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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: SAXS characterization of new thermoplastic elastomers synthesized via the chain-shuttling polymerization process**	**Experiment number**: MA-2453
Beamline: BM02	**Date of experiment**: from: 19/02/15 to: 21/02/15	**Date of report**: 09/12/15
Shifts: 6	**Local contact(s)**: C. Rochas	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

G. Stoclet, J.M. Lefebvre, T. Pinalie

Unité Matériaux Et Transformations (UMET) Equipe Ingénierie des Systèmes Polymères (ISP), Villeneuve d'Ascq, USTL (France)

Report:

This study was aimed at characterizing the structure at a nanometric scale of a new class of thermoplastic elastomers (TPEs). These TPEs are synthesized via a new method, to know chain-shuttling polymerization process, that allows to get access to multiblock copolymers with tunable structure and consequently tunable properties. Besides, the goal of this study is to characterize the blocks structure and their potential self-organization as a function of the elaboration parameters, in order to determine to elaboration parameters – structure relationships of these materials.
Particularly, the materials considered for this study are isoprene/styrene multiblock copolymers composed of hard blocks rich in Polystyrene and of soft blocks rich in Isoprene as schematized in figure 1

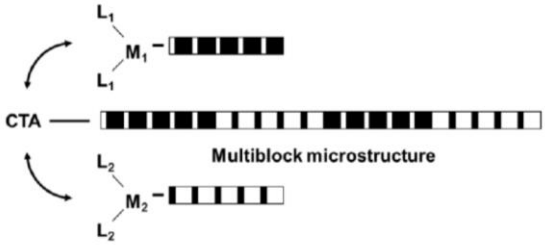


Figure 1. Schematic reprensentation of the synthesis method of the TPEs.

Samples synthesized under various conditions (meaning different catalysts ratios, monomers ratios, transfert agent concentrations…) have been analyzed by means of SAXS. The integrated intensity profiles have been calculated and the nanometer scale structure was deduced from modeling using the Irena macro as illustrated in figure 2.

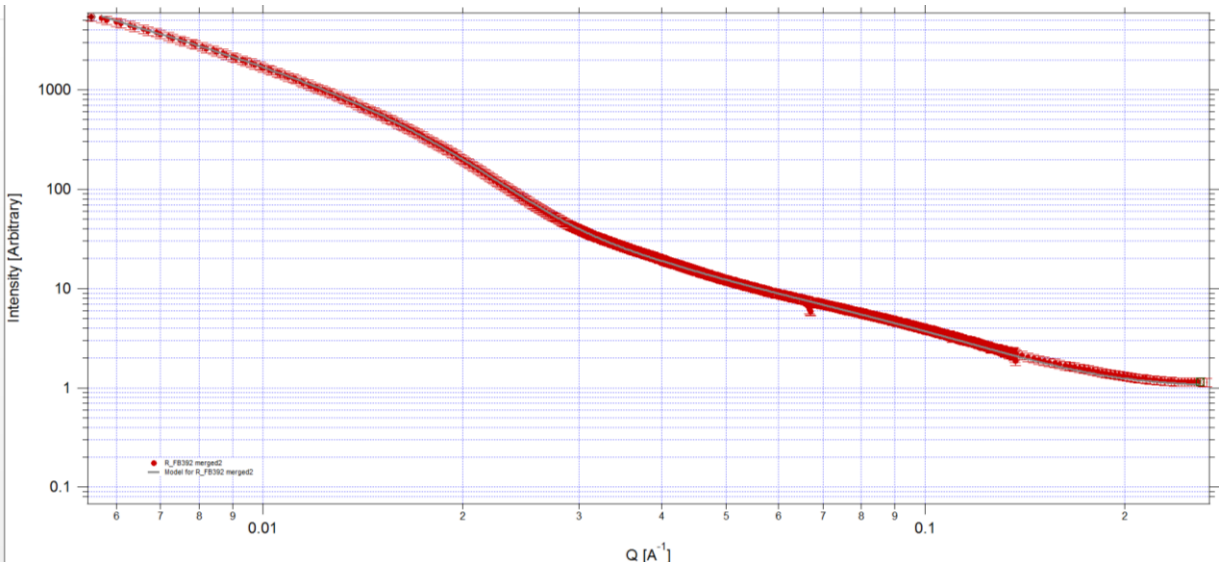


Figure 2. Integrated intensity profile of a TPE sample and modeling of the curve

The overall analyses indicate that the hard block has a disk-like shape and that they are embedded in the soft matrix, composed of the soft block. The relative concentration of the hard blocks as well as their characteristic lengths were determined. An example is depicted in figure 3 where it can be seen that the isoprene/styrene ratio in the synthesis solution strongly influences the concentration of hard blocks but not necessarily their mean diameter.

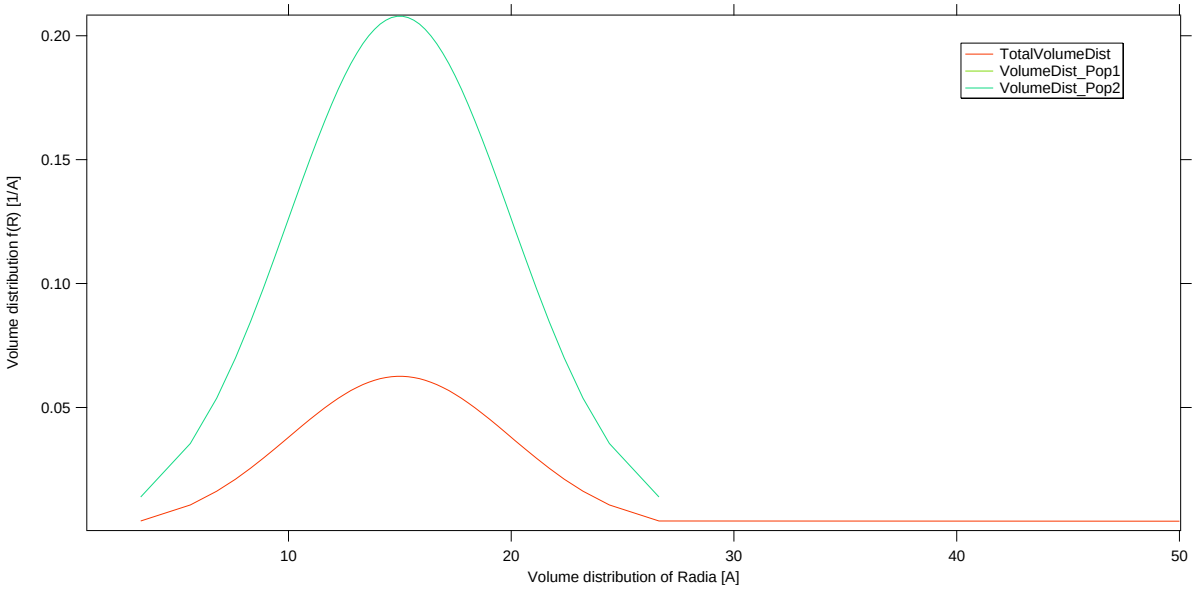


Figure 3. Size distribution of the hard block of two samples synthesized starting from two different Isoprene/Styrene ratios.

Complementary AFM analyses were carried out on the samples analyzed by means of SAXS. An example is reported in figure 4.

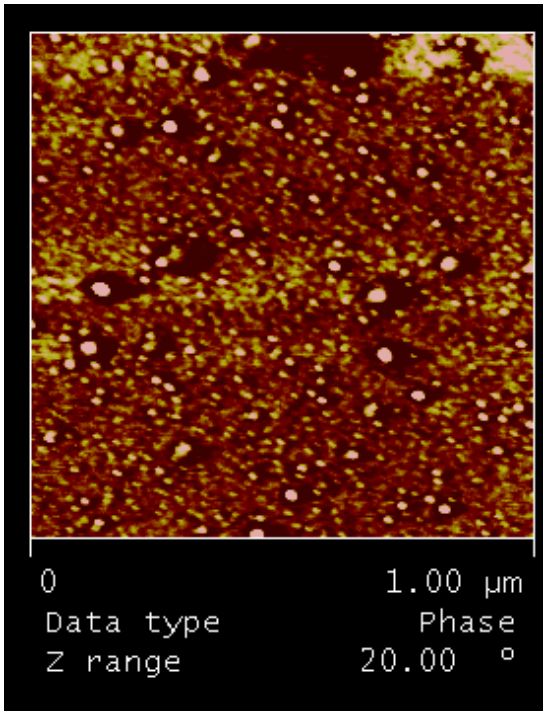
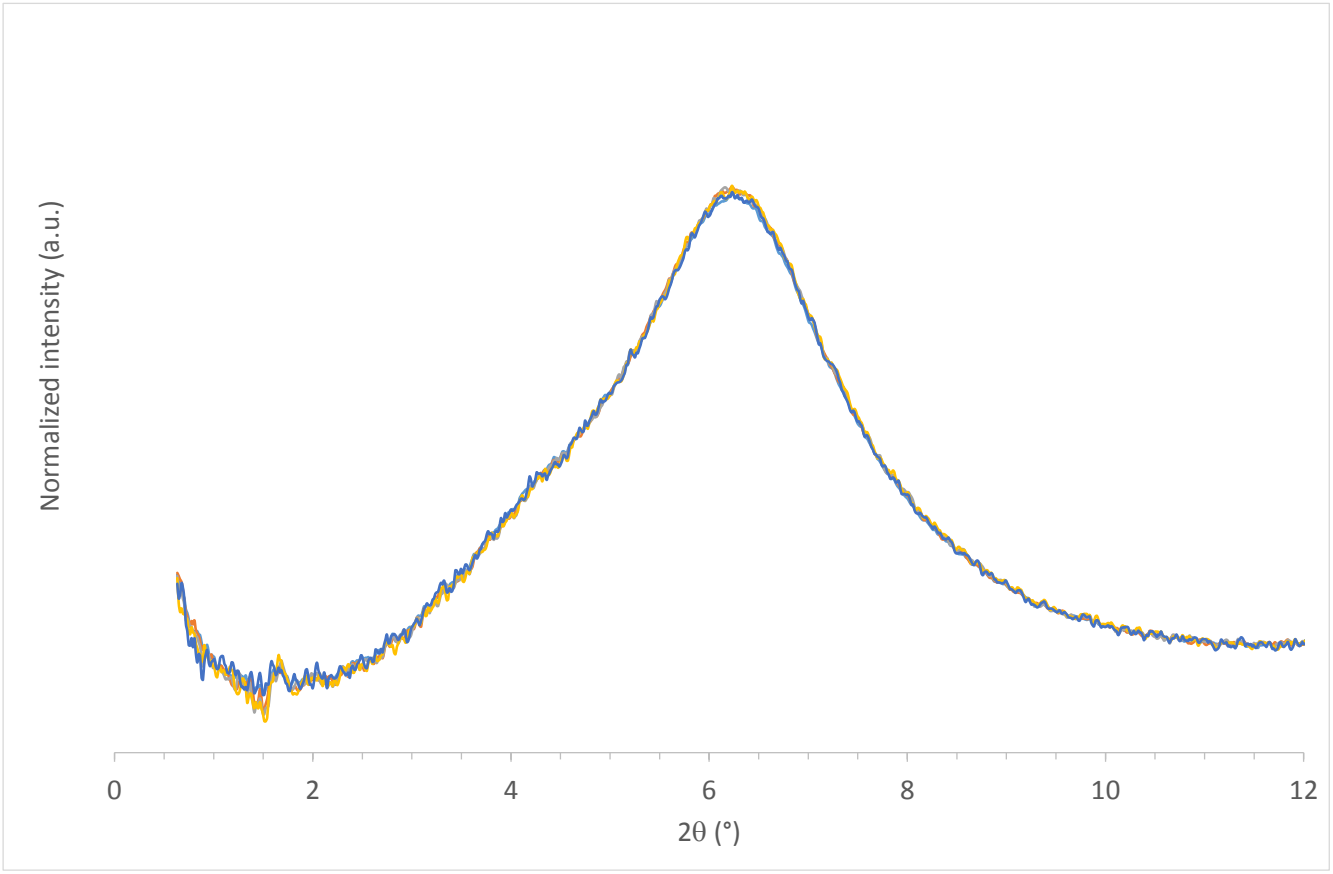


Figure 4. AFM micrograph of a TPE sample (corresponding to sample from figure 2).

A good agreement was found between the results obtained from those two techniques. The establishment of the synthesis conditions – structure relationships is still undergoing has no simple but rather complex relationships were found.

The second aim of the study was to characterize the strain-induced structural evolution of these materials upon strecthing. Besides TPEs know an increasing interest due to their shape memory behavior. More precisely, such materials are able to fully recover a previously applied deformation.
Samples of interest were thus uniaxially drawn and the associated structural evolution was followed by means of WAXS during the tensile test as well as during the subsequent retraction/recovery step. An example of a typical behavior observed is depicted in figure 5.

(a)



(b)

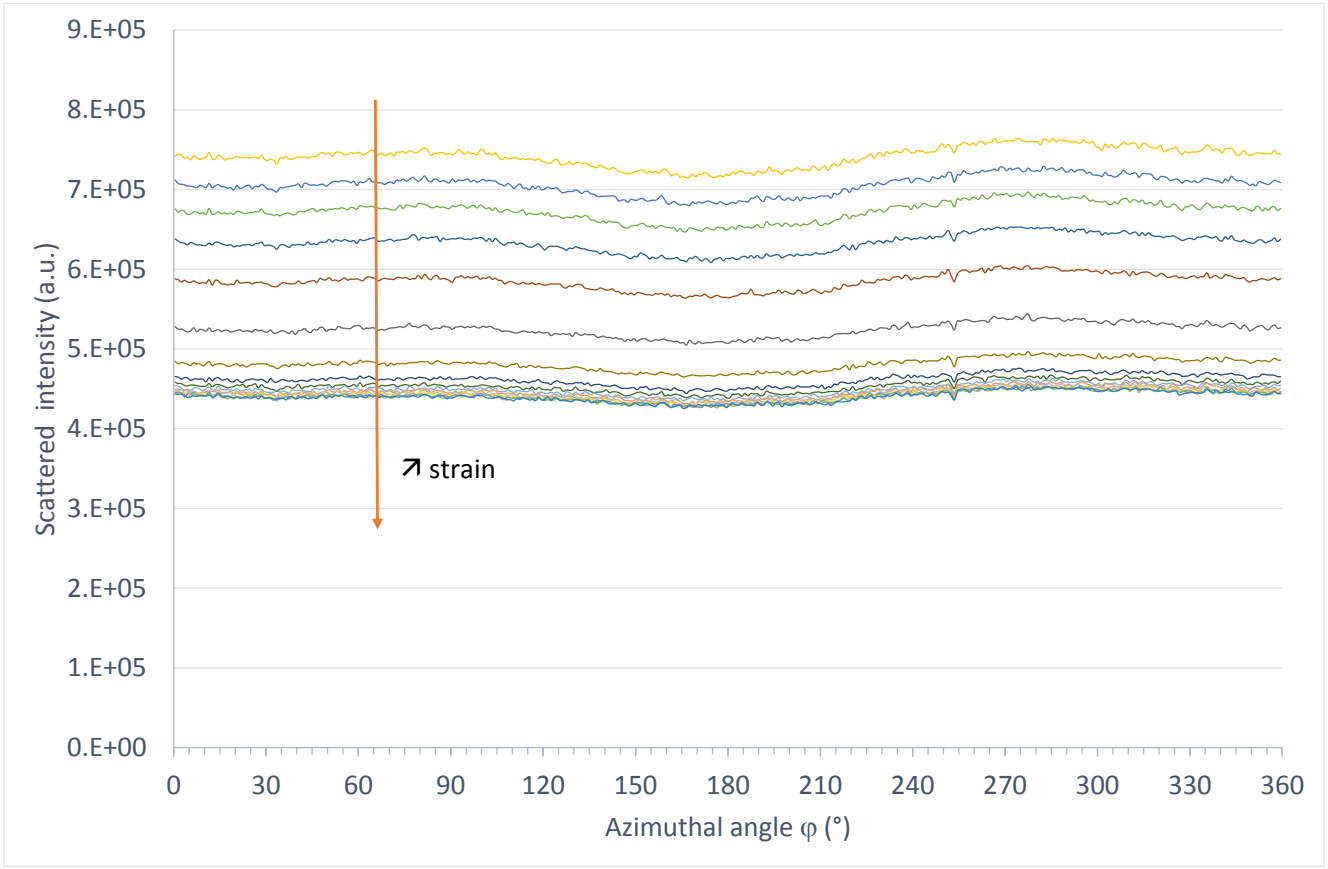


Figure 5. Evolution of (a) the radially and (b) the azimuthally integrated intensities profiles as a function of strain for a TPE sample.

As can be seen both radially and (b) the azimuthally integrated intensities profiles are constant whatever the deformation, tending to show that surprisingly there are no significant structural changes during drawing. Particularly there are no signs of macromolecular orientation upon stretching although strain levels as high as 1000% can be achieved with these TPEs.

This result, observed for all the studied samples remains unclear and unexplained, especially knowing that a complete retraction/recovery of the samples is observed when the sample is unloaded from the clamps of the tensile stage.

Conclusion

These experiments have allowed to progress regarding the structural characterization of this new class of Thermoplastic elastomers consisting in multiblock copolymers. The currently undergoing complementary experiments, will allow to determine the synthesis conditions-structure relationships.

Regarding the strain-induced structural evolution upon stretching, new and unsuspected results were obtained. An in depth analysis of the mechanical behavior of these materials, completed by mechanical behavior modeling, are currently under progress in order to explain the behavior observed.