

CARBON DIOXIDE-EPOXIDE COPOLYMERIZATION USING SUPPORTED ZINC CATALYSTS

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ABSTRACT

Carbon dioxide (CO₂) utilization for the production of value added products is an attractive chemical process, which offers several economic and environmental benefits. Being a green carbon source, CO₂ provides an alternative to the toxic phosgene which has a number of negative environmental impacts when used in the production of biodegradable polymers. However, this route of polycarbonate production, is hindered by the chemical inertness of CO₂, and to overcome this, catalytic systems are necessary to overcome this energy gap during the reaction. Therefore, this thesis reports the design of a highly active heterogeneous zinc glutarate-double metal cyanide composite catalyst (ZnGA/Zn₃[Cr(CN)₆]₂) for the carbon dioxide (CO₂) and epoxide copolymerization reaction.

The composite catalyst was synthesized in a rheological phase reaction using toluene as solvent, and characterized using Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (PXRD), Brunauer-Emmett-Teller (BET), and scanning electron microscopy (SEM). The metal composite catalyzed the solvent free reaction of propylene oxide (PO) and CO₂ to afford biodegradable polypropylene carbonate (PPC) copolymer that exhibited excellent properties. ¹H NMR, ¹³C NMR, FTIR and ESI-TOF mass spectrometry measurements confirmed PPC product formation. Under the optimized reactions conditions (50 bar CO₂, 70 °C, 24 h), the ZnGA/Zn₃[Cr(CN)₆]₂ composite catalyst gave PPC in high yield (47.9 g polymer/g catalyst, FCO₂ > 85 %) with a high molecular weight (4.2 kg/mol) and narrow polydispersity index of 2.2. The PPC also displayed good thermal stability, exhibiting a high decomposition temperature (10 % weight loss at 229 °C) and complete decomposition at 350 °C. Due to good thermal stability exhibited by the PPC formed, it was functionalized and tested in energy storage. PPC functionalization was achieved through thermal treatment, and FTIR analysis of the functionalized PPC (FPPC) showed that it retained all key functional groups observed in the original copolymer. The FPPC material exhibited excellent electrochemical properties such as a specific capacitance of 68.47 F/g and a current density of 0.3 A/g. In addition, the FPPC displayed good stability as an electrode material, with a capacitance retention rate of 98.5 % even after 9000 cycles at current density of 1.0 A/g. Finally, the ZnGA/Zn₃[Cr(CN)₆]₂ composite catalyst was also tested in the

copolymerization of styrene oxide (SO) and CO₂ producing the desired polystyrene carbonate in a yield of 26 g polymer /g catalyst (FCO₂ = 93 %). However, when the composite was tested in the copolymerization of 1, 2 epoxy hexane monomer with CO₂, only trace amounts of the desired copolymer were achieved.