ESRF	**Experiment title:** The role of the homopolymer matrix in the micellization characteristics of block copolymer / homopolymer blends	**Experiment number**: SC-2481
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Shifts: 9	**Local contact(s)**: Dr. Giuseppe Portale	*Received at ESRF:*

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Report:

This experiment is part of our ongoing research on the effect of the macromolecular architecture on the micellization properties of block copolymers / homopolymer blends, and it is considered to be the continuation of our previous experiment SC-2146. With the present experiment we intended to extend our investigation towards two directions: the influence of the homopolymer molecular weight (M_w) on the micellar characteristics, and the effect of the homopolymer matrix selectivity on the micellization of a series of graft copolymers. It is noted that the need for the study of the micellization with respect to the matrix characteristics was manifested by the theoretical studies that we carried; a simple thermodynamic model that describes the micellization of linear AB, AB_2 & A_2B graft and A_nB_n miktoarm copolymers within a B homopolymer matrix has been developped and, for this reason, the present experiment was designed in order to compare the results obtained with the theoretical ones.

The following sets of samples have been prepared and investigated by Small Angle X-ray Scattering (SAXS):

- A symmetric linear polyisoprene-b-polystyrene, IS, copolymer of low total molecular weight (~35k), a series of IS copolymers of higher total molecular weight (~100k) and varying composition, f_{PS}, thereinafter named SI, and a series of (polyisopene)$_2$(polystyrene), I_2S, graft copolymers of similar molecular weight and composition as the SI series, were blended with polyisoprene, PI, homopolymer of various M_w, namely 2k, 4k, 10k and 20k. Thus, the micelles that are formed consist of a polystyrene, PS, core and a PI corona.
- The I_2S graft copolymers were added in a low molecular weight (M_w ~3k) PS homopolymer, resulting in micelles formed by a PI core and a PS corona.

In all cases the copolymer concentration was 2wt% and the micellar characteristics were investigated with respect to M_w, f_{PS}, or both.

SAXS data were recorded on a two-dimensional position sensitive detector. Two different energies of the X-ray beam were used, 12keV and 8keV, each one for a different sample-to-detector distance, 1.5 m and

7 m respectively, and thus a wide scattering vector range was covered, $0.04 < q < 6.5$ nm^{-1}. The two-dimensional images were radially averaged around the center of the primary beam, in order to obtain the isotropic SAXS intensity profiles. The scattering patterns from a specimen of wet collagen (rat tail tendon) and Silver Behenate were used for calibration of the q scale of the scattering profiles. Lupolen and Eltex were used as reference samples for the intensity calibration in absolute units (cm^{-1}). The data have been normalized to the intensity of the incident beam (in order to correct for primary beam intensity decay) and corrected for absorption, background scattering and copolymer concentration. Two ionization chambers placed before and after the sample, were utilized for the measurement of the incident and the transmitted beam. The background correction was made by subtracting from the total intensity the contribution of density fluctuations evaluated from measuring pure PI or pure PS, for the corresponding set of samples. The samples were placed inside glass capillary tubes of 2 mm diameter and the measurements were conducted at room temperature. Through the analysis of the SAXS scattered intensity, the form factor of the micelles was derived, and thus the core radius, R_c, the micellar aggregation number, Q_m as well as the volume fraction of micelles in the blends were calculated.

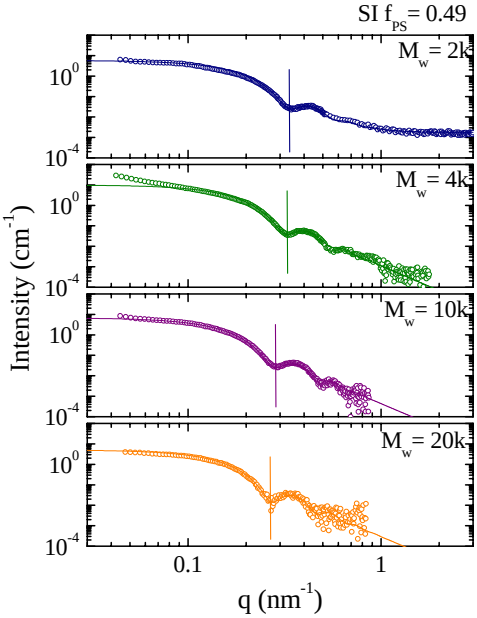

Figure 1: The SAXS intensity curves as a function of the scattering vector q for the 2wt% blends of the symmetric SI copolymer in the various PI matices, and the corresponding best fitting curves (solid lines).

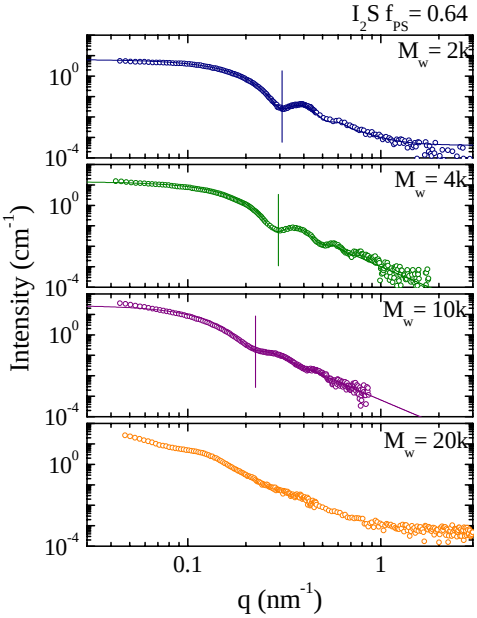

Figure 2: The SAXS intensity curves as a function of the scattering vector q for the 2wt% blends of the I_2S graft copolymer with f_{PS}=0.64 in the various PI matices, and the corresponding best fitting curves (solid lines).

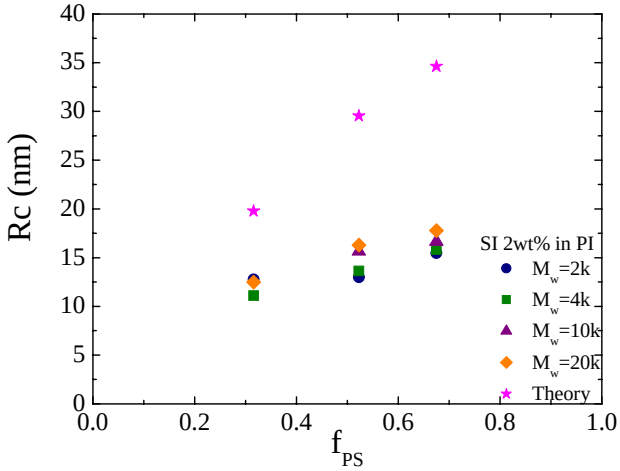

Figure 3: The core radius of the micelles formed within the 2wt% blends of the linear SI copolymers with the various PI matices, as a function of f_{PS} and M_w.

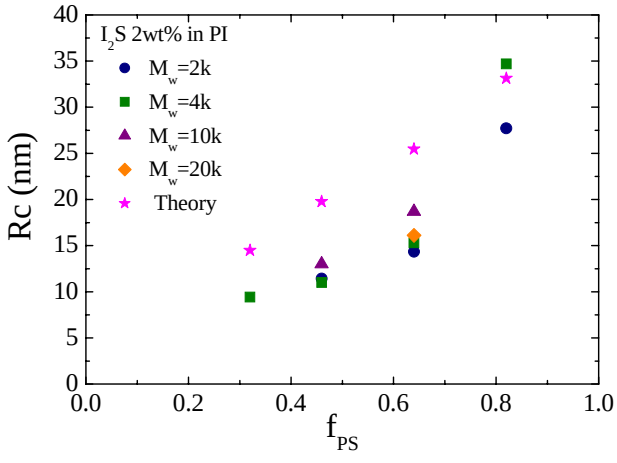

Figure 4: The core radius of the micelles formed within the 2wt% blends of the I_2S graft copolymers with the various PI matices, as a function of f_{PS} and M_w.

The scattering intensity profiles acquired for the blends of the linear SI copolymer with f_{PS} = 0.49 and the graft I_2S copolymer with f_{PS} = 0.64 in the various PI matrices are presented in Figures 1 and 2 respectively. Micelles are formed for all the blends and the characteristic features of the form factor of spherical particles are apparent in the profiles. For both copolymers, the position of the first minimum shifts towards lower q values as the M_w of the homopolymer matrix is increased, implying that the radius of the micellar core increases. This trend was further verified by the form factor analysis. The best fitting curves are designated by solid lines in Figures 1 & 2, while the fitting results concerning the core radius, R_c, are presented in Figures 3 & 4, for the linear and the graft copolymers respectively. The effect of the homopolymer M_w on the radius is presented along with the effect of the copolymer composition f_{PS}. The theoretical R_c values that are estimated by our model are also included in Figures 3 & 4 and despite the apparent disagreement with the experimental results, a trend to comply with them is observed as M_w is increased. This trend is more pronounced for the graft copolymer micelles, for which the length of the corona forming PI block decreases more abruptly with increasing f_{PS} than in the linear copolymer case, due to the grafting with the second PI block. Those observations actually confirm our predictions about the influence of the penetration of the homopolymer chains within the micelles corona on the micellar characteristics, but giving more details about this issue is beyond the scope of the present report.

It is interesting to note that the scattering profile of the blend of the I_2S graft with f_{PS}= 0.64 in the 20k M_w PI does not correspond to spherical micelles. A broad peak is observed around 0.12nm^{-1}, close enough to the theoretically calculated value for the scattering of the disordered diblock. Thus, macro-phase separation between the homopolymer and the copolymer is most probable to occur. Similar scattering profiles were also acquired for the I_2S grafts with f_{PS}= 0.82 and f_{PS}= 0.9, where the peak position shifts towards higher q values as M_w increases.

As far as the blends of the graft copolymers in the PS homopolymer are concerned, unfortunatelly, the experiments were not successful due to several problems encountered during the sample preparation, mainly because of the glassy nature of PS at room temperature and its high fragility at very low M_w, like that we used. Although several preparation methods have been applied in order to face these problems, no evidence on micelles formation was observed on the scattering profiles that were acquired.

Despite this slipup, the results obtained for the micellization of the PI homopolymer blends are evaluated to be very satisfactory, in particular combined with the theoretical predictions. Although the analysis of the profiles of the non-forming micelles blends is still ongoing, a publication is foreseen and will be soon in preparation.