

Theoretical and experimental investigation of the involvement of side chain functionalities in the mediation of regioselectivity during triazabicyclodecene (TBD)-catalyzed ring-opening polymerization of functional glucose carbonates

Yue Song¹, ysong@tamu.edu, Xin Yang², Michael B. Hall², Karen L. Wooley¹. (1) 3255 TAMU, Texas A&M University, College Station, Texas, United States (2) Department of Chemistry, Texas A&M University, College Station, Texas, United States

Glucose-based polymers with carbonate backbone linkages represent highly-functionalizable materials derived from sustainable natural resources. Ring-opening polymerization (ROP) using organocatalysts, a major strategy for the construction of glucose carbonate-based polymers, has demonstrated excellent performance in controlled polymerization. However, differential regiochemistries observed during ROP of cyclic carbonates derived from glucose and having carbonate vs. ether side chain functionalities presented an interesting challenge. Experimentally, highly regioselective ROP was achieved using glucose carbonate monomers with carbonate side chains, whereas regioirregularity was observed in the case of ether side chains. Given the importance of regiochemistry in regulating polymer properties, we undertook a comprehensive experimental and theoretical study to elucidate the mechanistic origins for the curious regiochemical differences in poly(glucose carbonates)s (PGC), providing structural details for the ring-opening process. Unimers and dimers from ROP initiation and propagation processes, respectively, were isolated by chromatography and identified by a combination of 1D and 2D NMR analyses. The glucose carbonate monomer with carbonate side chains exhibited regioisomeric preference of C-O4 bond cleavage, as revealed by ¹H-¹³C heteronuclear multiple-bond correlation (HMBC) spectroscopy, leading to O6-to-O4 polymerization direction and a head-to-tail regioregular structure of the resulting carbonate-substituted PGC. In contrast, both C-O4 and C-O6 bond cleavages were observed in ROP of glucose carbonates with ether side chains, resulting in regioirregularity of the final ether-substituted PGC. Density functional theory (DFT) calculations were carried out to understand the regioselectivity of the reactions based on different monomer structures. Overall, this work provides a fundamental understanding of the regiochemistry of organocatalytic ROP of cyclic glucose carbonates with varying side chain chemistry.

