EMULSION THIOL-ENE PHOTOPOLYMERIZATION: TOWARD GREENER METHODS FOR SYNTHESIS OF POLYSULFIDE LATEXES

Cuong Minh Quoc Le,[a,b] Marc Schmutz [c] and Abraham Chemtob [a,b]

[a] Université de Haute-Alsace, CNRS, IS2M UMR7361, F-68100 Mulhouse, France
[b] Université de Strasbourg, France
[c] Institut Charles Sadron, CNRS, UPR 22, Université de Strasbourg, 23 Rue du Loess, BP 84047, 67034 Strasbourg, Cedex 2, France

Emulsion polymerization process, considered as a green technique, offers a range of synthetic routes to polymer particles of variable size from nano- to micrometer range[1]. This technology has resulted in high tonnage industrial applications, including coatings or inks, as well as niche applications in drug delivery and immunoassay. However, the conventional approach for conducting an emulsion polymerization process relies exclusively on chain-growth radical polymerization using thermal or redox radical initiators. Therefore, finding new means to expand this process industrially beyond chain radical polymerization is highly desirable. Herein, we report the successful photoinitiated thiol-ene radical polyaddition of an emulsion based on two bifunctional monomers diallyl phthalate and 2,2-(ethylenedioxy)diethanedithiol. After 20 min irradiation (λ_{max} = 385 nm, 3.7 mW cm^{-2}), polymerization has resulted in a conversion above 99%, a coagulum-free poly(thioether) latex with a solids content of 10 wt%, a number-average molecular weight of 14 kDa, and an average particle diameter of 60 nm. Reaction kinetics, particle size distribution, and molecular weight progress have been studied in detail. The mechanism dictating particle formation have also been investigated. It is found that the polymer particle is mainly formed by the precipitation of oligo-radicals (homogeneous nucleation) even when the concentration of surfactant exceeds its critical micellar concentration[2]. The dispersion's solids content can reach as high as 40% with a reasonable molecular weight (> 4 kDa). In contrast to a conventional thermally induced polymerization, temporal control is demonstrated through sequential "on-off" cycles, and tunable molecular weight is achieved by precise energetic dosage of radiation. Additionally, low monomer residues latex as well as a facile process up-scaling are the other key advantages of this process. This new step photopolymerization in emulsion thus opens an avenue for the synthesis of linear polysulfide latex without high energy homogenization and at low irradiance.

[1] F. Jasinski, P. B. Zetterlund, A. M. Braun and A. Chemtob, *Progress in Polymer Science*, 2018, **84**, 47-88.

[2] C. M. Quoc Le, M. Schmutz and A. Chemtob, *Macromolecules*, 2020, **53**, 2369-2379.