PhD proposal

Funding	Ministère de l'Enseignement supérieur et de la Recherche
Contract	Doctoral contract (3 years)
Laboratory	C2P2 : Chemistry, Catalysis, Polymers and Processes (UMR 5265) Université Claude-Bernard-Lyon-1
Discipline	Polymer / Physical-chemistry/ Colloid
Deadline for application	April 1, 2020
Start date	September 1, 2020
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Model polyethylene nanoparticles for the study of (nano)plastics in the ocean

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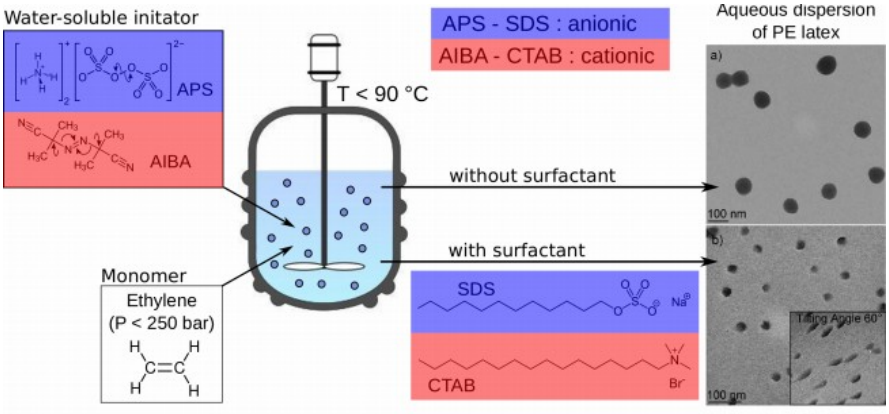
Polyethylene (PE) is the most mass-produced polymer, it represents 90% of the plastic waste accumulated in the center of oceanic gyres (i.e. "plastic continents"). [1] Following their photochemical degradation, these waste are gradually fragmented into micro-plastics (< 5 mm) and potentially into nano-plastics (< 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. Recently, we have succeeded in obtaining PE nanoparticles of controlled size (10 < D < 1000 nm) and of low polydispersity by radical polymerization of ethylene in emulsion (figure below). [6-7] These dispersions are well suited for studying the effects of micro / nano-plastics of PE in the environment.



It is estimated today that 250,000 tonnes of plastic are floating in the oceans [8] which represents less than 5% of the plastic debris inputs into the ocean (between 4.8 and 12.7 million tonnes of plastic enter the oceans every year). Where is the missing (micro) plastic? Several hypotheses have been put forward: bioaccumulation by marine organisms and/or their accumulation in sediments.

To answer this question, the development of a model study system will require (1) (1) the synthesis of ^{13}C or fluorescent labeled PE nanoparticles enabling the bioaccumulation of PE nanoparticles to be studied in the food chain (collaboration with the Le Mans Institute of Molecules and Materials / Fabienne Lagarde). (2) A precise physico-chemical characterization of the structure and morphology of nanoparticles is necessary and will be carried out using very large research infrastructures (Synchrotron-SAXS and SANS). In addition to characterizing the size, dispersity and morphology of nanoparticles, particular attention will be paid to their surface properties which will be varied using various stabilizing systems (ionic, steric, pickering, etc.). In order to extrapolate the laboratory results in the field, it is essential to identify and model as precisely as possible the mechanisms involved in their colloidal stability. Therefore it is necessary to precisely quantify the interaction energies (electrostatic, van der Walls ...) in order to simulate their aggregation (Smoluchowski coagulation equation) by including the effects of polydispersity and anisotropy of nanoparticles.

Skills and Experience of the future PhD student

Students with a master's degree or an engineer in materials science, chemistry, physical chemistry. Experience in polymer synthesis as well as analytical tools and polymer characterization techniques is desired. Experience with colloid and surface chemistry will be a plus. Finally, the candidate must demonstrate great curiosity and an interest in the diffusion of synchrotron light.

References

[1] Ter Halle, Alexandra, *et al.* "To what extent are microplastics from the open ocean weathered?." *Environmental Pollution* 227 (2017): 167-174.

[2] Ter Halle, Alexandra, *et al.* "Nanoplastic in the North Atlantic subtropical gyre." *Environmental science & technology* 51.23 (2017): 13689-13697.

[3] Gigault, Julien, *et al.* "Marine plastic litter: the unanalyzed nano-fraction." *Environmental Science: Nano* 3.2 (2016): 346-350.

[4] Thompson, Richard C., *et al.* "Plastics, the environment and human health: current consensus and future trends." *Philosophical Transactions of the Royal Society B: Biological Sciences* 364.1526 (2009): 2153-2166.

[5] Sharma, Shivika, and Subhankar Chatterjee. "Microplastic pollution, a threat to marine ecosystem and human health: a short review." *Environmental Science and Pollution Research* 24.27 (2017): 21530-21547.

[6] Grau, Etienne, *et al.* "Aqueous Dispersions of Nonspherical Polyethylene Nanoparticles from Free Radical Polymerization under Mild Conditions." *Angewandte Chemie International Edition* 49.38 (2010): 6810-6812.

[7] Billuart, Guilhem, *et al.* "Free radical emulsion polymerization of ethylene." *Macromolecules* 47.19 (2014): 6591-6600.

[8] Eriksen, Marcus, *et al.* "Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea." *PloS one* 9.12 (2014): e111913.

[9] Jambeck, Jenna R., *et al.* "Plastic waste inputs from land into the ocean." *Science* 347.6223 (2015): 768-771.