Mechanistic Studies on the Copolymerization of Epoxide with Carbon Dioxide

Kyoko Nozaki
Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, JAPAN, *e-mail nozaki@chembio.t.u-tokyo.ac.jp

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Abstract Speech

Carbon dioxide (CO₂) is an attractive C₁ feedstock because it is abundant on the earth, inexpensive, and less toxic. The metal-catalyzed copolymerization of epoxide with CO₂ is one of the most promising applications. Among various catalysts so far developed, cobalt/salen complexes were known as the most active catalyst. Recently, we reported that metal(IV)-based catalysts such as titanium and germanium, and iron/corrole complexes are also applicable to this reaction. Herein, we report studies on reaction mechanism of the metal-catalyzed epoxide/CO₂ copolymerization. Especially, kinetic studies and quantum-chemical analysis were employed in order to reveal the relationship between the catalyst structure and the catalyst performance.

Kinetic studies were conducted under the reaction conditions shown in Scheme 1 for the reported six complexes (Figure 1). Based on the dependence of the initial polymerization rate on catalyst concentration, we concluded that the rate determining step (RDS) was the ring opening of epoxide for each complex.

DFT studies were performed for this copolymerization system. In the calculation, t-butyl groups were omitted for simplification for M–salen and M–boxdipy complexes. For Fe–corrole complexes, trivalent complexes without axial chloride ligand were used since the Fe (IV) species is known to be easily reduced to Fe (III) species. The DFT results showed that the alkoxide complex was the most stable and the epoxide-coordinating complex was the most unstable (Figure 2). As shown in Figure 3, the negative correlation between ΔG and TOF for PPC existed, and logarithm of TOF and ΔG had a linear correlation.

In this research, we demonstrated the correlation between the catalytic activities and ΔG estimated by DFT studies. We believe this result will impact the future catalyst design for the copolymerization.

REFERENCES