

Cationic Polymerization via Activation of Alkoxyamines Using Photoredox Catalysts



M. Konya



M. Uchiyama



K. Satoh



M. Kamigaito



Hybrid Catalysis

The front cover artwork is provided by the group of Prof. Masami Kamigaito at the Department of Molecular and Macromolecular Chemistry, Nagoya University (Japan). The image shows cationic polymerization via the mesolytic cleavage of alkoxyamine triggered by an excited cationic Ir(III) catalyst under blue LED irradiation, in contrast to radical polymerization via the homolytic cleavage under heat. Read the full text of the Article at 10.1002/cptc.201900148.

What prompted you to investigate this topic/problem?

We have been wondering if the carbon–oxygen bond of alkoxyamine, which is generally used as a mediator for radical polymerization, somehow can be activated to generate a carbocation for cationic polymerization to widen the scope of controlled polymerization reactions using alkoxyamine.

What is the most significant result of this study?

Alkoxyamines indeed generate cationic species via mesolytic cleavage induced by photoredox iridium catalysts under visible-light irradiation to induce the cationic polymerization of various vinyl monomers.

What new scientific questions/problems does this work raise?

Another challenge is how to regenerate alkoxyamines via reversible capping of the propagating carbocationic species with nitroxide anions for controlling the cationic polymerization reactions.

Who designed the cover?

We described a simple idea of the cover to a professional designer (Mr. Masaya Matsukawa at YAP Co. Ltd.), who realized the final version through discussion more finely than we had expected.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Number JP18H04647 in “Hybrid Catalysis for Enabling Molecular Synthesis on Demand” and JP18H03917. We thank Dr. F. Ariura (Arkema) for providing a nitroxide, Prof. H. Shinokubo, Prof. Y. Miyake, Ms.

H. Takekoshi (Nagoya University) for CV analysis, and Prof. C. Boyer (University of New South Wales) for discussion on photopolymerization.

