



	<b>Experiment title:</b> SAXS measurement of waterborne polymer/clay nanocomposites.	<b>Experiment number:</b> 16-02-66
<b>Beamline:</b> BM16	<b>Date of experiment:</b> from: 18/07/09 to: 21/07/09	<b>Date of report:</b> 22/07/10
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**Names and affiliations of applicants (\* indicates experimentalists):**

**Ms. Audrey Bonnefond\*, Dr. Matej Micusik\*, Dr. Jose Ramon Leiza\*, Dr. Maria Paulis\***

Universidad del País Vasco / Euskal Herriko Unibertsitatea

Joxe Mari Korta Zentroa

Avda. Tolosa, 72

20018 Donostia-San Sebastián

Spain

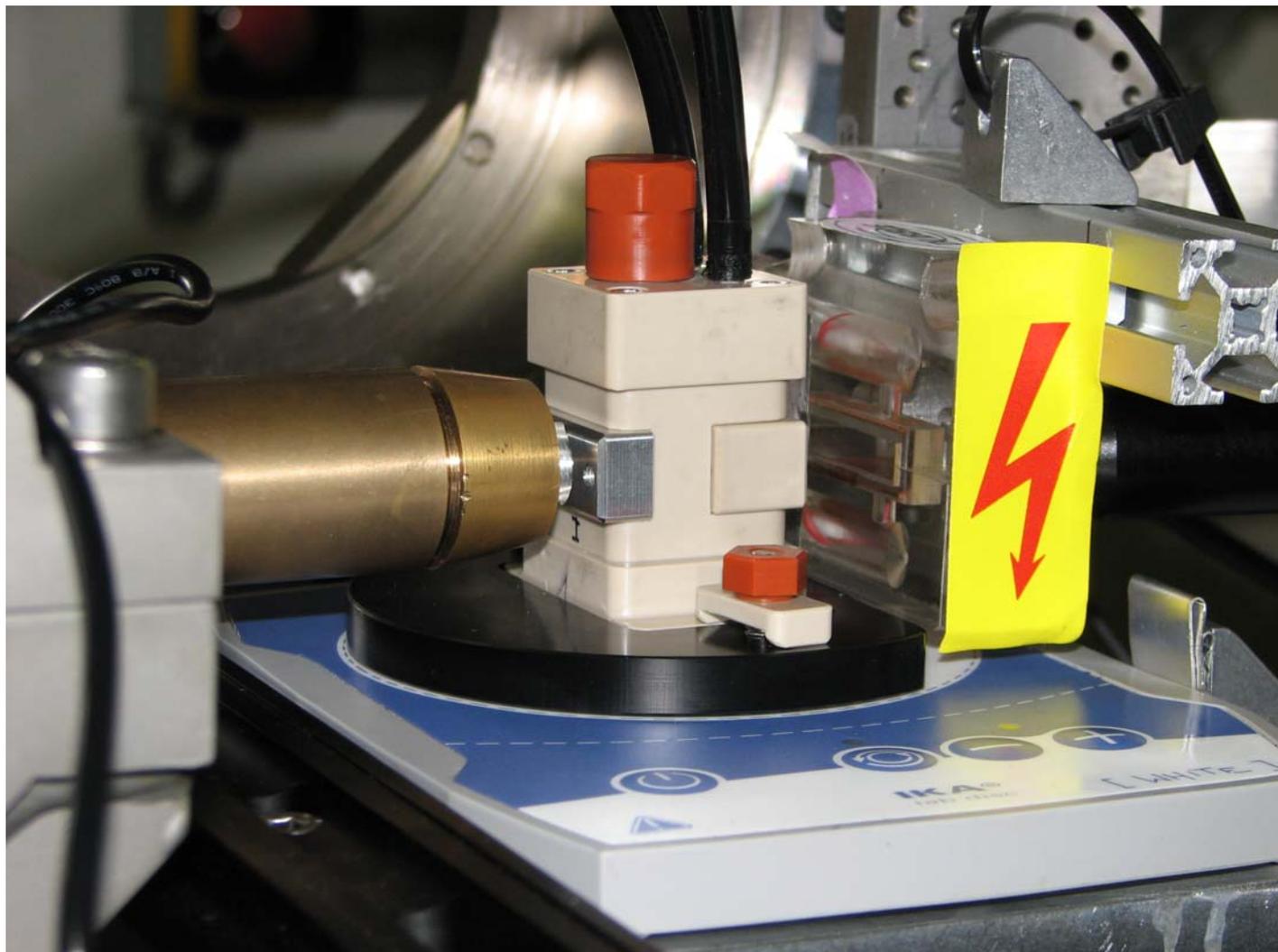
**Report:**

In previous stays at BM 16 beam line, different static and on-line measurements had been carried out, using either static sample holders both for solids or liquids and the equipment prepared by us for the on-line measurements. After the two prototypes used for this type of measurements in the last two stays in Grenoble, this time we have improved the design of the agitated and thermostated cell, in order to decrease the path crossed by the beam and facilitate the agitation inside the cell (see Figure 1). Therefore all the measurements that will be reported in these lines were carried out with this new cells.

First of all the different swelling capacity of the in-house modified MA16-MMT in the monomers in the presence of non-ionic emulsifiers will be presented. Then the on-line measurements of emulsion and miniemulsion reactions carried out in-situ in the measuring cell will be presented.

All these small-angle X-ray scattering (SAXS) measurements were carried at the Spanish CRG beamline BM16 in the European Synchrotron Radiation Facility in Grenoble, with the technical aid of Dr. Francois Fauth. Two configurations were used. The first one with a wavelength of the monochromatic X-ray of  $\lambda=1.386\text{\AA}$  (8.94 KeV, Yb\_L3 edge), at a sample to detector distance of 6m, and the second one at  $\lambda=0.9795\text{\AA}$  (12.6578 KeV, Se edge) and with a sample to detector distance of 2.52m. A 2-D detector

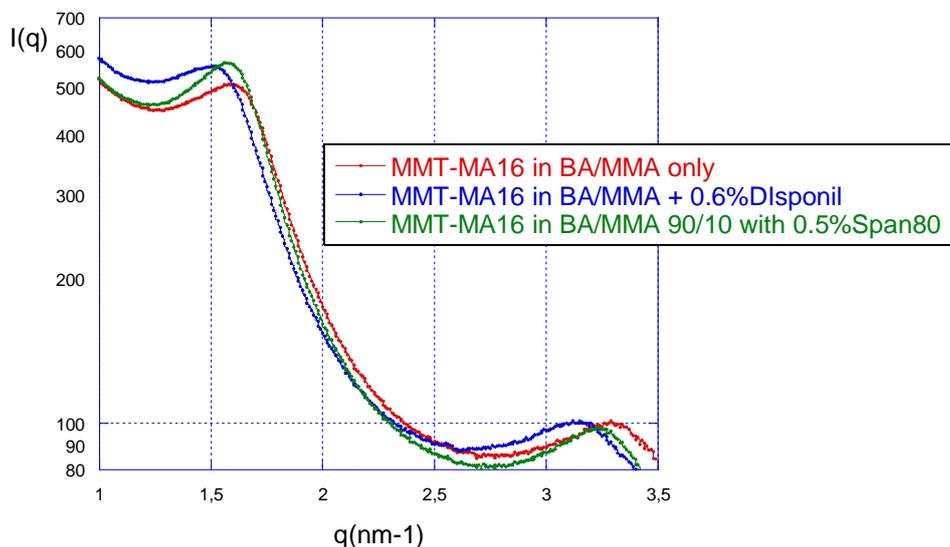
marCCD165 was used and the signal was treated (corrected for background) and converted to 1D through a Fit2D software. The scattering angle was calibrated by a silver behenate standard.



**Figure 1.** New design of the agitated and thermostated cell used for the on-line measurements.

- i) **SAXS measurements MA16 modified MMT dispersed in monomers with non-ionic emulsifiers.**

Figure 2 shows the SAXS profiles of the MA16/MMT hydrophobic clay dispersed in a 10/90 mixture of MMA/BA alone, and with Span 80 and Disponil non-ionic emulsifiers.



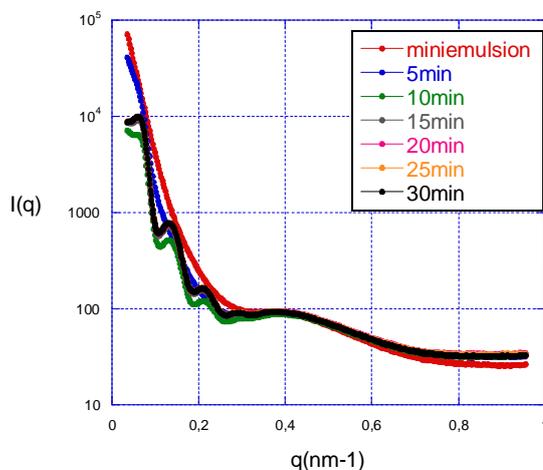
**Figure 2.** SAXS profiles of MA16/MMT dispersed in monomers with different non-ionic emulsifiers.

As it can be seen, the MA16/MMT swells even more in the monomers when non-ionic emulsifiers are present in the mixture. Disponil seems to be a better swelling compound than Span 80, as the interlayer space is highest with this non-ionic emulsifier.

## ii) On-line SAXS measurements of miniemulsion polymerization reactions.

As it has been said before, on-line measurements of the miniemulsion polymerization were carried out in the third generation of agitated and thermostatised cells.

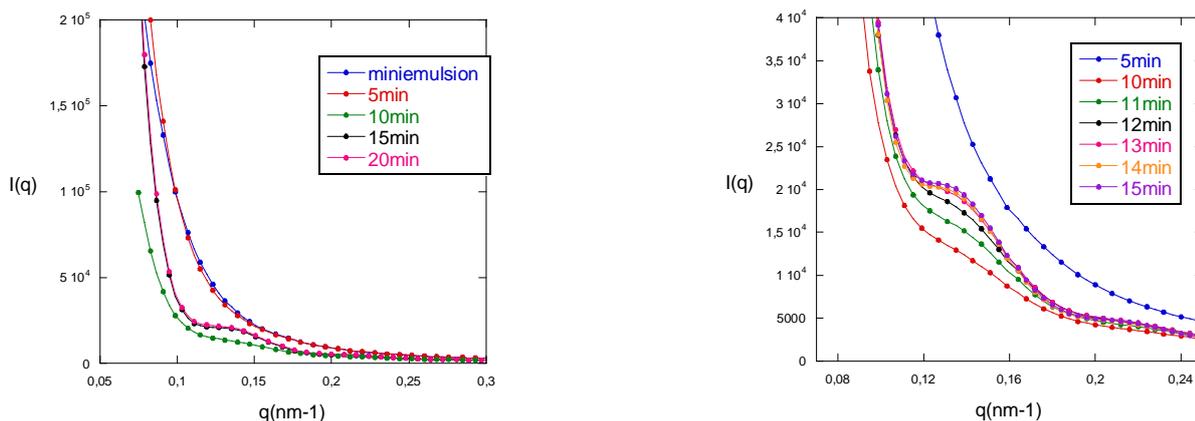
First of all the blank miniemulsion polymerization of MMA/BA 50/50, at 30% solids content with 2% Dowfax as emulsifier, 1%  $\text{NaHCO}_3$  as tampon, 3% of HD as costabilizer and 1.5% KPS as initiator was carried out. Figure 3 presents the spectra obtained at the beginning of the reaction (miniemulsion) and as the reaction proceeded. From 30 minutes on, the spectra did not change any more.



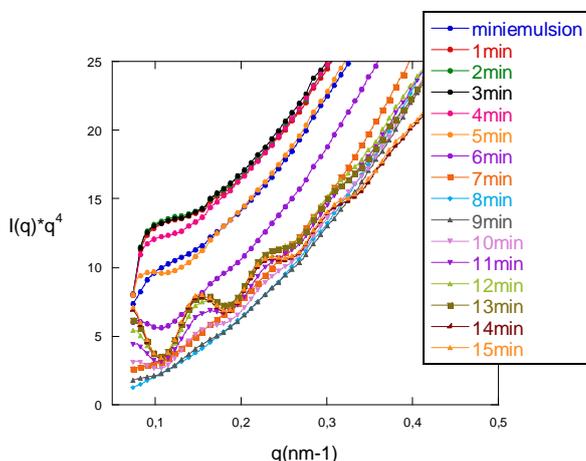
**Figure 3.** SAXS profiles of the on-line miniemulsion polymerization of MMA/BA 50/50 at 30% S.C. with 1.5% of KPS.

As it can be seen, the miniemulsion itself does not present any fringe (except for a broad peak due to the Dowfax). But at 10 minutes of reaction, the fringes start to appear and do not move their position along the polymerization, suggesting a droplet nucleation mechanism. The Porod plot of the spectra showed a particle size of 81 nm.

Then MMT-MA16 (F2) modified clay was incorporated to the miniemulsion polymerization of MMA/BA 10/90, with 2% Dowfax, 3% SA, 1%NaHCO<sub>3</sub> and 0.23%Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>. Figure 4 presents the SAXS spectra of the miniemulsion and of the reaction and Figure 5 the I(q)\*q<sup>4</sup> vs q curves along the reaction.



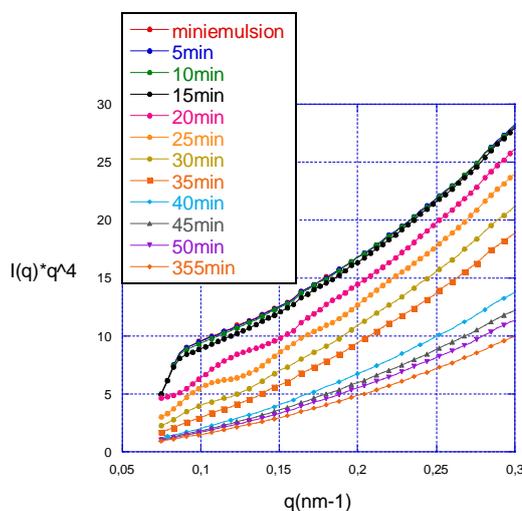
**Figure 4.** SAXS profiles of the on-line miniemulsion polymerization of MMA/BA 10/90 with MMT-MA16, 2% Dowfax as emulsifier and 1.5% KPS as initiator.



**Figure 5.** I(q)\*q<sup>4</sup> vs q curves of the on-line miniemulsion polymerization of MMA/BA 10/90 with MMT-MA16, 2% Dowfax as emulsifier and 1.5% KPS as initiator.

As it can be seen, the fringes start to appear at 10 minutes in this case, and they do not move again along the reaction. The average particle size obtained from the Porod's plot was in this case 82nm. The conversion obtained in this reaction was 85%, and the particle size measured by light scattering (Malver, Nanosizer) was 96nm.

Finally the miniemulsion polymerization of MMA/BA 10/90 with MMT/MA16 was carried under the presence of an anionic (Dowfax, 2%) and a non-ionic (Disponil, 0.78%) surfactant, with 1% KPS as initiator (1% NaHCO<sub>3</sub> 0.23% Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>). Figure 6 presents the  $I(q)*q^4$  vs  $q$  curves along this reaction.



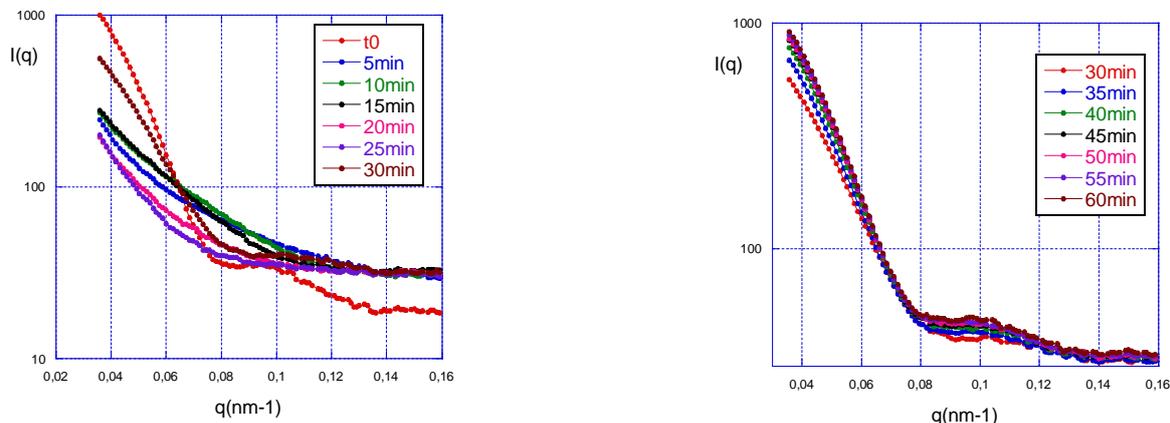
**Figure 6.**  $I(q)*q^4$  vs  $q$  curves of the on-line miniemulsion polymerization of MMA/BA 10/90 with MMT-MA16, 2% Dowfax and 0.78% Disponil as emulsifiers and 1.5% KPS as initiator.

As it can be observed, some fringes appeared at 20 minutes of reaction, showing a particle size of 94 nm, but then they disappeared. The final particle size was 178nm (measured by light scattering), but the conversion was not above 50% and some coagulum appeared in the latex (4%). Therefore it can be said that either due to the different emulsifier or to the lower initiator concentration, this reaction did not proceed completely and suffered some coagulation.

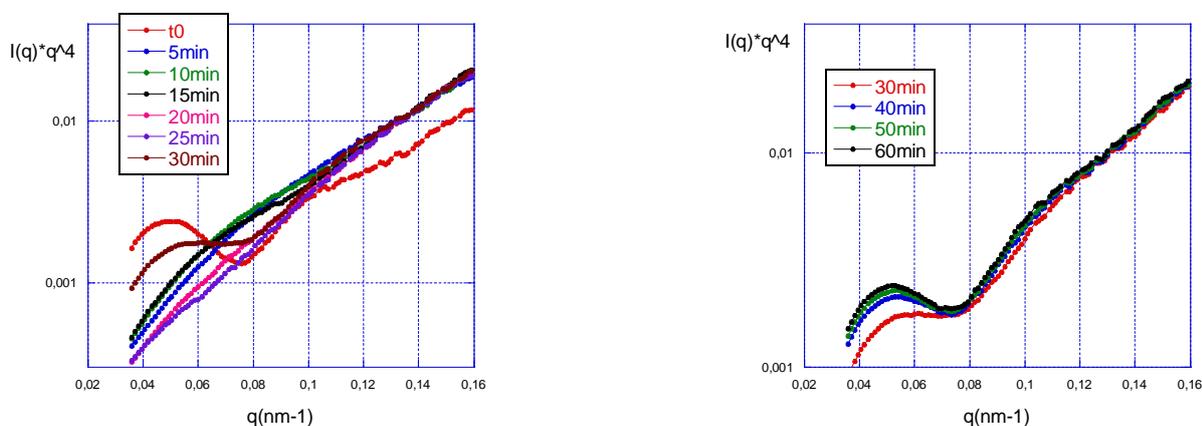
### iii) On-line SAXS measurements of emulsion polymerization reactions.

Once seen that we were able to follow miniemulsion polymerization reactions in-situ by SAXS, we tried to follow emulsion polymerizations too. We tried both styrene polymerizations and methyl methacrylate /butyl acrylate polymerizations.

First we tried the emulsion polymerization of styrene at 10% solids content, with two emulsifier concentrations in water: 2mM and 20mM. Figures 7 and 8 present the results obtained in the emulsion polymerization of S with 2mM of SLS in water, and 1% KPS as initiator.



**Figure 7.** SAXS profiles of the on-line emulsion polymerization of styrene, with 2mM SLS as emulsifier and 1% KPS as initiator.

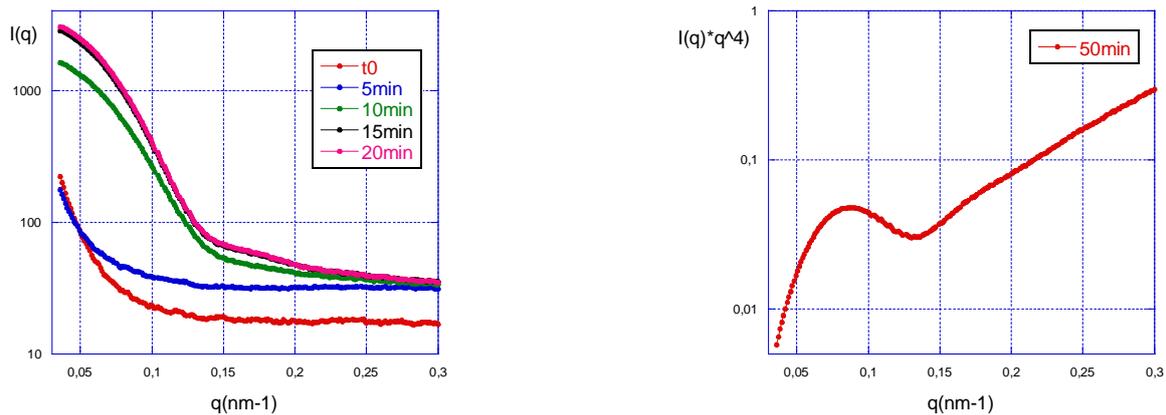


**Figure 8.**  $I(q) \cdot q^4$  vs  $q$  curves of the on-line emulsion polymerization of styrene, with 2mM SLS as emulsifier and 1% KPS as initiator.

At time 0, there are some fringes that disappear after 5 minutes. At 30 minutes new fringes appear that do not disappear or move up to 120 minutes. This is strange, because we would expect particles that grow during the emulsion polymerization, from the monomer diffusing from the monomer droplets. However it must be said that the conversion at the end was rather low (35%). Nevertheless the particle size obtained by the Porod plot (116nm) and that obtained by light scattering (118nm) were in agreement.

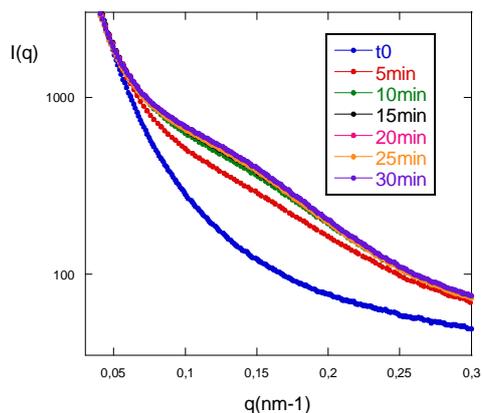
When the S polymerization at 20mM SLS was tried with 1% KPS, no fringes were observed in the spectra. In this case the final conversion was just 11% and the average particle size measured by light scattering, 70nm. Maybe there was not still polymer enough to be detectable by SAXS.

Finally the in-situ emulsion polymerization of MMA/BA at 10% solids content with and without clay was studied. First the blank emulsion polymerization with 2mM of SLS and 1% of KPS was studied. Figure 9 presents the SAXS spectra obtained during the reaction and the  $I(q) \cdot q^4$  vs  $q$  curve after 50 minutes of reaction. It can be seen that some fringes appear after 20 minutes of reaction that do not move up to 50 minutes. The final conversion of the reaction was 20% and the particle size measured by light scattering 64nm, while the one calculated by SAXS was 72nm.



**Figure 9.** SAXS spectra and  $I(q)*q^4$  vs  $q$  curve of the on-line emulsion polymerization of MMA/BA 50/50, with 2mM SLS as emulsifier and 1% KPS as initiator.

Then the emulsion polymerization of MMA/BA 50/50 with 1% NaMMT was carried out. This time 20mM of SLS was used, as the presence of clay is a destabilizing factor for the reaction. 1.5% of KPS was used as initiator. Figure 10 presents the spectra along the reaction. As it can be seen, no fringes can be observed as there were in the case of the blank miniemulsion, even if in this case the final conversion (32%) was higher than in that case. Probably the presence of the clay dispersed in the water hinders the presence of the fringes.



**Figure 10.** SAXS spectra of the on-line emulsion polymerization of MMA/BA 50/50 with 1% NaMMT, with 20mM SLS as emulsifier and 1.5% KPS as initiator.

As a conclusion it can be said that the particle formation in emulsion and miniemulsion polymerization can be followed in-situ with the new cell by SAXS, but that the achievement of high conversions is still lacking.