Model polyethylene nanoparticles for the study of nanoplastics in the oceans

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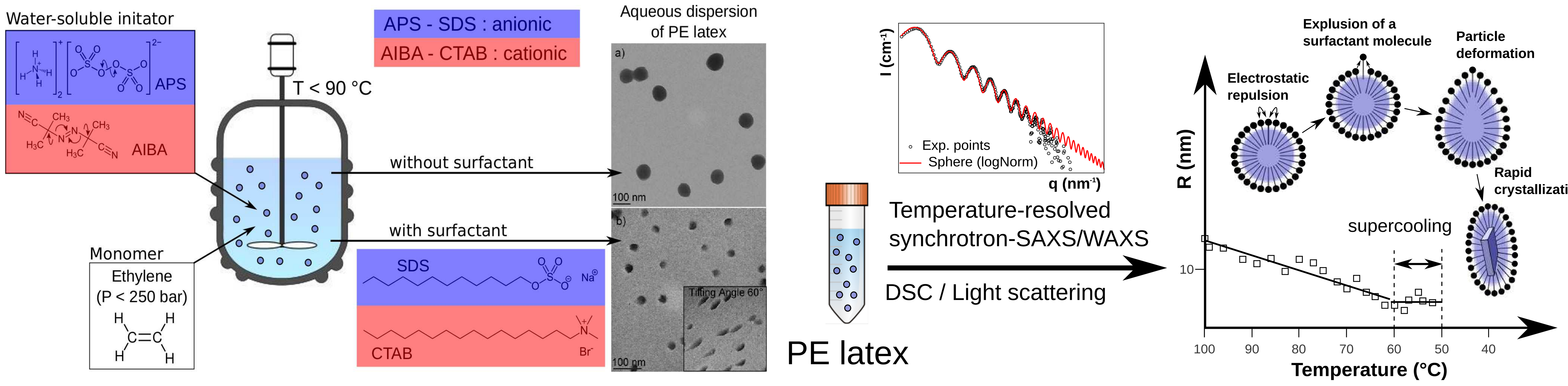
Introduction

Polyethylene (PE) is the most mass-produced polymer, it represents 90% of the plastic waste accumulated in the center of oceanic gyres (i.e. "plastic continents").[1] Following their photochemical degradation, these waste are gradually fragmented into micro-plastics (< 5 mm) and potentially into nano-plastics (< 1 µm).[2-3] Due to their small size, micro / nano-plastics are easily integrated into the food chain with possible toxic effects. [4-5] However, most biological and physico-chemical studies on micro-plastics are carried out with polystyrene nanoparticles because it remains difficult to synthesize PE nanoparticles. Model PE dispersions can be obtained by emulsification of the molten polymer, but this process produces particles of high size and dispersity.[6-7]



Relationship between surface charge, crystallinity and morphology

In the presence of surfactant (cationic or anionic) the nanoparticles obtained are anisotropic and have a very strong supercooling. Temperature-resolved synchrotron scattering was used to propose a novel mechanism explaining the origin of this enhanced supercooling in accordance with the evolution of the particle morphology and surface properties.[6] Our work is currently focused on the synthesis of PE nanoparticles using various stabilization in order to better control their size, morphologies and surface charge. The use of neutral initiator and surfactant allowed us to obtain spherical nanoparticles of controlled size (10 < D < 1000 nm) and of low polydispersity and therefore to extend the size range accessible via this synthesis process. **These dispersions are well suited for studying the effects of micro / nano-plastics of PE in the environment**.

Average diameter (nm)	PDI	ζ-potential (mV)
47.22	0.14	-73.2
45.44	0.2	-25.2
123.7	0.12	-0.7
71	0.146	24.8
36.19	0.303	51.7

Wide range of surface charges obtained by varying the initiator and the surfactant used during polymerization (anionic, neutral or cationic).

Surfactant exchange by dialysis after polymerization to tune both the charge and the size of the nanoparticles.

Perspectives

Synthesis of labeled PE nanoparticles (with ^{13}C or with a fluorophore) to better overcome the detection problems (by 2D NMR ^{13}C-13C or by fluorescence microscopy) and study their bioaccumulation depending on their size and their surface properties

Physico-chemical study and modeling of their fragmentation and their aggregation in a complex medium (in presence of salt, extracellular polysaccharide produced by microalgae and inorganic particles) could be performed to simulate the natural processes encountered in the ocean.

References :

[1] Ter Halle et al. (2017) Environmental Pollution 227: 167-174.
[2] Gigault et al. (2016) Environmental Science: Nano, 3(2), 346-350.
[3] Ter Halleet al. (2017) Environmental science & technology, 51(23), 13689-13697.
[4] Grau et al. (2010) Angewandte Chemie International Edition, 49(38), 6810-6812.
[5] Billuart et al. (2014) Macromolecules, 47(19), 6591-6600.