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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Structural and conformational changes on stimuli-responsive polymersomes under Ultraviolet irradiation	**Experiment number**: SC-4276
Beamline:	**Date of experiment**: from: 04/03/2016 to: 07/03/2016	**Date of report**: 22/01/2018
Shifts: 9	**Local contact(s)**: SZTUCKI Michael	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

In this experiment we proposed to study changes in the UV and temperature responsive polymersomes under two particular external stimuli: Ultraviolet (UV) light and temperature. By combining USAXS and WAXS with simultaneous UV irradiation we obtained information on the mechanism of modification of the polymersome membrane for drug delivery applications.

<u>Scientific Background</u>.

Polymeric vesicles, also known as polymersomes, represent a remarkable type of supramolecular structures formed by spontaneous self-assembly of amphiphilic block copolymers (BCs) in selective solvents whose growing interest is related to their potential for nanocontainers or nanoreactors applications among others.[1] These structures are hollow spheres with a polymeric hydrophobic bilayer isolated from the internal cavity and outer space by hydrophilic coronas. Stimuli responsive polymersomes are attracting lot of interest since they provide a roadmap to activate the delivery of the encapsulated compound in a controlled manner. Among the different stimuli, light is considered a very versatile one since it can be remote, temporal and spatially controlled. In general, light responsive polymer vesicles include azobenzene groups as a constituent block. Azobenzene groups isomerizes under illumination.[2] Temperature is also a very interesting stimulus, in particular for bio applications, since unhealthy tissues might show slightly high temperature than healthy ones. There are polymers, which are soluble in water, that become insoluble when heated over a certain temperature, called lower critical solution temperature (LCST). Recently, the group of

Prof. Luis Oriol have synthetized series of amphiphilic linear−dendritic block copolymers (LDBCs) that combined the responses to both mentioned stimuli. These systems self-assemble in water [1] and that have been shown to encapsulate both hydrophilic and hydrophobic compounds.

Experimental.

Simultaneous synchrotron Small Angle X-Ray Scattering (SAXS) and Wide Angle X-ray Scattering (WAXS) data were collected at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) on the beam-line ID02, with a wavelength of 1 Å. SAXS results were collected with the detector at a samples-to-detector distances of 30m 5m and 1m giving a q-range of observed q-range of $2 \cdot 10^{-3}$ nm^{-1} < q < 6.99 nm^{-1}. A detector located at closer distance from the sample allows the collection of the wide angle X ray scattering signal from the sample in a q-range of 6.2 nm^{-1} < q < 50 nm_{-1} 2D data were radially averaged and standard reduction procedures (subtraction of air scattering) were applied.

Results and discussion.

Several set of samples were studied. Experiments under UV irradiation were performed at room temperature, and SAXS patterns were collected while the sample was irradiated with a UV lamp (Phillips PL-S 9W) placed at a distance of 10 cm. On the other hand side chain azobenzene homopolymers and corresponding poly(methyl methacrylate) block copolymers have been synthesized by modification of polymeric scaffolds having pendant alkyne groups using azides from 2,2-bis(hydroxymethyl)propanoic acid decorated with two motifs, either two azobenzenes or one azobenzene and one biphenyl. These systems were prepared in the form of films by solution casting. a solution of the polymer in toluene 1% (w/w) (40 µL) at 6000 rpm during 60 s over an amorphous silicon substrate. Films were dried for 24 h at 30 ºC under vacuum, and annealed for 24 h at 150 ºC under vacuum.

Figure 1 shows the scattering obtained for P70AZO/AZO-b-PMMA20k. At low angle, the scattering can be described as arising from a Gaussian distribution of spheres with a mean diameter of 18 nm and a another contribution of smaller particles centered around 3 nm. These results are consistent with other obtained by Transmission Electron Microscopy (TEM).

In the case of P70CNB/AZO-b-PMMA20k (Figure 1) the scattering can be described as arising from a Gaussian distribution of particles with average diameter 5.2 nm, and this was also corroborated by TEM (Figure 2). The comparatively, higher tendency to phase segregation of P70AZO/AZO-b-PMMA block copolymers can be tentatively associated to the liquid crystalline behavior of the functionalized block.

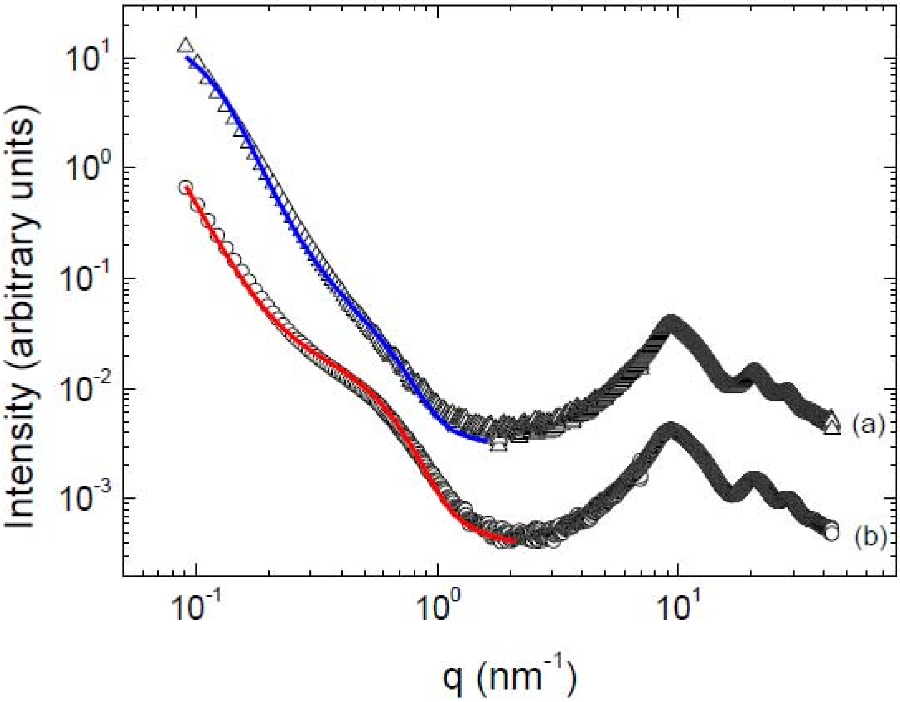

Figure 1. SAXS intensity as a function of the scattering vector of (a) P70AZO/AZO-b-PMMA20k (blue line, triangles), (b) P70CNB/AZO-b-PMMA20k. (red line, circles)

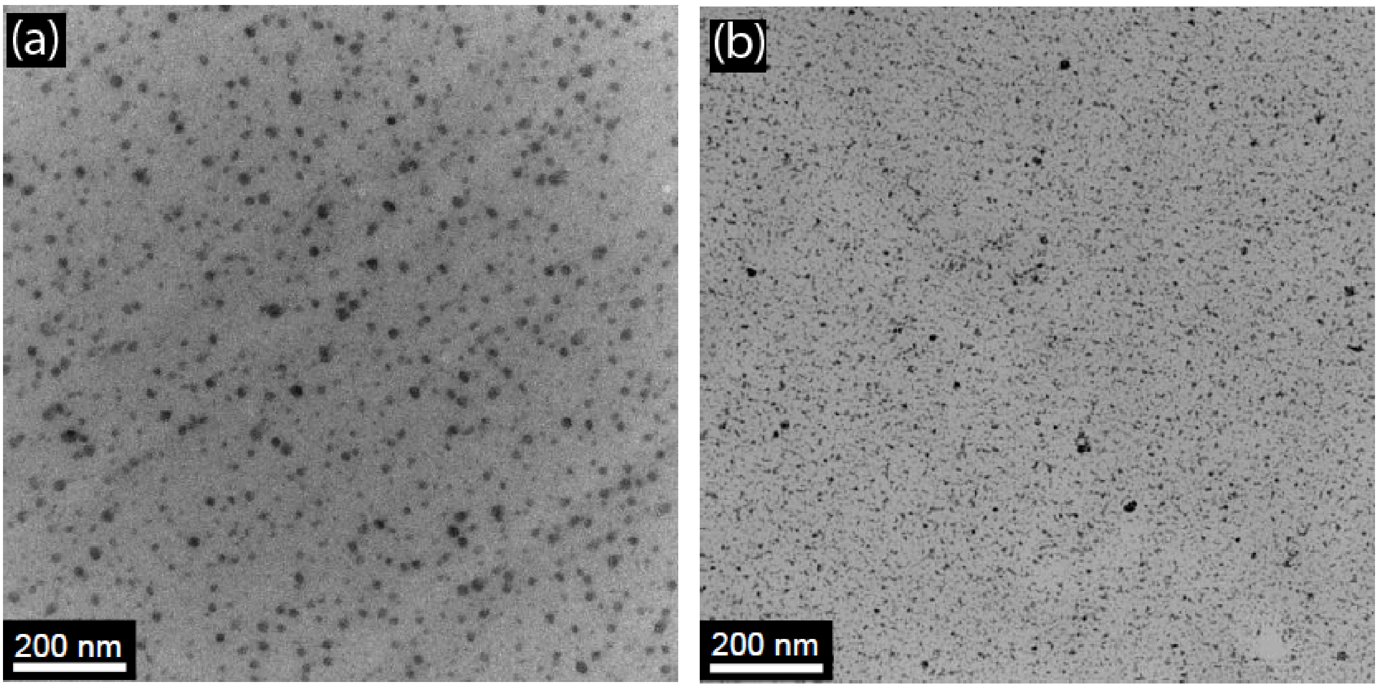

Figure 2: TEM images of the block copolymers (a), P70AZO/AZO-b-PMMA20k and (b) P70CNB/AZO-b-PMMA20k.