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Thesis title: Porous scaffolds of crosslinked poly(ε-caprolactone) *via* single-step high internal phase emulsion-ring opening polymerization

Abstract

Porous polymeric scaffolds available in form of monoliths, rods, beads, and films etc. have gained significant interest over past two decades due to their fascinating properties and applications in various fields. Amongst various techniques to prepare porous polymeric scaffolds, emulsion templating in the form of high internal phase emulsion (HIPE, volume fraction of dispersed phase, $\phi_d \geq 0.74$) polymerization is highly admired for being a single step process to synthesize porous scaffolds (known as polyHIPE) of interconnected pore-morphology, tailor-made properties, and customized functionalities. Aqueous and non-aqueous HIPE templates i.e. water-in-oil (w/o), oil-in-water (o/w), and oil-in-oil (o/o) stabilized using emulsifiers and/or Pickering stabilizers have been used to synthesize scaffolds suitable for various applications such as selective-sorption, adsorption, water-purification, and tissue engineering etc. Amongst different available polymerization chemistry, free radical polymerization is the most employed route in HIPE templating to synthesize porous scaffolds from unsaturated vinylic monomers. Very few reports are available on HIPE templated scaffold synthesis using other polymerization chemistry such as ATRP, RAFT, ROMP and step growth. Other polymerization routes such as ring opening polymerization (ROP) to synthesize porous scaffolds for tissue engineering based on a biodegradable aliphatic polyester specifically poly(ε-caprolactone) (PCL) by HIPE templating are scantly covered. All the PCL based scaffolds derived from HIPE templating are either based on pre-synthesized high molecular weight PCL or low molecular weight PCL macromers. Both of those approaches are multistep processes and require use of organic solvents to obtain low viscosity PCL solution for emulsification of dispersed phase during HIPE preparation. The scaffolds also showed poor mechanical strength and are of limited use especially in tissue engineering. Thus, there is an immense need and research prospects to generate mechanically strong PCL scaffolds in a single step using monomer (ε-caprolactone) (CL) as the continuous phase of HIPE.

In this study, we developed a single step synthesis of HIPE templated crosslinked PCL scaffolds *via* high internal phase emulsion-ring opening polymerization (HIPE-ROP). The challenges

associated with preparation of stable HIPEs of CL and its polymerization to obtain crosslinked PCL scaffolds were overcome by judicious selection of dispersed phase, n-hexadecane, emulsifier, pluronic F127 and magnetic stirring (1500 rpm). CL-HIPEs were prepared by dispersing n-hexadecane in continuous phase of HIPE

and HIPEs were polymerized *via* HIPE-ROP at 120 °C for 8 h in non-inert condition. Bis-(ε-caprolactone-4-yl) (BCY) was used as crosslinker which was melt-dissolved in CL and it effectively crosslinked the PCL chains during stannous octoate, $Sn(Oct)_2$ catalyzed HIPE-ROP. Different generations of crosslinked PCL scaffolds were synthesized by varying the crosslink density (X_c) and ϕ_d. Polymer yield (>95%) and gel content values (>98%) signified high efficacy of adopted parameters for HIPE-ROP performed with moisture sensitive monomers and catalyst. The crosslinked PCL scaffolds were of interconnected pore-morphology, high porosity, high mechanical strength and possessed significant liquid uptake. The effect of dual confinement on crosslinked PCL chains locked in typical polyHIPE morphology caused by ϕ_d and X_c was clearly reflected on the melting and crystallization temperatures of crosslinked PCL scaffolds. Further, to resolve the concerns related to high emulsifier content, synthesis of crosslinked PCL nanocomposite scaffolds at relatively low emulsifier concentration was demonstrated by incorporating nano-graphene oxide dots, as Pickering stabilizer, in the continuous phase of HIPE. The *in-vitro* cell-growth and biomineralization experiments and controlled hydrolytic degradation study of crosslinked PCL scaffolds proved the suitability of synthesized crosslinked PCL scaffolds in tissue engineering. Overall, the single step HIPE-ROP process developed in this work paved a new route to prepare emulsion templated crosslinked scaffolds of other lactones and lactides. The HIPE-ROP process executed using as received monomers and reagents has high potential for commercial viability by conversion from a batch to a continuous process.