

Insight into the mechanism of the catalysis of urethane formation by organotin(IV) dicarboxylate using experimental and computational methods

Ransi Devendra^{1,3*}, Neil R. Edmonds^{1,4}, Tilo Söhnel^{1,2}

¹School of Chemical Sciences, University of Auckland, New Zealand

²Centre of Green Chemical Science, University of Auckland, New Zealand

³Uroxsys Ltd. Auckland, New Zealand

⁴Department of Mechanical Engineering & Centre of Advanced Composite Materials, University of Auckland, New Zealand

Polyurethane is made by reacting a polyisocyanate with a polyol. Organotin dicarboxylates are used as catalysts for this reaction. However, a deeper understanding of the mechanism in catalysis is essential in the polyurethane product manufacture. Although catalysis of aromatic and aliphatic isocyanates using organotin dicarboxylate in urethane formation was claimed to have the same mechanism for both, our work showed that they were different. In this work, we investigated urethane formation for both aliphatic and aromatic isocyanates in the presence of different organotin carboxylate compounds as catalysts using experimental and computational methods. In experimental methods, kinetic studies and FTIR analysis were used. As the computational method, the DFT/B3LYP-D3 functional with the LANL2DZ basis set for tin and the 6-31G* basis set for light elements was used. The results from the experimental and theoretical studies showed that an alkoxide complex was formed initially by the interaction between organotin di-carboxylate catalyst and alcohol. Then the interaction between alkoxide complex and isocyanate molecule was modelled using a computational method. This interaction resulted in the formation of organotin carbamate and carboxylic acid. Then the newly formed organotin carbamate was computationally modelled to interact with alcohol or carboxylic acid to form the urethane and to regenerate the active catalyst. By using thermochemical data from the computational investigation, it was possible to show that aliphatic isocyanates can be more sensitive to the carboxylic ligand content of the organotin carboxylate catalyst compared to aromatic isocyanates in urethane formation. Based on these findings, different mechanisms for aromatic and aliphatic isocyanates in urethane formation can be proposed when an organotin dicarboxylate is used as a catalyst. The new knowledge from our studies was essential to minimize the viscosity increase in storage of urethane pre-polymer when synthesised using organotin dicarboxylate as the catalyst.

Keywords: Urethane, Catalyst, Organotin dicarboxylate, Computational

*Corresponding author. School of Chemical Sciences, University of Auckland, New Zealand.
Email address: rdev012@aucklanduni.ac.nz