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New agitated and thermostatized cell for *in situ* monitoring of fast reactions by synchrotron SAXS

Maria Paulis, Audrey Bonnefond, Matej Mičušik‡ and Jose R. Leiza*

Institute for Polymer Materials, POLYMAT and Grupo de Ingeniería Química, Dpto de Química Aplicada, University of the Basque Country, Joxe Mari Korta zentroa, Tolosa Etorbidea 72, 20018 Donostia-San Sebastián, Spain. E-mail: jrleiza@ehu.es

A thermostatized and agitated sample cell for synchrotron small-angle X-ray scattering (SAXS) measurements of liquid samples (homogeneous or heterogeneous) has been developed. The cell is composed of a compact main body with inlet and outlet windows for the beams of light. The volume of the cell is approximately 0.8 ml and the distance between the windows is 5 mm to allow accurate SAXS measurements. The cell is thermostatized by means of a jacket that surrounds the sample holder and it is connected to a thermostatic bath. In addition, the cell has a top and a bottom lid that allow easy cleaning and maintenance without demounting the optical windows. The cell has been used to run SAXS measurements of liquid samples and, for the first time, a mini-emulsion polymerization reaction has been monitored by SAXS.

Keywords: synchrotron SAXS; on-line monitoring; agitated and thermostatized cell; (mini)emulsion polymerization.

1. Introduction

The *in situ* monitoring of fast chemical reactions in the liquid heterogeneous phase by synchrotron small-angle X-ray scattering (SAXS) is not straightforward because of the lack of appropriate sample cells. In the case of homogeneous phase reactions, these can be carried out in sealed and thermostatized cells without agitating the reactants (*e.g.* Hannemann *et al.*, 2007; Hu *et al.*, 2008; Tanaka *et al.*, 2007). On the other hand, reaction samples have also been analysed *ex situ* after withdrawing them from an outer agitated and thermostatized reactor. Nevertheless, the monitoring of fast and heterophase reactions (such as dispersed phase polymerizations) requires the use of agitated and thermostatized cells.

Alison *et al.* (2003) proposed the use of a novel plug-flow reactor for *in situ* SAXS and wide-angle X-ray diffraction measurements of crystallization processes. However, the proposed reactor requires the continuous movement of the sample at very high flow rates, which can be detrimental for shear-sensitive formulations such as polymeric dispersions stabilized by surfactants. Grunwaldt *et al.* (2005) developed a sample cell for *in situ* measurements with a capacity of 10 ml, which can be agitated, thermostatized and pressurized. Nevertheless, it was designed for X-ray absorption measurements, not for X-ray diffraction, as the relatively large dimensions of the cell decrease the diffraction efficiency. Several patents describe the development of cells for *in situ* measurements of reactions, but they do not provide agitation (Takaaki *et al.*, 1985) or they are not small enough to be used in X-ray diffraction analysis (Tsutomu & Shingo, 2004).

In this work we describe a recently patented (Paulis & Leiza, 2009) reaction cell that is small enough to be used for X-ray diffraction analysis (specially suited for synchrotron SAXS facilities or similar), which can be thermostatized and mechanically agitated in order to monitor in real-time fast chemical reactions, such as emulsion polymerization reactions. Furthermore, cleaning and maintenance of the cell is straightforward. As well as a description of the cell, this work presents two examples of potential applications of the cell. In the first, we analyzed latex samples to measure the particle size of the dispersion and compared the results with conventional dynamic light scattering (DLS) techniques. In the second, we explored the possibility to *in situ* monitor a polymerization reaction. The experiment chosen was the synthesis of waterborne hybrid polymer/clay nanocomposites. *In situ* SAXS measurements allowed the determination of the encapsulation state of the montmorillonite platelets in the polymer particles during the polymerization.

2. Description of the cell

The cell is depicted in Fig. 1. It comprises a compact body (*A*) made of polyether ether ketone (PEEK) that contains the reaction/sample vessel (*B*) with inlet and outlet optical windows (*C* and *D*). The optical (flat) windows [see Fig. 1(*c*) for a detailed design of the optical window parts] are attached to the main body by means of two parts (on either side of the main body) that contain the optical material (a thin circular film, 12 mm in diameter, made of kapton, mica or any other suitable material), which is sealed with O-rings. The outlet optical window was designed to collect the maximum amount of scattered light and therefore has a conical shape (see Fig. 1*c*, bottom). The reaction vessel is a cylinder with an inner diameter of 5 mm to allow its content to be mixed by means of a magnetic bar and for the beam of light to pass through. The reaction vessel (*B*) is surrounded by a cooling/heating jacket that can be connected to a thermostatic bath for temperature control. The main body is connected at the top and the bottom to two parts that seal the cell (*F* and *G*). These parts

‡ On leave from Slovak Academy of Sciences, Polymer Institute, Department of Composite Materials, Dúbravská cesta 9, 842 36 Bratislava, Slovakia.

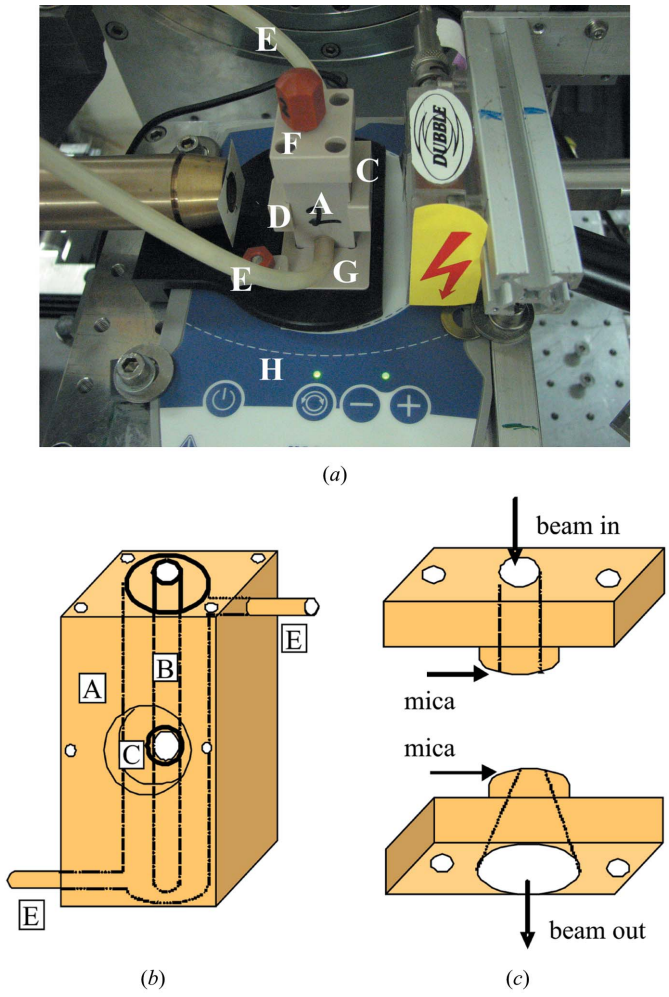

Figure 1
(*a*) Photograph of the cell used in the SAXS equipment showing the different parts. (*b*) Schematic of the cell main body. *A*, main body. *B*, reaction vessel. *C*, inlet optical window. *D*, outlet optical window. *E*, inlet and outlet of cooling/heating jacket. *F*, top cover. *G*, bottom cover. *H*, magnetic agitator. (*c*) Optical window parts: top, inlet; bottom, outlet.

can be easily mounted and demounted without needing to disassemble the optical windows, and hence cleaning and maintenance procedures are straightforward. The reaction mixture can be agitated by means of a magnetic agitator (*H*) as shown in Fig. 1(*a*). The temperature inside the sample cell can be measured before starting the reaction from the top lid (red nut in Fig. 1*a*). The cell set-up does not allow temperature to be monitored, but this is technically easy and will be implemented in future upgrade versions of the cell.

3. Representative examples of the potential applications of the cell

The cell was designed for carrying out SAXS measurements at the Spanish CRG beamline BM16 at the European Synchrotron Radiation Facility in Grenoble, France. The SAXS equipment was operated using a monochromatic X-ray beam (λ = 0.9795 Å, set at the Se *K*-edge for 12.6578 keV) with a sample-to-detector distance of 3.52 m. A two-dimensional detector, marCCD165, was used and the two-dimensional patterns were converted to $I(q)$ *versus* q plots using the *FIT2D* program (http://www.esrf.eu/computing/scientific/FIT2D/; Hammersley *et al.*, 1996). The samples were calibrated to the diffraction peaks of silver behenate.

The cell was first assessed by analyzing polymer latex samples. Polymer latexes can be synthesized by emulsion polymerization and other related techniques such as mini-emulsion, micro-emulsion and dispersion polymerization (Asua, 2007). The latex is a colloidal dispersion that is characterized by its particle size and distribution among other microstructural properties. DLS is a routine technique used to measure the particle size. SAXS has also been used to characterize the particle size of polymer colloids (Megens *et al.*, 1997; Finnefrock, 2000). In order to check the performance of the developed cell we characterized the particle size of a latex sample [methyl methacrylate (MMA)/butyl acrylate (BA)] synthesized by mini-emulsion polymerization by SAXS and compared the results with DLS measurements (Zetasizer Nano Series, Malvern Insruments, UK). Fig. 2(*a*) shows the diffraction pattern obtained for the latex in the sample cell at room temperature (278 K) and its Porod plot [$I(q)q^4$ *versus* q].

The scattering intensity achieved in the cell was comparable with that obtained in conventional cells available at BM16. The only difference was that the transmitted light through the cell was about 20% whereas in the conventional cell it was about 40%. The difference is due to the thinner (3 mm) dimensions of the conventional cell.

From the positions of the maxima and minima in the Porod plot an average particle size of 84.8 nm was obtained [from the slope in Fig. 2(*b*)]. Finnefrock's analysis (Finnefrock, 2000) also provided an average particle size of 85 nm. The particle size of the latex was also calculated by DLS and the value obtained (93 nm) was in good agreement with the results obtained by SAXS.

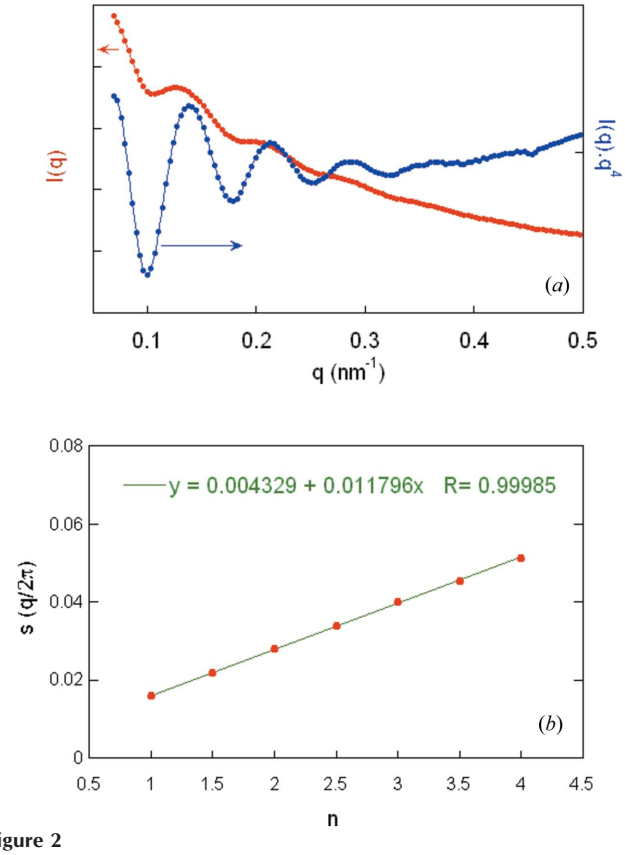

Figure 2
(*a*) SAXS diffraction pattern and Porod plot of a latex sample produced by mini-emulsion polymerization. (*b*) Regression for obtaining the particle diameter.

The second application was more challenging because we aimed to monitor *in situ* a mini-emulsion polymerization reaction. Polymer/clay nanocomposites are a new class of materials with improved properties provided by the high aspect ratio of the clay platelets; upon exfoliation they may render polymeric materials with enormous surface interaction area between the polymer and the clay. In order to synthesize such materials it is therefore necessary to homogeneously exfoliate the clay mineral in the host polymer matrix. Mini-emulsion polymerization has been reported to be suitable for incorporating water-insoluble compounds in the reaction loci (Asua, 2002). Therefore, if the clays are organically modified it should be feasible to incorporate them in the polymer particles. We have recently used SAXS to analyze the morphology of polymer/clay nanocomposite particles (Diaconu *et al.*, 2008, 2009). However, this time the aim was to *in situ* monitor the clay platelet association during the mini-emulsion polymerization carried out to synthesize the waterborne polymer/clay nanocomposites. This cannot be done in conventional SAXS sample cells because it is necessary to agitate the reactor content. It is difficult to assess the quality of mixing in the cell because it cannot be visualized from the small windows. However, when oil-in-water emulsions were polymerized (not shown here), stable latexes were obtained without phase separation. This is an indirect proof that mixing is reasonable in the cell.

The SAXS equipment was programmed to record a pattern every 30 s (1 s acquiring and 29 s standing). The mini-emulsion was prepared as follows. The organic phase contained the monomers MMA, BA and stearyl acrylate and the organically modified clay, labelled MA16-MMT (see Diaconu *et al.*, 2009), in the following amounts: 10 g, 90 g, 3.7 g and 3 g, respectively. A portion of this dispersion was first analyzed by SAXS and the pattern is shown in Fig. 3. The aqueous phase was composed of water and the surfactant mixture (1% Dowfax 2A1 + 0.6% Disponil AFX4060). Both phases were put together and agitated with a magnetic stirrer at 1000 r.p.m. for 15 min. Then the mixture was sonicated at 80% duty cycle and 80% power output for 15 min (Bandelin HD 2070 sonifier with probe tip MS72) to form a mini-emulsion. The required amount of this mini-emulsion was added to the cell and placed in the SAXS instrument (as shown in Fig. 1*a*), and the temperature was raised to 343 K. Then 0.5% wbm (weight based on monomer) AIBN initiator was injected and on-line monitoring of the reaction by SAXS was started. The solids content of the mini-emulsion was 26 wt%.

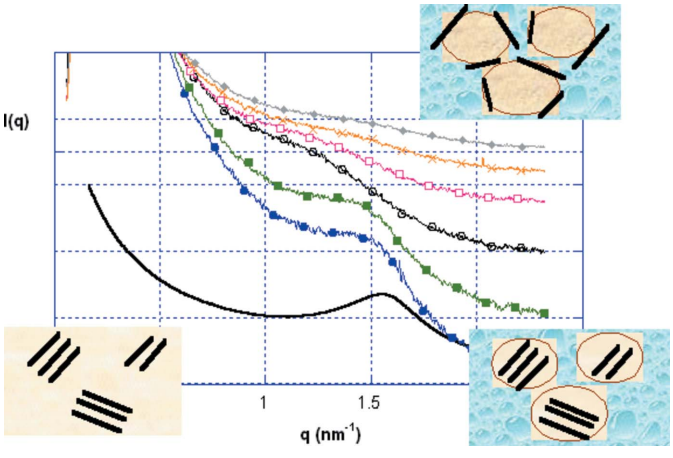

Figure 3
SAXS diffraction patterns of the *in situ* mini-emulsion polymerization reaction of MMA/BA in the presence of organically modified montmorillonite. Full line: MA16-MMT dispersed in monomer mixture. Filled circles: $t = 0$ min. Filled squares: $t = 5$ min. Open circles: $t = 10$ min. Open squares: $t = 15$ min. Crosses: $t = 20$ min. Filled diamonds: $t = 120$ min.

Fig. 3 shows a series of representative SAXS patterns collected during the polymerization. The solid line corresponds to MA16-MMT dispersed in the monomers and the symbols to the mini-emulsion polymerization at different polymerization times. For the clay monomer dispersion the pattern showed a peak at $q = 1.55$ nm^{-1}, corresponding to an average interlayer distance between platelets of 4.04 nm. The original MMT/MA16 dry clay had an interlayer distance of 1.89 nm [according to X-ray diffraction analysis (Diaconu *et al.*, 2009)]. This result indicates that the organically modified clay is swollen in the monomers mixture. In the patterns corresponding to the polymerization reaction the band assigned to the interlayer space of the MA16-MMT clay began to shift to lower q values, suggesting an increment of the interlayer space. As the reaction time progressed, this band practically disappeared. This indicated that the clay was mainly exfoliated in the latex (surface location of the platelets) as illustrated in Fig. 3 (top right).

4. Conclusions

A new sample cell for synchrotron SAXS measurements has been developed and tested. The cell allows either homogeneous or heterogeneous liquid samples to be analyzed. The cell can be agitated and thermostatized so that experiments can be performed over a broad range of temperatures. The cell was assessed by analyzing the particle size of latexes by SAXS and by *in situ* monitoring of the morphology of a polymerization leading to the production of waterborne polymer/clay nanocomposites. The latter results are promising and we envisage that this type of cell can be used to monitor on-line the early nucleation stages of emulsion polymerization processes.

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