

Magnetic Nanoparticle Supported Metal Alkoxide Catalysts for the Ring-opening Polymerization of ϵ -Caprolactone

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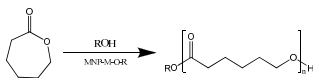
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Introduction

Magnetic nanoparticles (MNPs) have attracted attention as alternative catalyst supports because of their high external surface area, capability for facile surface modification and easy recoverability [1]. Functionalization of MNP with polymerization catalysts could facilitate a new generation of recyclable and recoverable polymerization catalysts for niche applications. Polymerization catalysts are routinely single use catalysts, as neither homogeneous (no easy recovery mechanism) nor heterogeneous (polymer clogs catalyst pores and entraps catalyst within the polymer product) are easily recoverable. Here we report MNP supported metal alkoxide catalysts for ring-opening polymerization (ROP) of ϵ -caprolactone as an example of a rare, recoverable and recyclable polymerization catalyst for synthesis of an important biodegradable poly(ester).

This work describes the preparation, characterization and kinetic activity of this new type of heterogeneous catalyst in the ROP of ϵ -caprolactone. Metal alkoxides are grafted onto the surface of spinel ferrite magnetic nanoparticles (CoFe_2O_4). The catalysts can be easily recovered from the reaction mixture via application of an external magnetic field and reused in subsequent reactions.



Scheme 1. ROP of ϵ -caprolactone, M: Al, Y

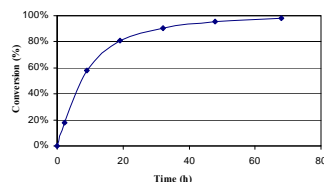


Figure 1. Kinetic data for the MNP supported aluminum isopropoxide catalyst.

Materials and Methods

The synthesis of cobalt spinel ferrite nanoparticles (CoFe_2O_4) followed a published microemulsion method [2]. MNP supported aluminum isopropoxide catalysts (MNP-Al-O-iPr) were prepared using aluminum isopropoxide as the precursor. For preparation of MNP supported yttrium isopropoxide catalysts (MNP-Y-O-iPr), [Tris(hexamethyldisilyl)amide]yttrium ($[\text{Y}(\text{N}(\text{SiMe}_3)_2)_3]$) was used as the precursor and isopropanol was added to endow the metal site with alkoxide ligands. Polymerization reactions were carried out under N_2 . In the glove box, catalysts were mixed with ϵ -caprolactone, isopropanol, dodecane, and toluene. After reaction, the catalysts were recovered under external magnetic field and the polymer was precipitated

and washed with cold hexanes. The supported aluminum isopropoxide catalysts were characterized by elemental analysis, FTIR, FT-Raman and transmission electron spectroscopy (TEM). The reaction conversion was determined using gas chromatography (GC) by following the monomer consumption. Polymer products were analyzed with gel permeation chromatography (GPC) and ^1H NMR.

Results and Discussion

Polymerization of ϵ -caprolactone is successfully demonstrated with the MNP supported metal isopropoxide (MNP-M-O-iPr, M: Al, Y) catalysts. The isopropyl end groups (δCH_3 at 1.2 ppm) were observed in the recovered polymer, in agreement with the proposed coordination-insertion mechanism [3]. The recovered polymer has a narrow PDI (M_w/M_n around 1.5) and the M_n from GPC is close to the theoretical value (Table 1). The reaction conversion reached 81% in 19 hours with MNP-Al-O-iPr supported catalysts (Figure 1). When using MNP-Y-O-iPr, the reaction reached 98% conversion in just 2 hours. All catalysts could be easily recovered from reaction solution upon application of an external magnetic field. The recovered catalysts were reused for the polymerization under the same conditions and polymers were recovered from the reaction systems that used recycled catalysts. The various methods for preparation of MNP supported metal alkoxide catalysts, characterization of the catalysts and polymer products, catalytic activity and recyclability of the catalysts will be discussed.

Table 1. ROP of ϵ -caprolactone (CL) with MNP supported metal isopropoxide catalysts

	Temp/ $^{\circ}\text{C}$	Time/h	Conv %	M_n (theory)	M_n (GPC)	M_w/M_n
MNP-Al-O-iPr	100	19	81	2047	1804	1.50
MNP-Y-O-iPr	100	2	98	2511	2306	1.60

Significance

This is the first reported MNP supported, recoverable and recyclable catalyst for polymerization using a metal catalyst that operates by the coordination-insertion mechanism. Acid catalysts based on porous silica for the ROP of ϵ -caprolactone, such as $\text{SBA15-SO}_3\text{H}$ [4], yttrium isopropoxide on porous silica [5], aluminium alkoxides on porous silica [6] are known, but diffusion and pore clogging is a significant problem with these systems. This new type of heterogeneous catalyst can be easily recovered and reused. In addition, the MNP supported Lewis acid catalysts can also be applied to other systems where reaction activity is limited by pore diffusion [7].

References

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