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Photolabile organic catalysts for delayed ring opening polymerization

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PURPOSE OF THE ABSTRACT

Photolabile polymerizations open the way for applications where a delayed reaction and/or a spatial control is required. The polymerization begins "on demand" when and where the irradiation is applied. Photolabile polymerizations developed so far usually involve radical processes that are sensitive to oxygen, limiting industrial applications. In order to get biodegradable, biocompatible and biosourced materials prepared with this technology, we decided to develop photolabile ring-opening polymerization (ROP) of cyclic esters and other cyclic monomers. While the ROP of cyclic esters is commonly catalysed by organometallic catalysts such as tin(II) 2-ethylhexanoate, organic catalysts such as guanidines, amidines and N-heterocyclic carbenes (NHC) have also been used effectively, then avoiding the presence of metallic residue in the final polymer. [1] This led us to the challenging development of photolabile NHCs. We recently reported the first photolabile NHC in the form of a tetraphenylborate imidazolium salt. [2] The expected carbon disulfide NHC adduct was isolated after the addition of carbon disulfide in an irradiated solution of this photolabile NHC. The photolabile NHC combined with a ruthenium precursor allowed the fast photopolymerization of norbornene after UV irradiation via a ring opening metathesis mechanism. However, this first generation of photolabile NHC revealed to be inefficient for the ROP of cyclic esters. A second generation of photolabile NHC was thus developed with counter anions known to undergo a photodecarboxylation such as ketoprofenate. [3] With such photobase generators (PBGs), ROP of lactide in solution was successfully achieved after irradiation at 365 nm (Figure 1). Obtained polymers (poly(lactide), PLA) were carefully characterized by SEC, ¹H NMR and MALDI TOF analyses. [4]

Finally, an interesting comparative study between the new photolabile NHC and a photobase generator (PBG) releasing triazabicyclodecene was conducted. Differences in the activity of the two systems were investigated (Figure 2).

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