Electronic Supplementary Information for Dalton Transactions

Recoverable & recyclable magnetic nanoparticle supported aluminum isopropoxide for ring-opening polymerization of ε-caprolactone

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Experimental Part

Chemicals and Materials. ε-caprolactone (Aldrich, 97%) and dodecane (Acros, 99%) were dried over CaH_2 and distilled at reduced pressure. Toluene (Aldrich, 99.8%) and isopropanol (^iPrOH, Aldrich, 99.5%) were dried by refluxing over sodium benzophenone and then distilled under Argon. Aluminum isopropoxide (Aldrich, 98+ %), cobalt (II) chloride (Alfa Aesar, anhydrous, 99.5%), iron (II) chloride (Alfa Aesar, anhydrous, 99.5%) were used as received.

Characterization. Molecular weights and molecular weight distributions of the polymer were determined by gel permeation chromatography (two Varian PLgel Mixed E columns, THF eluent, polystyrene calibration standards, and refractive index detector). ^1H NMR measurements were performed on a Varian Mercury Vx 400 ($CDCl_3$ solvent). The polymerization reaction conversion was monitored by gas chromatography (Shimadzu GC-2010, FID detector, SHRX5 column). Transmission electron microscopy measurements were performed on a JEOL 100CX-2. Elemental analysis was performed by Columbia Analytical Services (Tucson, AZ)

Catalyst preparation. The synthesis of cobalt spinel ferrite nanoparticles ($CoFe_2O_4$) followed a published microemulsion method.[1] $CoFe_2O_4$ support (0.7 g), which was dried under vacuum (180°C, overnight) prior to use, was suspended in dry toluene (27 ml). Then, aluminum isopropoxide (1.1 g) was added into the solution. The mixture was stirred at room temperature for 24 hours. The solid was then recovered under a magnetic field, washed with toluene three times, and dried under vacuum (150°C, overnight).

Polymerization of ε-caprolactone. A typical procedure is as follows: A pressure tube was charged with ε-caprolactone (12.1 mmol), ^{i}PrOH (0.55 mmol), dodecane (0.515 g), catalysts (1.77 mol %) and toluene (10 ml). The reaction mixture was stirred under nitrogen (100°C) while a GC was used to monitor the conversion. At set time intervals, 120 μL aliquots of the polymerization solution were taken. Of this amount, a 20 μL sample was added into acetone for GC analysis. THF (1 ml) and iPrOH (0.1mL) were added into the vial with the remaining 100 μL sample for GPC analysis (catalysts in the samples were removed before measurement). Once the expected conversion was reached, the reaction was terminated by addition of excess ^{i}PrOH, followed by toluene. The reaction vessel was put on a magnet for a long time to recover all the catalysts. The clean reaction solution was recovered and excess solvent was removed by rotovap, leaving an oily liquid. Polymers were then precipitated with cold hexane, washed with cold hexane and cold methanol a few times, and then dried under vacuum.

Catalyst recycle. When polymerization was complete, the reaction mixture was quenched with ^{i}PrOH and toluene. Catalysts were attracted to the bottom of the flask by an external magnet, washed three times with toluene, and then dried under vacuum (150°C, overnight). The recovered catalysts were then added into the reactor and reused according to the typical polymerization procedure.

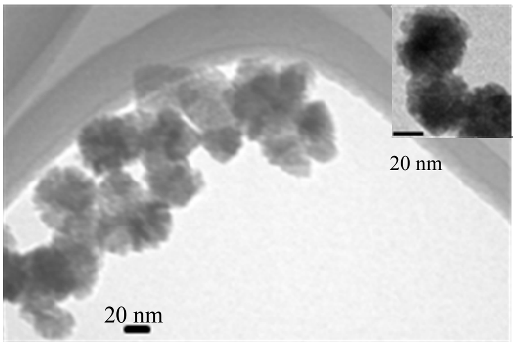

Figure S1. TEM images of MNP supported aluminium isopropoxide catalyst.

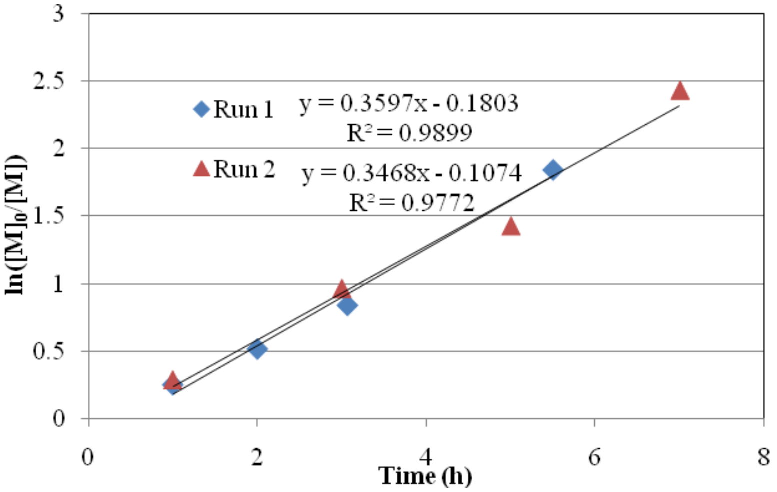

Figure S2. ln($[M]_0$/[M]) vs time for ROP of ε-caprolactone with fresh MNP supported aluminum isopropoxide. Reaction conditions: toluene, T= 100°C, $[Al]_0$=1.77 mol%, [Monomer]/[^{i}PrOH]=22. The apparent rate constant k_{app} = 0.360 h^{-1} was calculated by plotting –ln(1-conv.) vs time. A second run with *fresh* catalyst gave $k_{app} = 0.347\ h^{-1}$, yielding an average number of $0.35\ h^{-1}$. This experiment demonstrates the reproducibility of the polymerization.

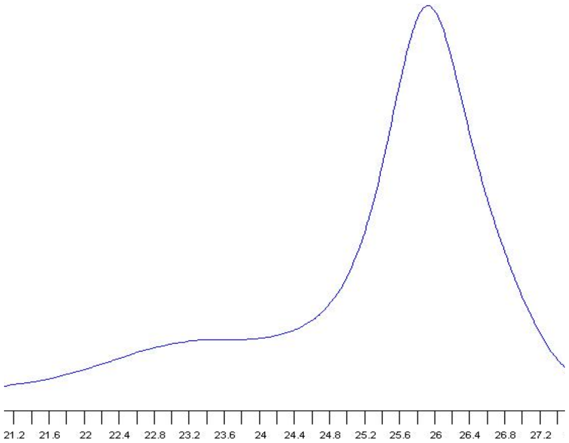

Figure S3. GPC curves of poly(caprolactone) produced by fresh MNP-supported aluminium isopropoxide catalyst, showing the small amount of high molecular weight polymer along with the large primary polymer peak. Changing GPC columns allowed better separation between peaks.

References

1. A. J. Rondinone, A. C. S. Samia and Z. J. Zhang, *Journal of Physical Chemistry B*, 1999, **103**, 6876-6880.