor peak and the form factor shoulder become more pronounced and move to lower q values, manifesting an increase in the length scales of the system. Within this range, their positions do not vary significantly, which is probably due to geometrical boundary conditions. We conclude that, at these low contents of D-acetone, the hydrogel has a similar network architecture as in pure D$_2$O: glassy domains from hydrophobic PMMA which are connected by the polyampholytic blocks. The only change is that D-acetone lowers the dielectric permittivity of the solvent and, hence, the weakens the repulsive electrostatic interactions between the charged DEA units on bridging polyampholytic blocks, which in turn, enhances their hydrophobicity. As a result, the middle blocks may shrink and partially merge with the hydrophobic PMMA cores, increasing the micellar dimensions. From mass conservation, the number of these larger micelles decreases, which may explain the increase in average distance between different cross-links in the network.

At D-acetone contents of 15, 20 and 30%, the scattering curves have very low intensity, the characteristic features are unchanged, but less pronounced and shifted to higher q values. In addition, strong forward scattering at $q < 0.15$ nm^{-1} appears. The latter is presumably due to large aggregates, being a result of clustering of the micelles into a network. We suppose that D-acetone dissolves part of the PMMA cores, releasing some of the PMMA chains, which may explain the decreasing radius of the PMMA cores. The less pronounced structure factor peak is presumably due to a lower fraction of micelles which are correlated. At this high D-acetone content, the pronounced screening of charges on the middle block provokes its severe shrinkage, which may explain a decrease in intermicellar distances and a reduced cross-linking functionality in the network.

We are currently analyzing the data quantitatively by model fitting.

The experiment was successful and the beamtime scientist was very helpful.

1. C. Tsitsilianis, T. Aubry, I. Iliopoulos, S. Norvez, *Macromolecules* **2010**, *43*, 7779.
2. C. Tsitsilianis, G. Gotzamanis, Z. Iatridi, *Eur. Polym. J.* **2011**, *47*, 497.