

**Experiment title:**

Quasi-Block Copolymers: Responsive Nano-structured Copolymers Consisting of Conventional and Supramolecular Blocks

Experiment number:

SC-2902

Beamline:

BM26B

Date of experiment:

from: May 21, 2010 to: May 24, 2010

Date of report:

May 21st, 2011

Shifts:

9

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Report:

The target of the research project for which the experiment at BM26 was performed is to create a new family of block copolymers consisting of a supramolecular block. Such copolymers, termed quasi-block copolymers (q-BCPs), should feature both the microphase separation-induced nano-structuration typical to block copolymers and the ability to tune the molecular weight of the supramolecular block using external stimuli.

The aim of the experiment at BM26 was to construct the phase diagrams of these copolymers both in solution and in the melt. Nearly 150 samples were prepared in capillaries and on kapton sheets and brought to ESRF for the experiment. Preliminary experiments performed prior to the experiment provided encouraging evidence for the formation of the q-BCP architectures. In solution, viscosity measurements performed on mixtures of the supramolecular polymer (**EHUT**) and end-functionalized polystyrene (either **PS-DiBUT** or **PS-TriBUT**) showed a much slower increase in viscosity with increasing **EHUT** concentrations compared to a mixture of **EHUT** and a "dead" PS (Figure 1). In the solid state, differential scanning calorimetry measurements (Figure 2) and surface probe microscopy images indicated the formation of microphase separated structures (Figure 3).

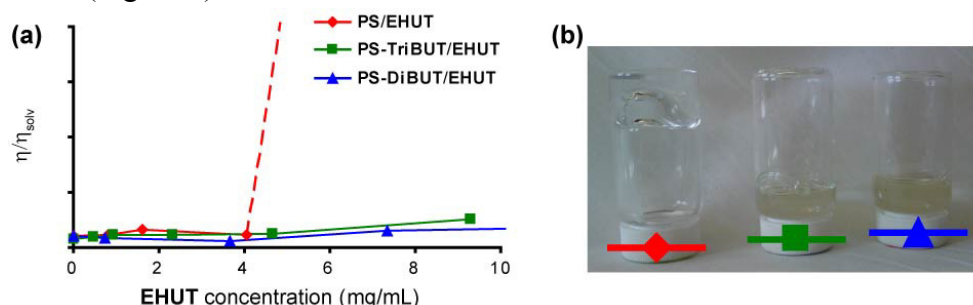


Figure 1. (a) Relative viscosities measured for the PS/EHUT, PS-DiBUT/EHUT, and PS-TriBUT/EHUT systems at constant PS-derivative concentration (7.4 mg/mL) and different EHUT concentrations in 7:3 CHCl₃:toluene. The dashed line represents reaching the maximum detection limit in the viscosity measurements of the next concentration. (b) Inverted vials containing mixtures corresponding to (a), demonstrating the strong effect on viscosity of the TriBUT and DiBUT end-functionalities.

Figure 2. DSC curves of blends of (a) PS and **EHUT** at different **EHUT**:PS ratios (x), (b) **PS-DiBUT** and **EHUT** at different **EHUT**:**PS-DiBUT** ratios. For comparison, the curves of the neat PS and **PS-DiBUT** are provided on top (green) and the neat **EHUT** curve is provided on the bottom (blue). Curves are offset for clarity.

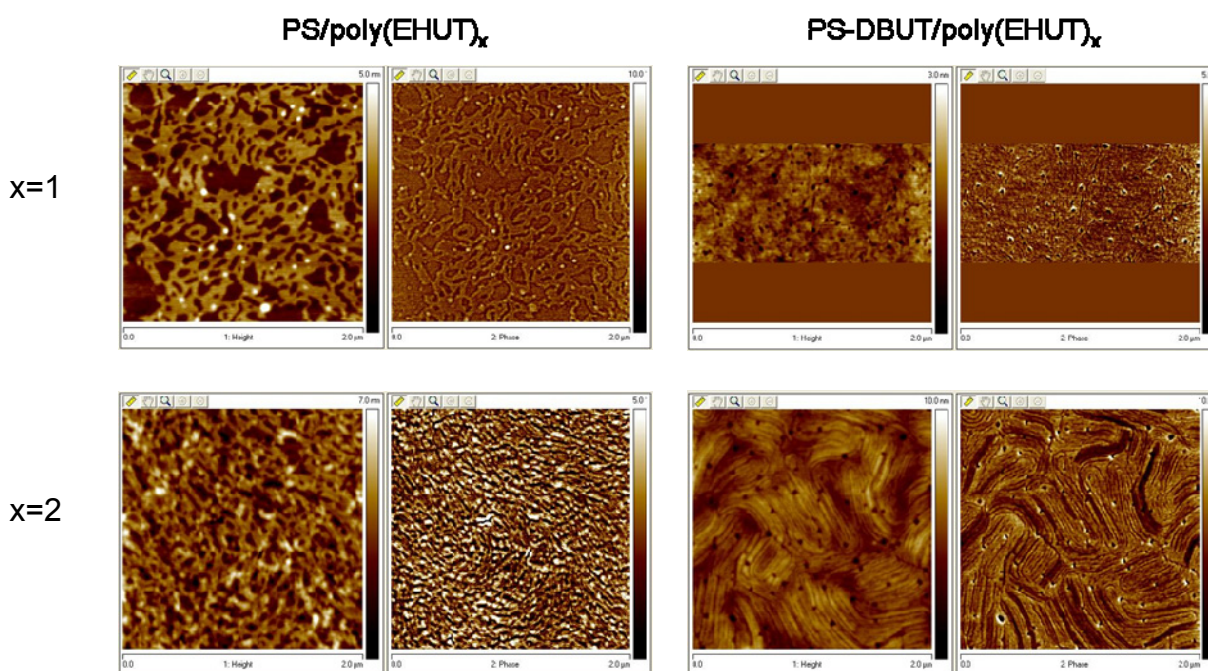
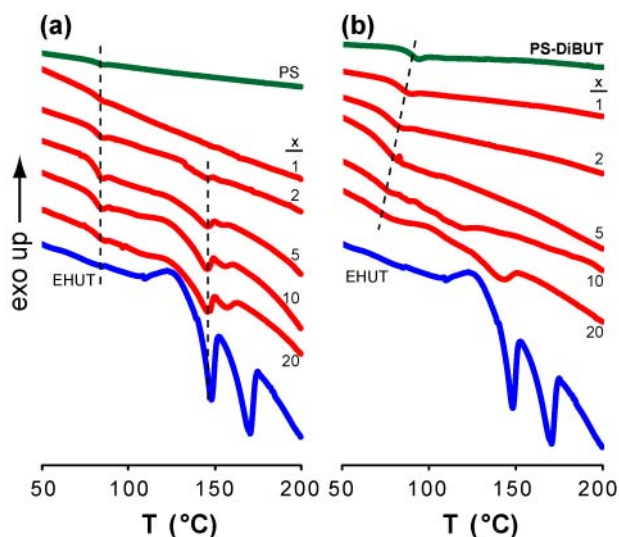


Figure 3. SPM images of blends of "dead" PS with **EHUT** and q-BCP forming **PS-DiBUT** with **EHUT**, at different **EHUT** mole ratios, demonstrating for the latter case either uniform films (at $x=1$) or the formation of periodic structures at high **EHUT** content ($x=2$) compared to the phase separated structures observed for the former at both **EHUT** contents.

None of the solution samples scattered X-rays at low angles despite our expectations that micelles will be formed, and despite the indirect evidence from viscometry demonstrating that q-BCP structures are formed in these solutions. The conclusion is that the conditions used for the solution samples (i.e., concentrations and solvent systems) were below the critical micelle concentration, and further studies are required to identify the appropriate conditions for micelle formation.

Melt samples also did not exhibit diffraction peaks at low angles, indicating that the phase separated structures observed by SPM were not sufficiently uniform in size. Nonetheless, poly(EHUT) features a peak at the wide angle region of the SAXS, which is attributed to the crystallization of the supramolecular polymer. Figure 4 shows that a similar peak was observed only in the control experiment, consisting of the "dead" PS polymer blended with EHUT. The absence of this peak in the **PS-DiBUT** and **PS-TriBUT** consisting samples indirectly indicates the formation of smaller domains of poly(EHUT), which is in line with the DSC and SPM data presented above.

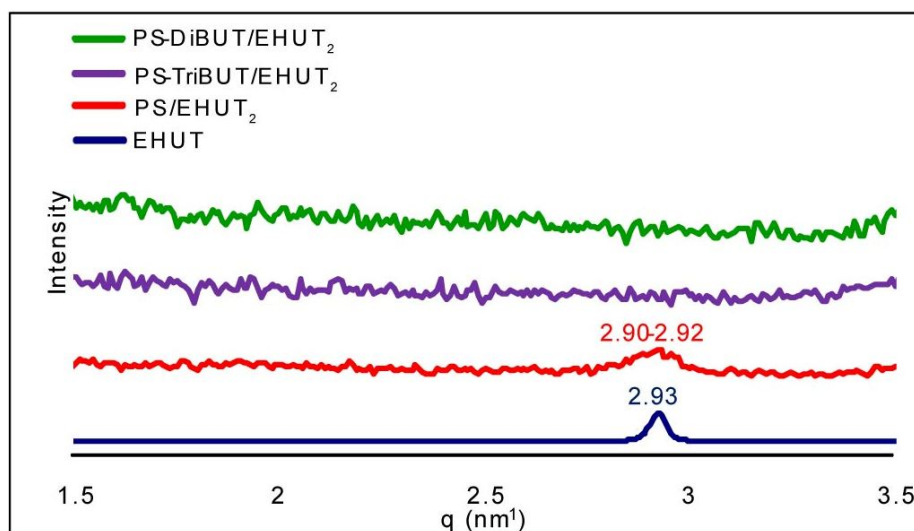


Figure 4. SAXS curves indicating the reduced crystallinity of EHUT in melts containing the end-functionalized polystyrenes. Values above the peak denote the corresponding spacing calculated in nm.

Spare time we had during the experiment was used for acquiring data on additional samples we brought, related to a different project (formation of hierarchical structures in block copolymer/organometallic surfactant systems). The results we obtained complemented data acquired during a previous experiment at ESRF, and were required for completing our understanding on the behavior of these systems. We are currently preparing this material for publication.