Biomimetic Polymers

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Abstract: We report here metal-free strategies using organocatalysis based on supramolecular recognition for the Ring-Opening Polymerization (ROP) of several Cyclic Phosphate Monomers (CPMs).

Keywords: Ring-Opening Polymerization, Cyclic Phosphate Monomers, organocatalysis

Introduction

Polymers with repeating phosphoester bonds in the backbone are structurally versatile compared to the conventional aliphatic polyesters such as PGA, PLA, PCL and their copolymers. One of their advantages is the easy functionalization of side chains due to the pentavalency of the phosphorous atom, allowing the introduction of bioative molecules and extensive modification of the physical and chemical properties of polymer.

Results and Discussion

The ROP of cyclic esters is a well-established process to provide linear polyesters with preditable molecular weight, narrow polydispersity and well-defined end-groups (Figure 1). To better fulfill the requirements of biomedical applications, we developped synthetic procedures that are metal-free (i.e., organocatalytic) using a variety of organoctalysts such as DBU, TBD, M-TBD and a bicomponent thiourea-tertiary amine. Among the metal-free organocatalysts studied, the bicomponent catalysts based on DBU and thiourea is by far the most efficient. This system, based on dual activation of both monomer by thiourea and initiator by DBU, was successfully implemented for the synthesis of PPEs with molecular weight up to 70.000 g.mol^{-1}, whereas the molecular weight distribution remains monomodal and narrow (PDI<1.10)[1]. Moreover, the undesired transesterification reactions are minimized, even at near-complete conversion that proves the efficiency and the robustness of the process. The chain extension experiment through the use of hydroxy end-capped PPEs as macroinitiators confirm the controlled/living nature of organo-catalyzed ROP of CPMs and pave the way to the synthesis of block copolymers and others more complicated architectures based on polyphosphates.

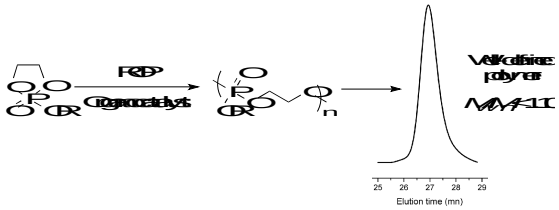

Figure 1: Synthetic pathway for the synthesis of well-defined polyphosphates by ROP.

Conclusions

These polymerizations procedures are expected to facilitate the synthesis of well-defined PPEs with various architectures and free of potentially toxic metal remnants for biomedical applications.

References

[1] B. Clément *et al.*, *Macromolecules*, **45**, (11) 4476 – 4486 (2012).

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