Communication ☒ Oral
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ε-THIONOCAPROLACTONE: A SUITABLE MONOMER FOR EMULSION COPOLYMERIZATION ?

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In recent years, the increasing demand for degradable polymeric materials has resulted in developing new copolymerization techniques, one of the most studied relying on radical ring-opening (co)polymerization (rRO(co)P).[1] This process enables to incorporate cleavable bonds, e.g. esters and thioesters, into the polymer backbone. The polymer can then undergo chemical degradation in response to specific stimuli, including aminolysis or hydrolysis. While this polymerization process presents promising results in homogeneous systems, its adaptation to emulsion polymerization is usually more challenging due to the hydrolytic susceptibility of the cyclic monomers involved.[2] Recently, thionolactones, a new class of monomers undergoing rROP when copolymerized with a wide range of vinyl monomers, raised interest for their ability to produce easily degradable thioester bonds in the backbone of the resulting copolymers.[3] Additionally, some thionolactones such as dibenzo[c,e]oxepane-5-thione (DOT) have proven to be compatible with emulsion and miniemulsion systems where hydrolysis was not observed. [3]

This project aims at studying the emulsion copolymerization of vinyl acetate with various thionolactones to produce (bio)degradable latexes. As a first approach, the polymerizability of ε-thionocaprolactone (TCL)[3] was assessed in emulsion. Many challenges were raised, questioning the relevancy of the use of such a monomer under these conditions. This paper will discuss our main results (hydrolysis pathway, impact on radical polymerization mechanism) and how experimental conditions need to be tuned to successfully copolymerize TCL in emulsion.

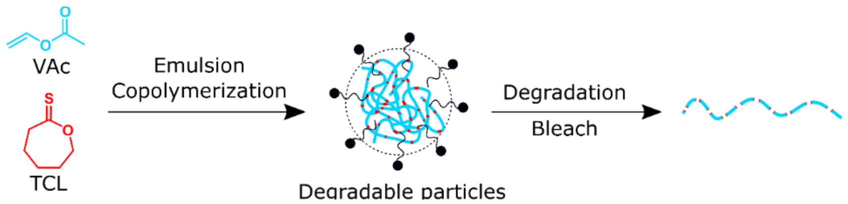

Figure: synthesis of degradable P(VAc-*co*-TCL) particles *via* emulsion copolymerization

[1] A. Tardy, J. Nicolas, D. Gigmes, C. Lefay, Y. Guillaneuf, *Chem. Rev.* **2017**, *117*, 1319–1406.
[2] B. R. Kordes, L. Ascherl, C. Rüdinger, T. Melchin, S. Agarwal, *Macromolecules* **2023**, *56*, 1033–1044.
[3] C. Lefay, Y. Guillaneuf, *Prog. Polym. Sci.* **2023**, 101764.