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Can X-rays be used to monitor polymerisations in supercritical CO_2? A study in SAXS

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Abstract

A versatile high pressure X-ray sample autoclave with diamond windows has been developed for conducting *in situ* time-resolved X-ray scattering experiments in the pressure and temperature regime required for polymerisation reactions in supercritical CO_2 ($scCO_2$) (**Figure 1, a**)).[1] Dispersion polymerisation in $scCO_2$ is an effective process for creating polymer microparticles free from solvent and monomer residue **(Figure 1, b)**. More recently, our group has demonstrated that block copolymer microparticles can also be created in this way in one-pot by using the reversible addition−fragmentation chain transfer (RAFT) process.[2] Such microparticles were shown to possess internal morphologies on the order 50 nm throughout, owing to the incompatibility of the two blocks that comprised the polymer chains **(Figure 1, b, insert)**. Here we detail an alternative synthesis route to these materials involving completely independent steps that exploits the livingness of RAFT-terminated PMMA microparticles and their ability to be redispersed in $scCO_2$. This not only enables a series of block copolymers to be created from a single RAFT dispersion synthesised PMMA homopolymer batch, thus improving reproducibility, but also adds flexibility by allowing the time and concentration requirements for each stage to be decoupled. The internal morphology development and evolution for a series of PMMA-*b*-PS block copolymer microparticles synthesised via this route was monitored via *in situ* small-angle X-ray scattering (SAXS) in our X-ray autoclave at 300 bars and temperatures and 65 °C. Together with offline kinetics experiments and post-mortem transmission electron microscopy imaging this approach provides remarkably detailed insights of the self-assembly processes of block copolymers in $scCO_2$ (**Figure 1, c**).

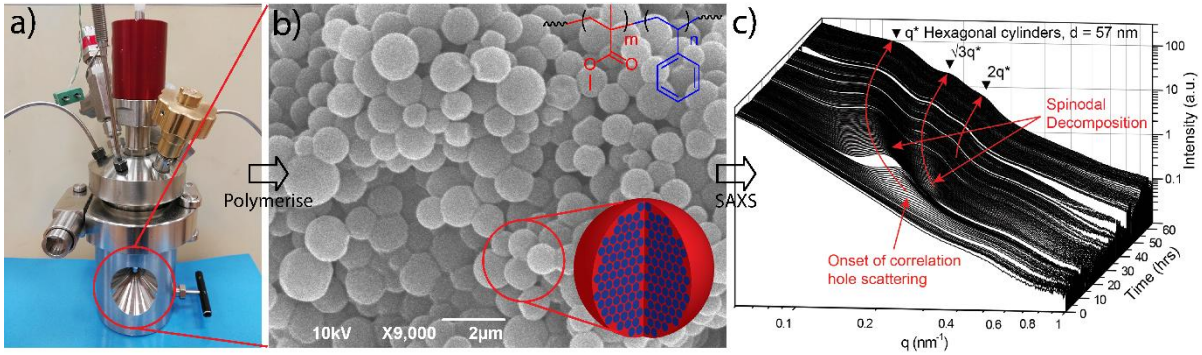

Figure 1. a) Autoclave built in-house with diamond windows for in situ SAXS monitoring of reactions. b) PMMA-b-PS block copolymer microparticles with internal structures, created via dispersion polymerisastion in $scCO_2$ at the synchrotron. c) In situ SAXS data collected throughout the polymerisation of PMMA-b-PS.

References

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[2] J. Jennings, M. Beija, A. P. Richez, S. D. Cooper, P. E. Mignot, K. J. Thurecht, K. S. Jack, S. M. Howdle, One-Pot Synthesis of Block Copolymers in Supercritical Carbon Dioxide: A Simple Versatile Route to Nanostructured Microparticles, *Journal of the American Chemical Society*, *134*, 2012, 4772-4781.