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THERMO-SENSITIVE AND BIODEGRADABLE BLOCK COPOLYMERS OBTAINED BY CONTROLLED POLYMERISATION

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Recently, LCBM has studied new catalysts for the ring-opening polymerisation (ROP) of ε-Caprolactone (ε-CL)[1]. Meanwhile, our French collaborators (LCPM) have been using the Atom Transfer radical polymerisation (ATRP) of methyl methacrylate to synthesize amphiphilic PMMA-grafted dextran glycopolymers (Dex-g-PMMA) with attractive surfactant properties [2].
This work was aiming at associating both expertises and thus combining to synthesize poly(ε-Caprolactone)-block-poly[oligo(ethylene glycol)methyl ether methacrylate] (POEGMA) copolymers using a bifunctional initiator. Thanks to their POGEMA block, such copolymers may exhibit a lower critical solution temperature (LCST) in aqueous medium and self-assemble in aqueous aggregates with various morphologies, such as micelles or vesicles. This propriety is very promising for biomedical applications such as enzyme recycling or drug delivery.
The two-step route for the synthesis of these copolymers is using either ATRP or ROP as first step and the other polymerisation secondly. Each polymerisation was studied carefully in order to control the macromolecular parameters of the copolymers. On the one hand, the ATRP of methacrylates bearing oligo(ethylene glycol) with different side-chains lengths was studied. Three different methacrylates were selected (MEO_2MA, MEO_5MA, MEO_9MA). Their ATRP was carried out in solution in toluene at 70 °C from two different intiators (Ethyl 2-bromoisobutyrate as model initiator or 2-hydroxyethyl-2-bromoisobutyrate as bifunctional initiator). Copper(I) bromide and *N*-propyl-pyridylmethanimine were used as catalytic system with or without initial addition of copper(II) bromide. On the other hand, ε-CL was polymerized in solution using tin octoate, tin tetrakis(phenylethynyl) and bismuth triflate as non-toxic catalysts.