



# Double hydrophilic polyphosphoester containing copolymers as efficient templating agents for calcium carbonate microparticles

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Titre Double hydrophilic polyphosphoester containing copolymers as efficient templating agents for calcium carbonate microparticles

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The use of calcium carbonate ( $\text{CaCO}_3$ ) microparticles is becoming more and more attractive in many fields especially in biomedical applications in which the fine tuning of the size, morphology and crystalline form of the  $\text{CaCO}_3$  particles is crucial. Although some structuring compounds, like hyaluronic acid, give satisfying results, the control of the particle structure still has to be improved. To this end, we evaluated the  $\text{CaCO}_3$  structuring capacity of novel well-defined double hydrophilic block copolymers composed of poly(ethylene oxide) and a polyphosphoester segment with an affinity for calcium like poly(phosphotriester)s bearing pendent carboxylic acids or poly(phosphodiester)s with a negatively charged oxygen atom on each repeating monomer unit. These copolymers were synthesized by a combination of organocatalyzed ring opening polymerization, thiol-yne click chemistry and protection/deprotection methods. The formulation of  $\text{CaCO}_3$  particles was then performed in the presence of these block copolymers (i) by the classical chemical pathway involving  $\text{CaCl}_2$  and  $\text{Na}_2\text{CO}_3$  and (ii) by a process based on supercritical carbon dioxide ( $\text{scCO}_2$ ) technology in which  $\text{CO}_3^{2-}$  ions are generated in aqueous media and react with  $\text{Ca}^{2+}$  ions. Porous  $\text{CaCO}_3$  microspheres composed of vaterite nanocrystals were obtained. Moreover, a clear dependence of the particle size on the structure of the templating agent was emphasized. In this work, we show that the use of the supercritical process and the substitution of hyaluronic acid for a carboxylic acid containing copolymer decreases the size of the  $\text{CaCO}_3$  particles by a factor of 6 ( $\sim 1.5 \mu\text{m}$ ) while preventing their aggregation.

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