ESRF	**Experiment title:** Macromolecular Architecture Effects on the Micellization Behavior of Block Copolymers in Homopolymer Matrices	**Experiment number**: SC-2146
Beamline: BM26B	**Date of experiment**: from: 03/12/2006 to: 05/12/2006	**Date of report**: 31-07-2007
Shifts: 6	**Local contact(s)**: Dr. Giuseppe Portale	*Received at ESRF:*

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Report:

We investigate the effect of macromolecular architecture on micellar formation and micelle characteristics of block copolymers in homopolymer matrices. A series of (polyisoprene)$_2$(polystyrene), I_2S, graft copolymers with constant total molecular weight and varying composition, f_{PS}, and a series of symmetric (polyisoprene)$_n$(polystyrene)$_n$ (I_nS_n) miktoarm star block copolymers, with n identical pairs of arms, are added to a low molecular weight polyisoprene homopolymer matrix and the blends are investigated by small-angle X-ray scattering (SAXS) as a function of f_{PS} or n, respectively, of the copolymer concentration and the temperature.

SAXS data were recorded on a two-dimensional position sensitive detector using an X-ray wavelength of 1.55 Å. Two different sample-to-detector distances were used, 1.5 m and 7.5 m, thus a wide scattering vector range was covered, $0.04 < q < 3.7$ 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. The samples were placed inside glass capillary tubes of 2 mm diameter and the measurements were conducted at the temperature range 25°C – 160°C. Through the analysis of the SAXS scattered intensity, the form factor of the micelles was derived, and thus the polystyrene core radius, R_c, the micellar aggregation number, Q_m, as well as the micelle number density, N, and the polystyrene volume fraction in the core, n_{PS}, were calculated.

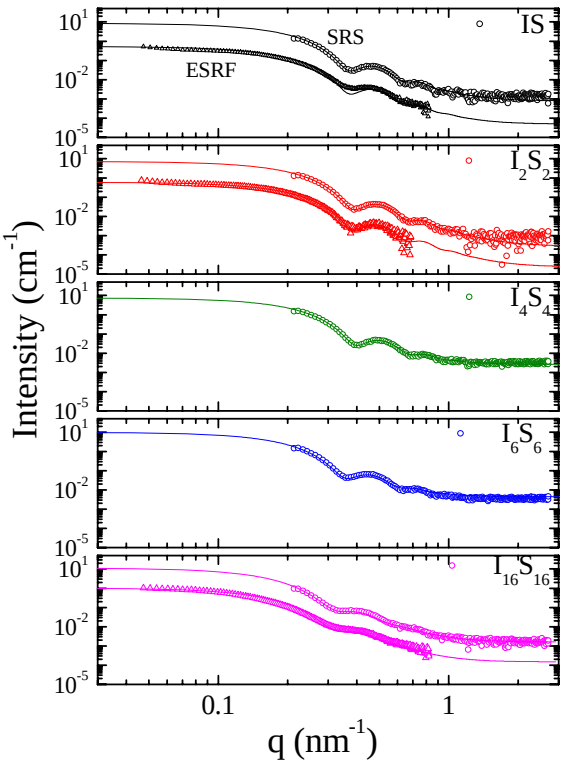

Figure 1: The SAXS intensity curves as a function of the scattering vector q for the 2wt% blends of the various I_nS_n miktoarm copolymers in PI. The curves obtained at ESRF are presented shifted by an order of magnitude for clarity.

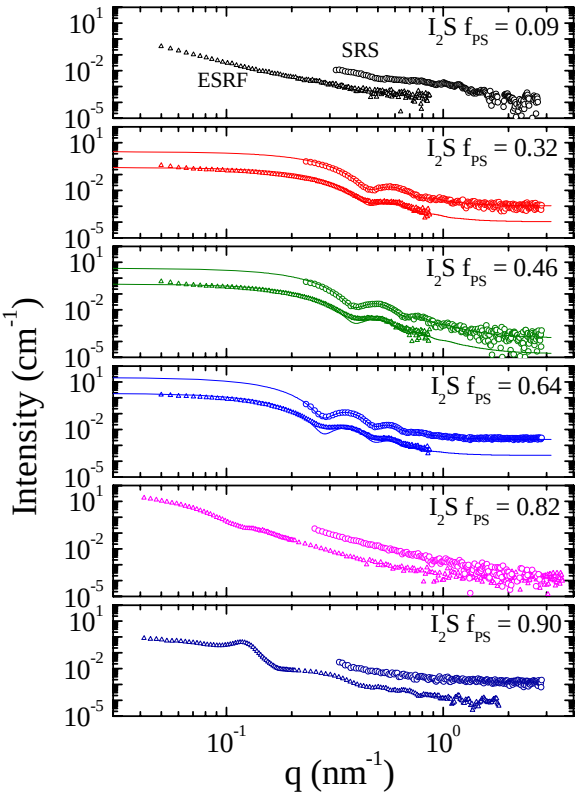

Figure 2: The SAXS intensity curves as a function of the scattering vector q for the 2wt% blends of the various I_2S graft copolymers in PI. The curves obtained at ESRF are presented shifted by an order of magnitude for clarity.

Although test measurements of the 2wt% concentration of the I_nS_n and I_2S samples were previously conducted at the Synchrotron Radiation Source (SRS) at Daresbury Laboratory, Warrington, UK, on station 16.1, additional scattering profiles were collected in ESRF in order to detect the scattering in the low q range, which is essential for the correct determination of the scatterers shape and the intensity in forward direction, I_0. Figures 1 and 2 present comparatively the profiles acquired in both instruments for the two series of samples and the corresponding fitting curves. The experimental curves are in such a good agreement with each other that only one fitting curve can describe well both of them.

The analysis of the profiles concerning the 2wt% concentration of the I_nS_n copolymers (with 19k polystyrene and 15k polyisoprene blocks) revealed that micelles are obtained for all *n* values (Fig. 1), with a micellar core radius that is independent of *n* whereas the aggregation number decreases with *n* following an n^{-1} power law. The number density of micelles in the mixture and the polystyrene fraction in the core are constant as well, signifying that in the range of molecular weights investigated the functionality of the junction point of the copolymer does not influence the micellar characteristics. A simple thermodynamic model has been developed that describes theoretically the micellization of A_nB_n copolymers within a B homopolymer matrix. The model agrees very well with the experimental data both qualitatively and quantitatively. These data are reported in a manuscript already submitted for publication.

For constant concentration (2wt%) of the I_2S grafts (M_n~90000), micelles are formed only above a certain polystyrene volume fraction (f_{PS}=0.32), while the core size as well as the aggregation number increase with increasing f_{PS} (Fig. 2). Moreover, the number density decreases with f_{PS}, in accordance with mass balance, whereas there is strong evidence that the polystyrene volume fraction in the core increases. These results are compared to those for the respective linear diblock copolymers and different trends are revealed. The two copolymers with the higher PS content are of special interest, since their scattering

patterns differ substantially from those of the other samples, although one would have expected them to form spherical micelles as well. Especially the last blend seems to prefer to macro-phase separate, forming domains of ordered block copolymer embedded in the PI matrix. A paper related to this study is prepared and will be soon submitted for publication.

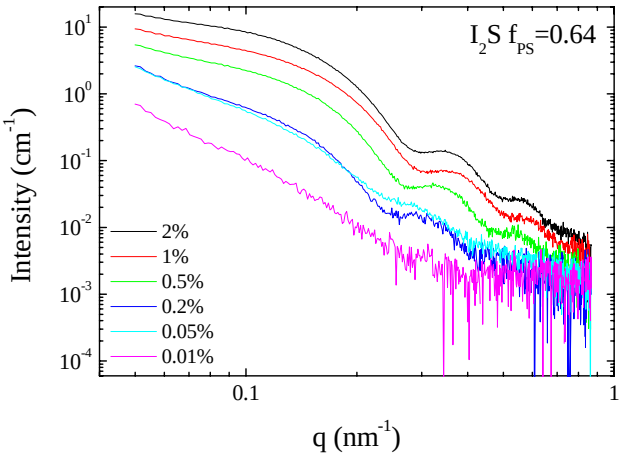

Figure 3: The SAXS intensity curves for the various concentrations of the I_2S (f_{PS}=0.64) graft copolymer within PI.

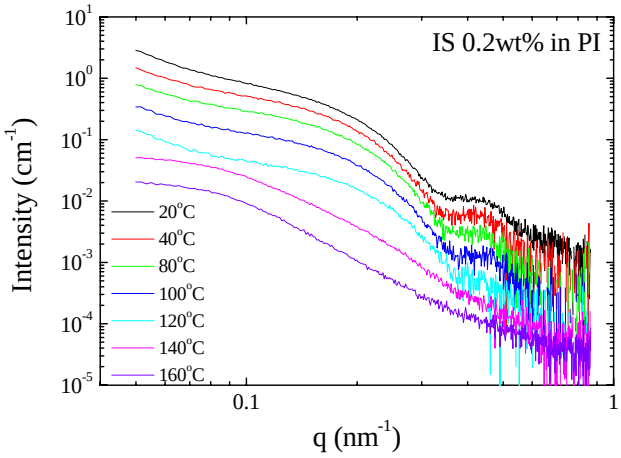

Figure 4: The SAXS intensity curves for the 0.2wt% blends of the IS copolymer within PI, for various temperatures. The curves have been arbitrarily shifted vertically for clarity.

Finally, the effects of copolymer concentration and temperature on the formation and characteristics of micelles were studied, in order to determine the critical micelle concentration (CMC) and temperature (CMT), respectively, and their dependence on the macromolecular architecture. In Figures 3 and 4 two characteristic sets of measurements are presented, the first refering to the concentration effect on the micellization and the second to the temperature effect. Above CMC, the concentration affects only the number of the micelles present and not their characteristics, while the percentage of free chains increases as the concentration decreases until the system reaches the CMC, below which only free chains exist in the mixtures. As far as the temperature effect is concerned, the structure of the micelles is affected by the temperature increase but not their number density. Strangely, most of the samples did not exhibit CMT below the highest studied temperature, that is 160^{o}C, and a new series of measurements appear to be necessary for the completion of this study. The analysis of the data concerning the concentration and the temperature effects is still ongoing, but yet promissing that another publication will come up.