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In Situ Generated Ruthenium-Arene Catalyst for Ring-Opening Metathesis Photopolymerization Through Photolabile N-Heterocyclic Carbene (NHC) Ligand

Abstract

Since its discovery in the 1950s, olefin metathesis has evolved from a restricted use in petroleum cracking processes to the standard method for creating C-C double bonds. Progress has been driven by a range of increasingly advanced and well-defined olefin metathesis catalysts. Nevertheless, these developments have predominantly benefited preparative organic chemistry, and to a lesser extent, the synthesis of polymer materials. Many useful polymers such as poly(norbornene) or poly(dicyclopentadiene) can be prepared by ring-opening metathesis polymerization (ROMP), and have led to successful commercial applications. However, their implementation at industrial scale has been held back by the lack of ambient stability and processability of most late transition metal-based catalysts.^[1] Designing ROMP catalysts in a way that allows the on-demand release of highly reactive alkylidene species is a very attractive goal to ease storage, handling and processing.^[2] UV-vis radiation is certainly one of the most sought after activating stimuli because it enables, among other advantages, room-temperature process and spatial control.^[3] So far, though, only radical and cationic chain-growth processes have enabled photopolymerization to be harnessed as a technology.^[4] In an effort to improve ROMP photocatalyst performance, versatility, latency and ease of synthesis, we have designed an indirect activation method based on a metathesis inactive Ru complex converted into an active system by a photogenerator of N-heterocyclic carbene (NHC) ligand.^[5] So far, all latent NHCs are triggered thermally or mechanically,^[6] and the synthesis of an efficient photolabile NHCs is unprecedented. With this new photocatalytic system, full conversion of norbornene was achieved in less than 3 min.

References

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