

Living/controlled anionic polymerization of glycolide in fluoroalcohols: Toward sustainable bioplastics and pentacrystalline quintopolymer

Pengfei Zhang, Viko Ladelta and Nikos Hadjichristidis*

King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia, 23955

Ring-opening polymerization (ROP) is a promising approach to accessing well-defined polyesters with superior (bio)degradability and recyclability. However, the living/controlled polymerization of glycolide (GL), a well-known sustainable monomer derived from carbon monoxide/dioxide, has never been reported due to the extremely low solubility of its polymer in common solvents. Herein, we disclose the first living/controlled anionic ROP of GL in strong protic fluoroalcohols (FAs), which are conventionally considered incompatible with anionic polymerization. Well-defined polyglycolides (PGA, $\bar{D} < 1.15$, M_n up to 55.4 kg mol⁻¹) are obtained at room temperature for the first time. NMR titration and computational studies revealed that FAs simultaneously activate the chain end and monomer without being involved in initiation. Low-boiling-point FAs and PGA can be recycled through simple distillation and sublimation at 220 °C in vacuo, respectively, providing a promising sustainable alternative for tackling plastic pollution problems.

Well-defined multicrystalline multiblock polymers are essential model polymers for advancing crystallization physics, phase separation, self-assembly, and improving the mechanical properties of materials. However, due to the different chain properties and incompatible synthetic methodology, multicrystalline multiblock polymers with more than two crystallites are rarely reported. Herein, by combining the newly developed fluoroalcohol-assisted ring-opening polymerization, polyhomologation, and “catalyst switch” strategy, we synthesized the first pentacrystalline pentablock quintopolymer, polyethylene-*b*-poly(ethylene oxide)-*b*-poly(ϵ -caprolactone)-*b*-poly(L-lactide)-*b*-polyglycolide (PE-*b*-PEO-*b*-PCL-*b*-PLLA-*b*-PGA). The novel “fluoroalcohol-assisted catalyst switch” strategy enables the first successful incorporation of a high melting point polyglycolide into the complex multiblock polymer. 1D/2D variable temperature (VT) liquid- and solid-state NMR spectroscopy (e.g. VT ¹H–¹³C INEPT NMR, VT ¹H–¹³C CP-MAS NMR, ¹H–¹³C CP–MAS WISE NMR, etc), X-ray diffraction, and differential scanning calorimetry revealed the existence of five different crystalline phases.