Experimental report

26/04/2019

Proposal:	**9-11-1877**	**Council:**	4/2018

Title: Asymmetric, gradient-like block-copolymers: solution behaviour as a function of pH

Research area: Chemistry

This proposal is a new proposal

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Samples: $(C_3H_3O_2)_x(C_7H_{12}O_2)_y$-b-$(C_3H_3O_2)_y(C_7H_{12}O_2)_x$ x=1k y=4k
$(C_3H_3O_2)_x$-b-$(C_3H_3O_2)_y(C_7H_{12}O_2)_y$-b-$(C_7H_{12}O_2)_x$ x=4k y=6k
$(C_3H_3O_2)_x$-b-$(C_7H_{12}O_2)_y$ x=10k y=10k
$(C_3H_3O_2)_x$-g-$(C_7H_{12}O_2)_y$ x=10k y=10k
$(C_3H_3O_2)_x$-b-$(C_7H_{12}O_2)_y$ x=5k y=5k
$(C_3H_3O_2)_x$-g-$(C_7H_{12}O_2)_y$ x=5k y=5k
$(C_3H_3O_2)_x(C_7H_{12}O_2)_y$-b-$(C_3H_3O_2)_y(C_7H_{12}O_2)_x$ x=2k y=8k
$(C_3H_3O_2)_x$-b-$(C_3H_3O_2)_y(C_7H_{12}O_2)_y$-b-$(C_7H_{12}O_2)_x$ x=2k y=3k

Instrument	Requested days	Allocated days	From	To
D11	3	2	24/09/2018	26/09/2018

Abstract:

Gradient copolymers, whose composition varies continuously as a function of chain length, are an intriguing class of materials whose synthesis needs particular care. For this reason alternative 'gradient-like' copolymers, with asymmetric structures intermediate between a gradient copolymer and a block-copolymer, are industrially valuable. They should mimic the behaviour of gradient copolymers, but are easier to synthesize.

We synthesized a library of copolymers based on acrylic acid and butyl acrylate monomers and characterized their self-assembling behaviour as a function of pH. Dynamic Light Scattering and cryo-TEM experiments prove that the hydrodynamic size and morphology of the self-assemblies change as a function of pH in a way which depends on the monomer distribution along the copolymer chain. A detailed investigation on the structural features of the self-assemblies and their evolution as a function of pH, only possible through neutron scattering, is needed in order to better understand the structure-properties relationship and thus inspire polymer design.

Asymmetric, gradient-like block-copolymers: solution behaviour as a function of pH

Gradient copolymers may be considered as intermediate species between block and random copolymers. Many other intermediate species may also be considered, some of which are shown in Figure 1. The aim of the experiment was to investigate this kind of polymers, incorporating block, gradient and random segments in order to understand the relation between copolymer composition and self-assembled structures in solution.

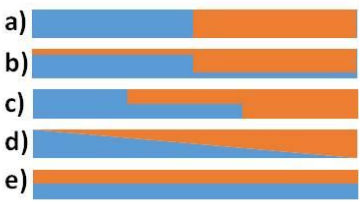

Figure 1. Schematic representation of asymmetric A/B copolymer structures: (a) block containing two homopolymer segments (b) diblock copolymer containing two random blocks (c) triblock copolymer with intermediate random block (d) linear gradient copolymer (e) random copolymer.

We have chosen a series of copolymers based on acrylic acid (monomer A) and butyl acrylate (monomer B). They possess the same total molecular weight and mean composition, but different mean monomer distribution along the chain, as depicted in Figure 1a-d: $A_{0.5}$-b-$B_{0.5}$ (block, B), $A_{0.5}$-g-$B_{0.5}$ (gradient, G), $A_{0.4}B_{0.1}$-$A_{0.1}B_{0.4}$ (diblock, D) and $A_{0.2}$-$A_{0.3}B_{0.3}$-$B_{0.2}$ (triblock, T) copolymers (the index is the weight percentage of each monomer) with M_n= 10 kDa and 20kDa.

In our SANS experiment on D11 we measured 1% wt D_2O buffered solutions (pH=4, 5, 7 and 10) in order to study how the hydrophilic nature of the copolymers, tuned by the protonation of the acrylic acid groups, influences the morphology of the assemblies. Samples have been measured in a wide q range (between 2 10^{-3} and 0.5 $Å^{-1}$). The main results are represented in Figure 2.

In the case of the block copolymer, phase separation was observed at pH 4, so the supernatant solution was analysed. Aggregation occurs at pH 4 when acrylic moieties are protonated and still large aggregates of spherical micelles are present in solution, as indicated by the low q increase of the scattering intensity (Figure 2a). At pH 10, an interaction peak at 0.11 nm^{-1} (57 nm) probably indicates a repulsion between spherical micelles in bigger aggregates (low q trend). This is in accordance with cryo-TEM experiments, where spherical micelles are always observed.

For all investigated systems the size of the assemblies diminishes when the pH increases, as witnessed by the shift of the curves towards high q values. This decrease in size is accompanied by a change in the shape of the curves indicating a morphological transition. We have begun the data analysis of the more representative curves (samples 10D, 10T and 20D) in order to capture the main features of the morphological transition. Depending on the system and the investigated pH, form factors corresponding to vesicles, cylinders or a mixture of cylinders and spheres were used to describe the data. The scattered length density was estimated to be 4.4 10^{-6} $Å^{-1}$ for the hydrophobic butyl acrylate forming the interior of the self-assemblies. The results of the fitting are reported in Table 1. Even if the quality of the fits has to be improved in some cases, the main features of the self-assemblies in the samples are captured.

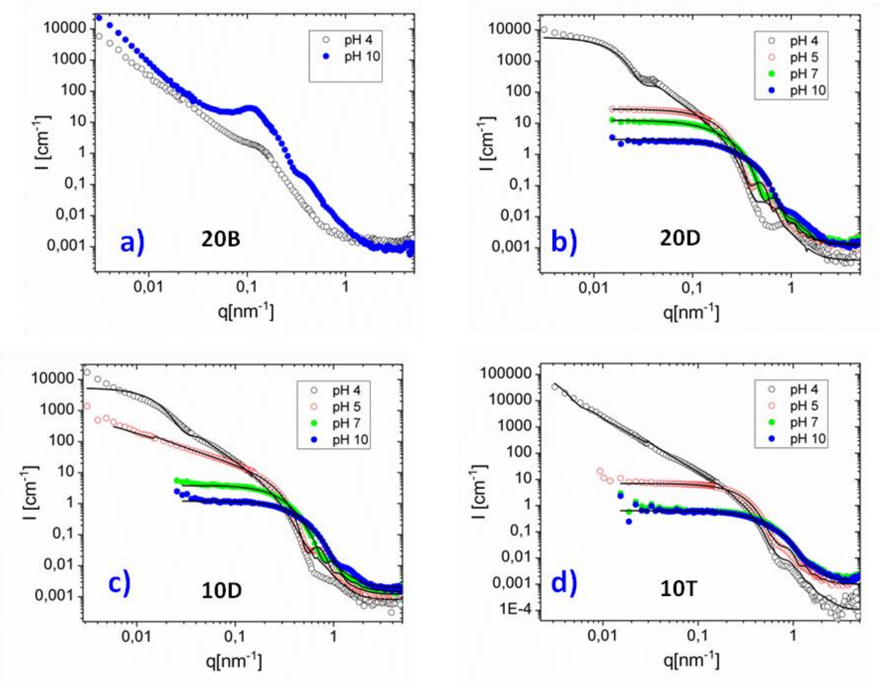

Figure 2. SANS curves and preliminary fits of samples 20B, 20D, 10D and 10T

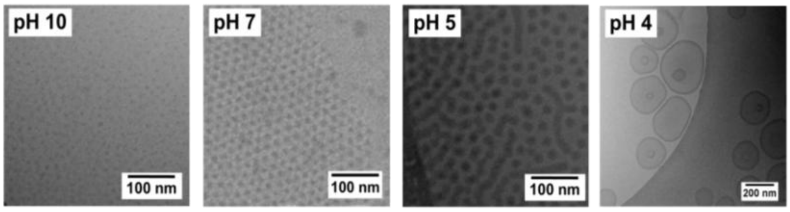

Figure 3: Representative cryoTEM images of aqueous solutions of sample 10D at pH 10, 7, 5 and 4.

This transition can be rationalized in terms of the changing hydrophilicity of the copolymer due to the deprotonation of acrylic units as a function of pH. This causes an increase in the hydrophilic/hydrophobic ratio of the copolymer and of the electrostatic repulsions in the hydrophilic shell. Both factors induce a decrease of the micellar aggregation number. The presence of elongated micelles together with spheres is observed at higher pH for the 10T and 20D copolymers. It is remarkable that the cross-section of the elongated micelles is very similar to the spheres' diameters.

Table 1. Sizes in nm of the self-assembled morphologies found in solution at different pH.

pH			10D	10T	20D
4	Vesicles	R	90	> 600	
		d	11	9.5	
5	Long cylinders	L	> 600		
		R	7.1		
	Elongated micelles	L		16.4	29
		R		6.7	13
	spheres	R		6.1	11.8
7	Elongated micelles	L	16.5	12	36
		R	5.1	2.7	8.2
	spheres	R		1.5	8.2
10	Elongated micelles	L	13	12	20
		R	3	2.7	5.2
	spheres	R		1.5	4.5

This preliminary data analysis will next be extended to the remaining copolymer systems (20G and 20T, see Figure A), whose diffraction patterns show qualitatively similar morphological transitions. The SANS analysis has allowed us to validate the morphological transitions previously observed by cryoTEM for a subset of the samples, and confirmed that this system is a rare example of a pH-responsive two-component block copolymer which undergoes the full range of sphere/cylinder/vesicle morphological transitions. The pH-induced order-order transitions are not observed in block copolymers containing two homopolymer segments, but require the component hydrophilic and hydrophobic monomers to be distributed in a controlled manner between the block copolymer segments. This finding will have significant ramifications for the future design of stimuli-responsive copolymers.

Annex

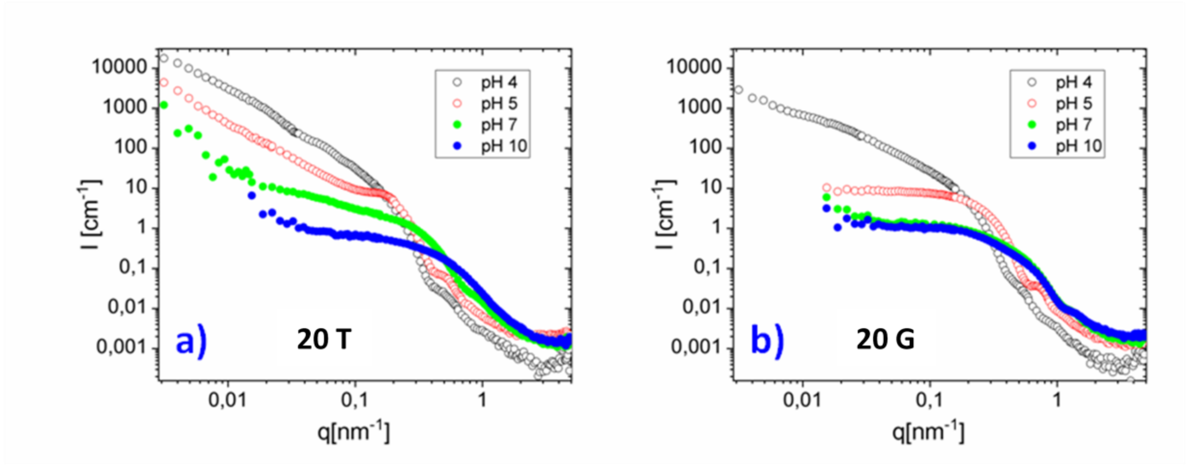

Figure A. SANS curves of samples 20T and 20G.