

Supplementary Information

The catalytic performance of metal complexes immobilized on SBA-15 in the ring opening polymerization of ϵ -caprolactone with different metals (Ti, Al, Zn and Mg) and immobilization procedures

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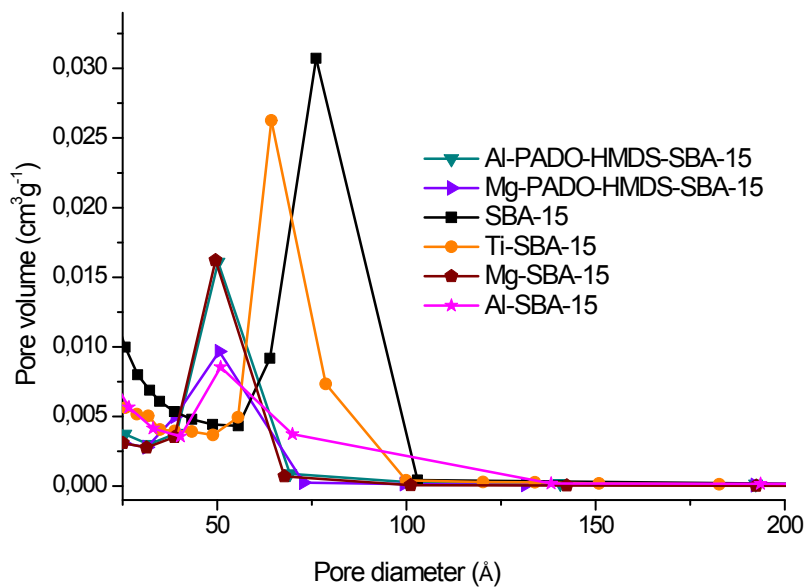


Fig. S1. Pore Size distribution of SBA-15 and hybrid materials determined by BJH method.

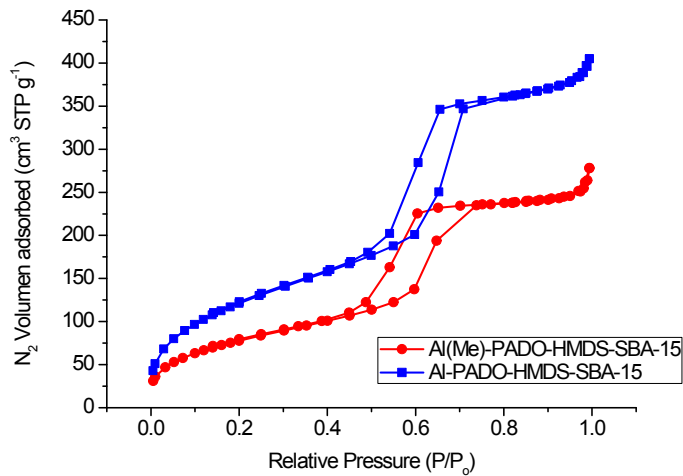


Fig. S2. Nitrogen adsorption-desorption isotherms profiles of Al-PADO-HMDS-SBA-15 and Al(Me)-PADO-HMDS-SBA-15

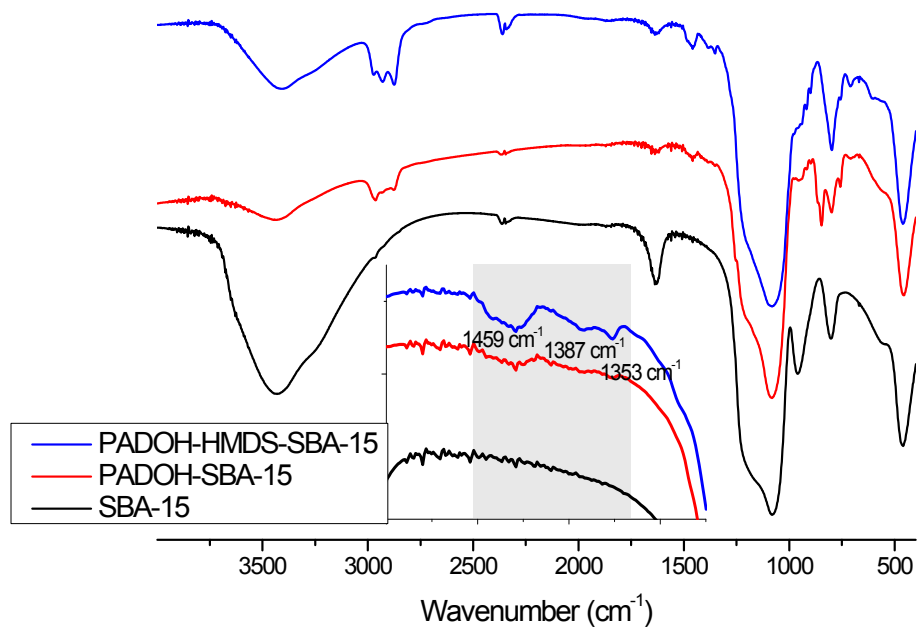


Fig. S3. FTIR spectra of SBA-15, PADOH-SBA-15 and PADOH-HMDS-SBA-15

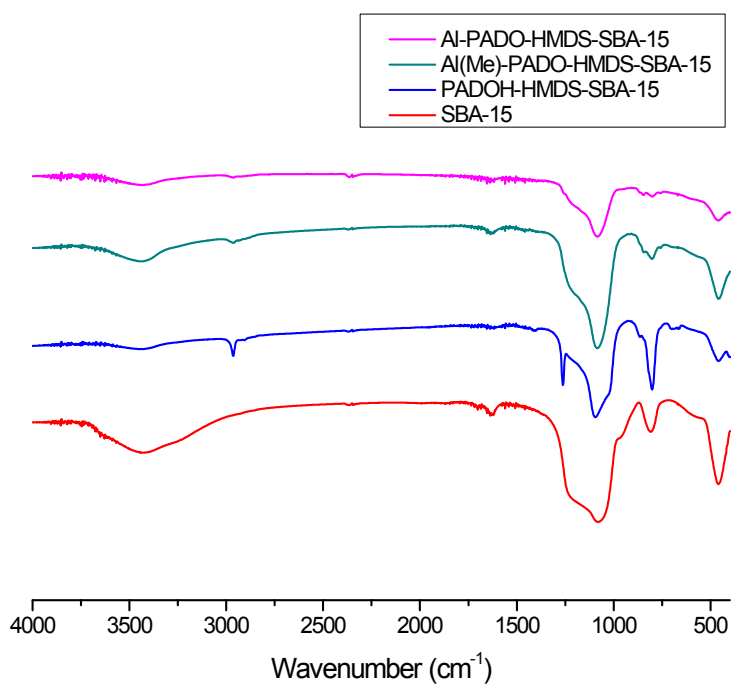


Fig. S4. FT-IR spectra of SBA-15, PADOH-HMDS-SBA-15; Al-PADO-HMDS-SBA-15 and Al(Me)-PADO-HMDS-SBA-15

Synthesis and Characterization of homogeneous metal complexes

Synthesis of complex Ti-PADO

Ti(OⁱPr)₄ (0.95 mL, 3.19 mmol) was added to a CH₂Cl₂ solution (25 mL) of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane] 65% in ethanol (1.62 mL, 3.19 mmol). The resulting mixture was stirred at room temperature for 4 h. The solvent and the remaining isopropyl and ethyl alcohol were removed under vacuum. The resulting product was isolated as colourless oil after being rinsed twice with cold pentane. ¹H NMR (400 MHz, CDCl₃) δ = 0.62 (t, 2H, Si-CH₂-CH₂-CH₂-N); 1.12 (t, 9H, OCH₂CH₃); 1.17 (d, 12H, OCH(CH₃)₃); 1.60 (m, 2H, Si-CH₂-CH₂-CH₂-N); 2.52 (t, 2H, Si-CH₂-CH₂-CH₂-N); 3.63 (q, 6H, OCH₂CH₃); 4.34 (bs, 3H, OCH(CH₃)₃); 2.67 and 3.50-3.68 (m, 4H, N-((CH₂)-OH)₂). ¹³C{H} NMR (400 MHz, C₆D₆) δ = 8.7 (Si-CH₂-CH₂-CH₂-N); 21.8 (OCH₂CH₃); 18.9 (Si-CH₂-CH₂-CH₂-N); 26.5 (OCH(CH₃)₃), 29.7 (Si-CH₂-CH₂-CH₂-N); 51.6 (Si-CH₂-CH₂-CH₂-N); 58.7 (OCH₂CH₃); 76.5 (OCH(CH₃)₃). FT-IR (KBr disk, cm⁻¹) 710 (m), 801 (s), 935 (s), 955 (w), 1106 (s), 1281 (m), 1378 (m), 1464 (m), 2876 (m), 2924 (8m), 2972 (m).

Synthesis of complex Zn-PADO

ZnMe₂ 2M in toluene (0.98 mL, 3.03 mmol) was added to a toluene solution (25 mL) of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane] 65% in ethanol (1.00 mL, 3.03 mmol) at 0 °C. The reaction evolves with methane elimination as temperature increases to room temperature. The solution was stirred for 4 h, afterwards the solvent was removed in vacuo, and the resulting solid washed with hexane (2×10 mL) to give complex **Zn-PADO** as a white solid. Yield 88 %. ¹H NMR (400 MHz, CDCl₃) δ = 0.66 (t, 2H, Si-CH₂-CH₂-CH₂-N); 1.15 (t, 9H, OCH₂CH₃); 1.64 (m, 2H, Si-CH₂-CH₂-CH₂-N); 2.55 (t, 2H, Si-CH₂-CH₂-CH₂-N); 3.63 (q, 6H, OCH₂CH₃); 2.71 and 3.75-3.81 (m, 4H, N-((CH₂)-OH)₂). ¹³C{H} NMR (400 MHz, C₆D₆) δ = 8.9 (Si-CH₂-CH₂-CH₂-N); 21.1 (OCH₂CH₃); 18.9 (Si-CH₂-CH₂-CH₂-N); 29.7 (Si-CH₂-CH₂-CH₂-N); 51.2 (Si-CH₂-CH₂-CH₂-N); 58.8 (OCH₂CH₃); 203.4 (N-((CH₂)-O)₂). FT-IR (KBr disk, cm⁻¹) 710 (m), 796 (s), 935 (s), 1106 (s), 1266 (m), 1379 (m), 1464 (m), 2876 (m), 2924 (m), 2972 (m).

Synthesis of complex Al-PADO

AlMe₃ 2M in toluene (1.05 mL, 2.1 mmol) or a toluene solution of Al(OⁱPr)₃ (1.00 g, 4.9 mmol) was added to a toluene solution (25 mL) of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane] 65% in ethanol stoichiometrically at 0 °C. The so obtained solutions were stirred for 4 h, afterwards the solvent and the by-products obtained were removed in vacuo, and the resulting solid washed with hexane (2×10 mL) to give complex **Al-PADO** as a white solid. Yield 95 and 88 %, respectively. ¹H NMR (400 MHz, CDCl₃) δ = 0.63 (t, 2H, Si-CH₂-CH₂-CH₂-N); 1.17 (t, 9H, OCH₂CH₃); 1.22 (bs, 3H, Al-OCH₂CH₃), 1.61 (m, 2H, Si-CH₂-CH₂-CH₂-N); 2.54 (t, 2H, Si-CH₂-CH₂-CH₂-N); 3.63 (q, 6H, OCH₂CH₃); 2.71 and 2.60-3.77 (m, 4H, N-((CH₂)-OH)₂). ¹³C{H} NMR (400 MHz, C₆D₆) δ = 9.3 (Si-CH₂-CH₂-CH₂-N); 21.4 (OCH₂CH₃); 19.3 (Si-CH₂-CH₂-CH₂-N); 51.5 (Si-CH₂-CH₂-CH₂-N); 52.4 (Si-CH₂-

CH₂-CH₂-N); 52.6 (OCH₂CH₃); 199.34 (N-((CH₂)-O)₂). FT-IR (KBr disk, cm⁻¹) 724 (s), 748 (m), 785 (s), 903 (s), 942 (s), 991 (m), 1103 (s), 1278 (m), 1383 (m), 1452 (m), 2870 (m), 2926 (m), 2970 (m).

Synthesis of complex Mg-PADO

Mg(ⁿBu)₂, 1 M in heptane (3 mL, 3.03 mmol) or a toluene solution of Al(OPrⁱ)₃ (1,00 g, 4,9 mmol) was added to a toluene solution (25 mL) of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane] 65% in ethanol (1.00 mL, 3.03 mmol) at 0 °C. The reaction evolves with butane elimination as temperature increases to room temperature. The so obtained solutions were stirred for 4 h, afterwards the solvent and the by-products obtained were removed in vacuo, and the resulting solid washed with hexane (2×10 mL) to give complex **Mg-PADO** as a white solid. Yield 91 %. ¹H NMR (400 MHz, CDCl₃) δ = 0.66 (t, 2H, Si-CH₂-CH₂-CH₂-N); 1.16 (t, 9H, OCH₂CH₃); 1.20 (bs, 3H, Al-OCH₂CH₃), 1.64 (m, 2H, Si-CH₂-CH₂-CH₂-N); 2.56 (t, 2H, Si-CH₂-CH₂-CH₂-N); 3.67 (q, 6H, OCH₂CH₃); 2.73 and 2.56-3.80 (m, 4H, N-((CH₂)-OH)₂). ¹³C{H} NMR (400 MHz, C₆D₆) δ = 9.8 (Si-CH₂-CH₂-CH₂-N); 22.1 (OCH₂CH₃); 19.9 (Si-CH₂-CH₂-CH₂-N); 54.3 (Si-CH₂-CH₂-CH₂-N); 55.1 (Si-CH₂-CH₂-CH₂-N); 53.8 (OCH₂CH₃); 201.6 (N-((CH₂)-O)₂). FT-IR (KBr disk, cm⁻¹) 751 (m), 802 (s), 1022 (s), 1100 (s), 1263 (m), 1387 (m), 1460 (m), 2867 (m), 2923 (m), 2968 (m).

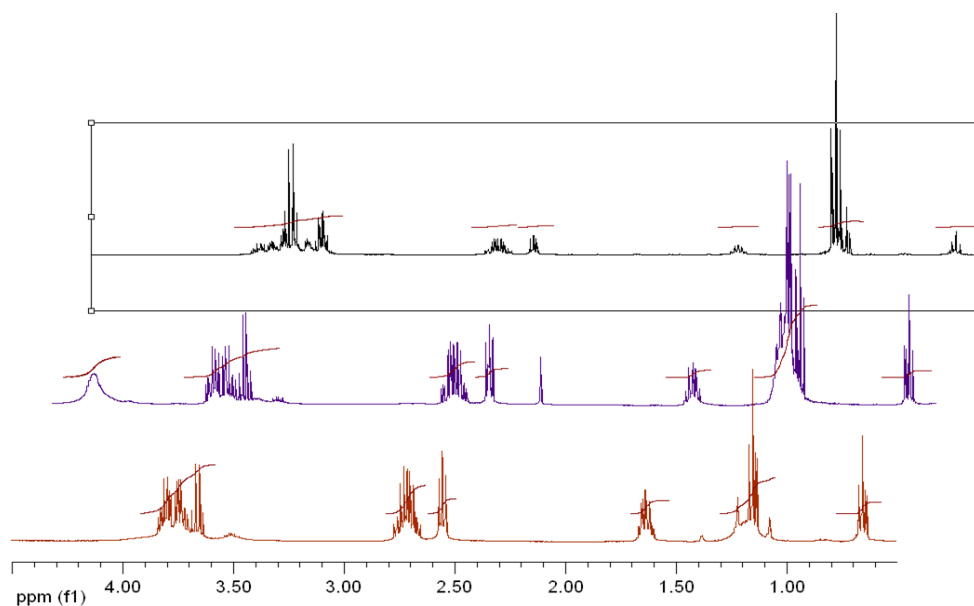


Fig. S5. ^1H NMR spectra in CDCl_3 (From up to down) of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane] in EtOH, titanium and zinc complexes with the acronyms Ti-PADO and Zn-PADO, respectively.

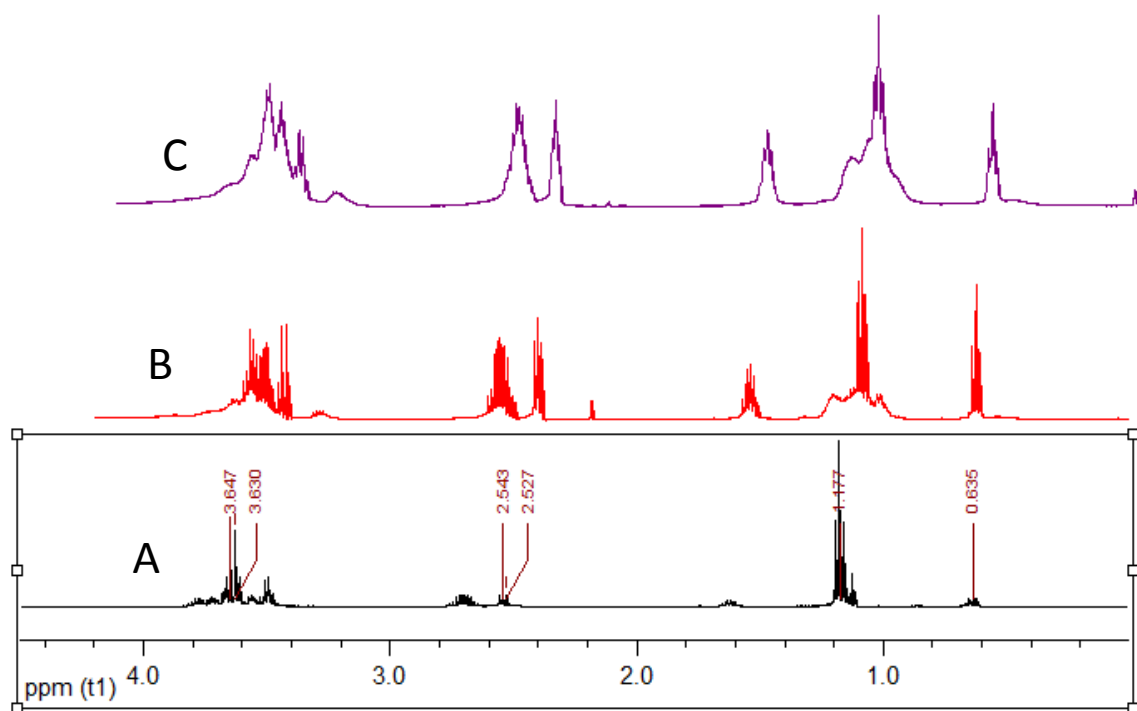


Fig. S6. ^1H NMR spectra in CDCl_3 (From down to up) of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane] in EtOH, aluminum complex synthesized by reaction with $\text{Al}(\text{O}^i\text{Pr})_3$ or AlMe_3 , with the acronym Al-PADO.

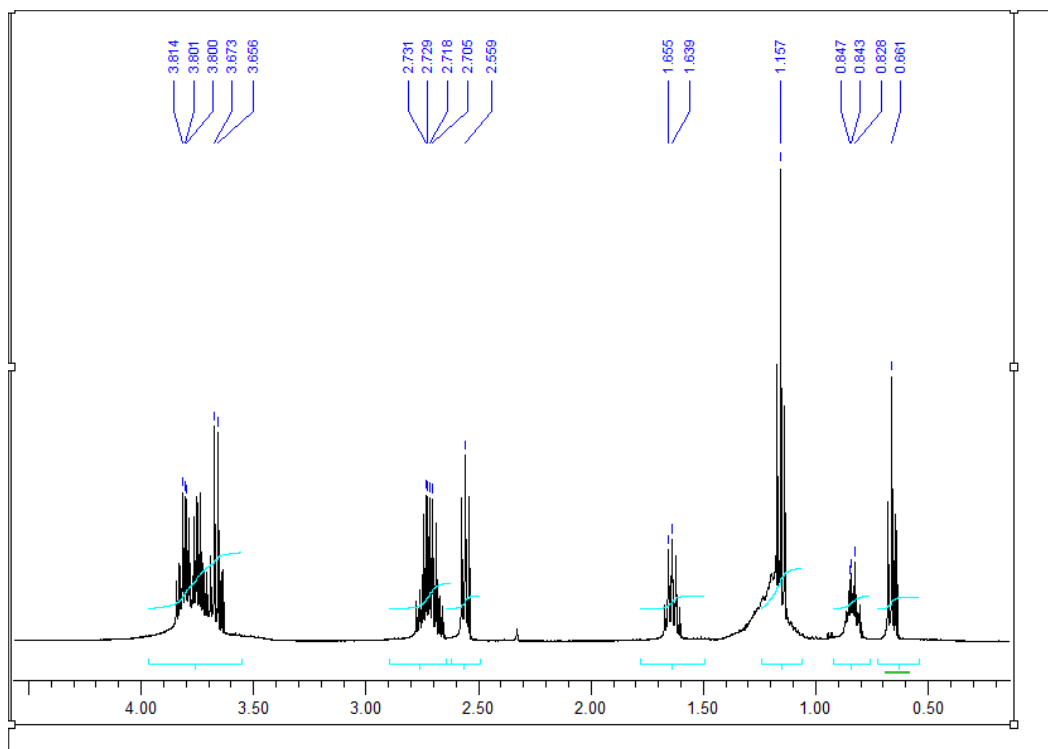


Fig. S7. ¹H NMR spectra in CDCl₃ of magnesium complex synthesized by reaction 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane] in EtOH with Mg(ⁿBu)₂, with the acronym Mg-PADO.

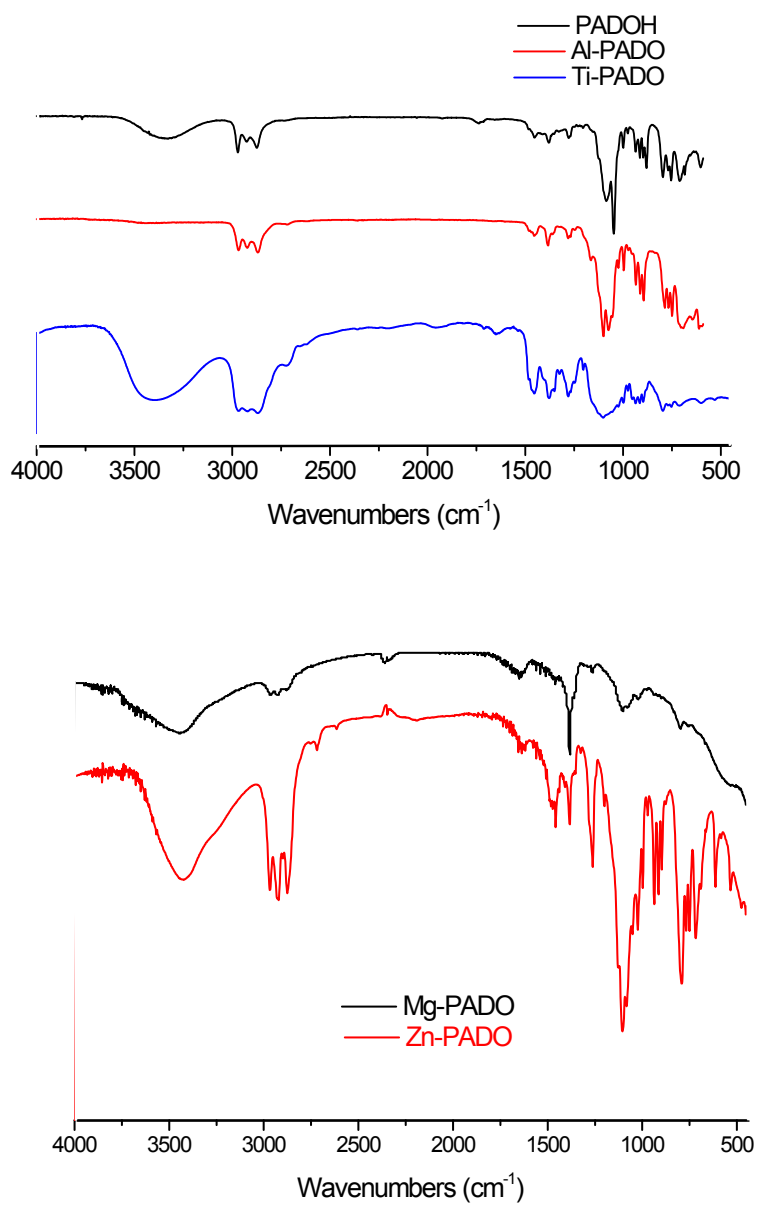


Fig. S8. FT-IR spectra of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane (PADOH) in EtOH, Ti-PADO, Al-PADO, Mg-PADO and Zn-PADO

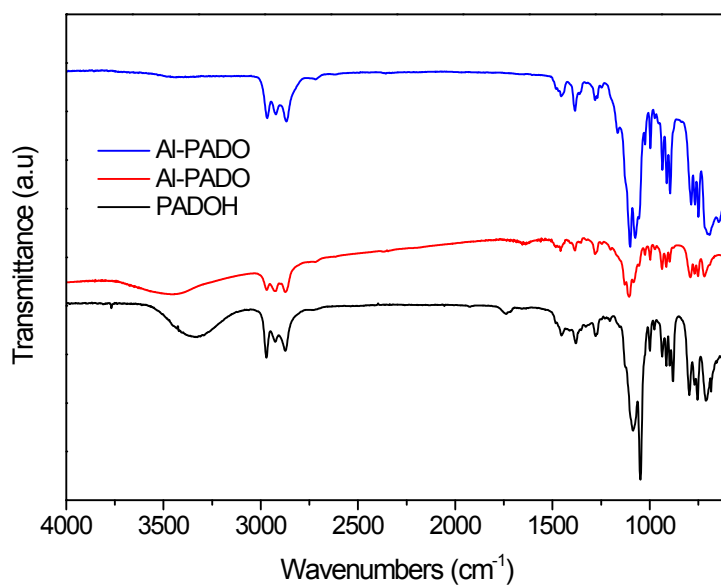


Fig. S9. FT-IR spectra of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane (PADOH) in EtOH, aluminum complex synthesized by reaction with Al(OⁱPr)₃ or AlMe₃, with the acronym Al-PADO.

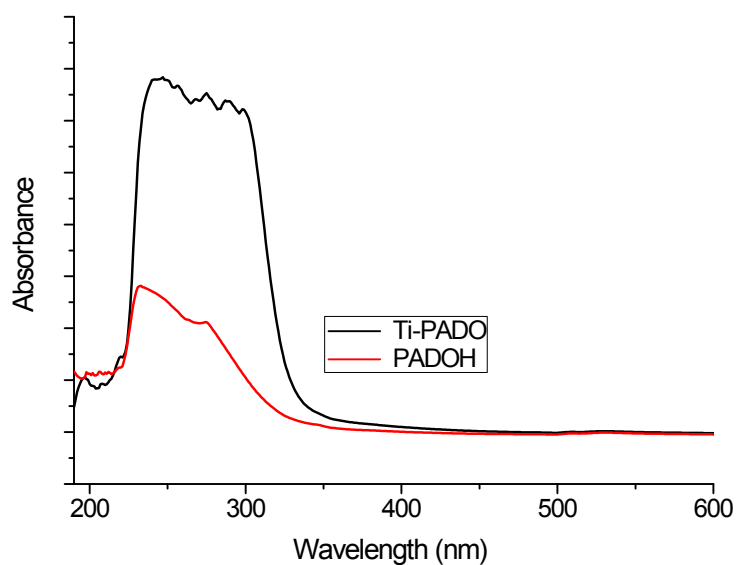


Fig. S10. UV-Vis spectra of 3-[Bis(2-hydroxyethyl)amino]propyl-triethoxysilane (PADOH) and Ti-PADO complex in CH₂Cl₂.

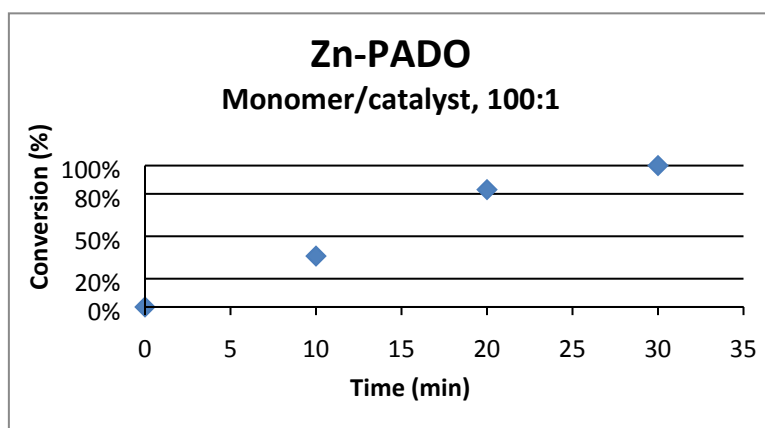


Fig. S11. Plot of conversion as a function of reaction time in ϵ -caprolactone polymerization initiated with Zn-PADO complex, at room temperature, with $(M_0/I_0) = 100$.

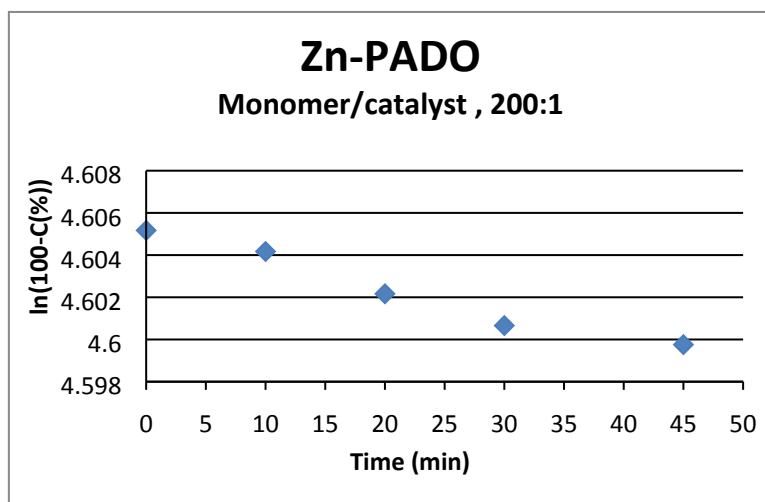


Fig. S12. Plot of $\ln(100-C(\%))$ as a function of time in ϵ -caprolactone polymerization initiated with Zn-PADO complexes at rt, with $[M_0/I_0] = 200$. C (%) corresponds to the degree of conversion in percent.

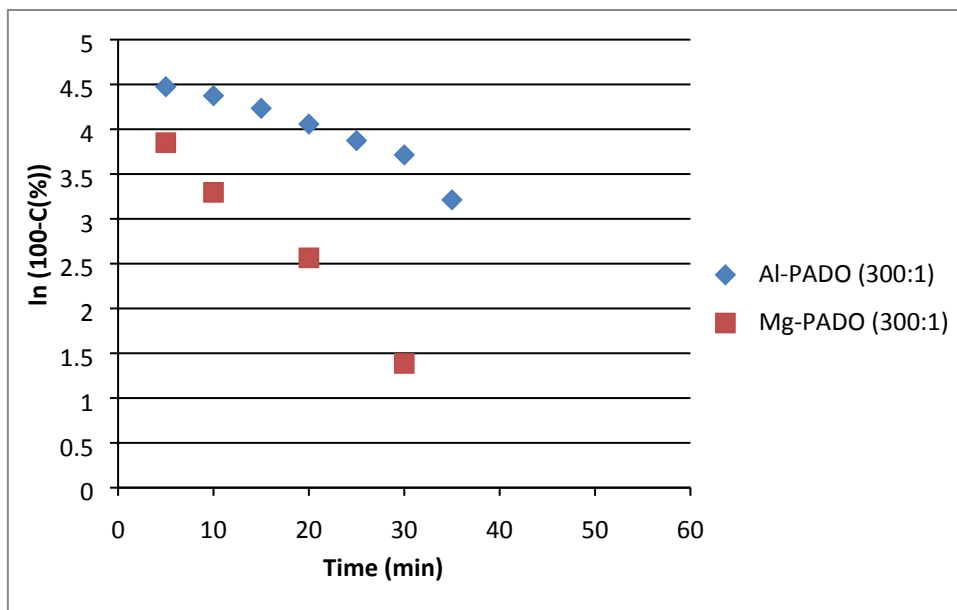


Fig. S13. Plot of $\ln(100-C(\%))$ as a function of time in ϵ -caprolactone polymerization initiated with Zn and Al-PADO complexes at rt, with $[M_0/I_0] = 300$. C (%) corresponds to the degree of conversion in percent.

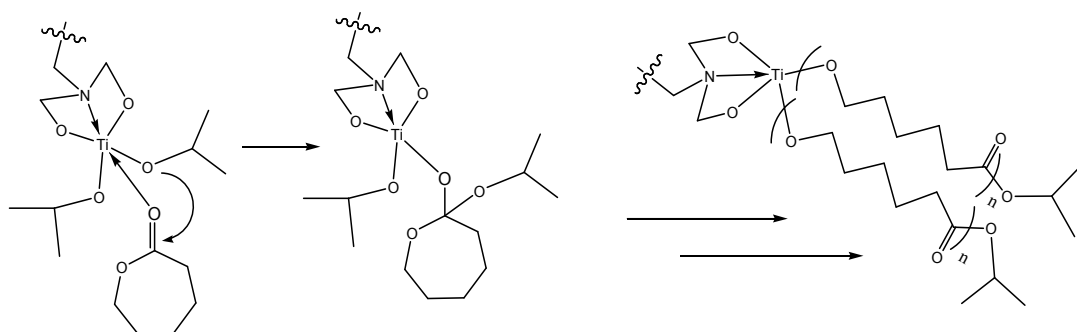
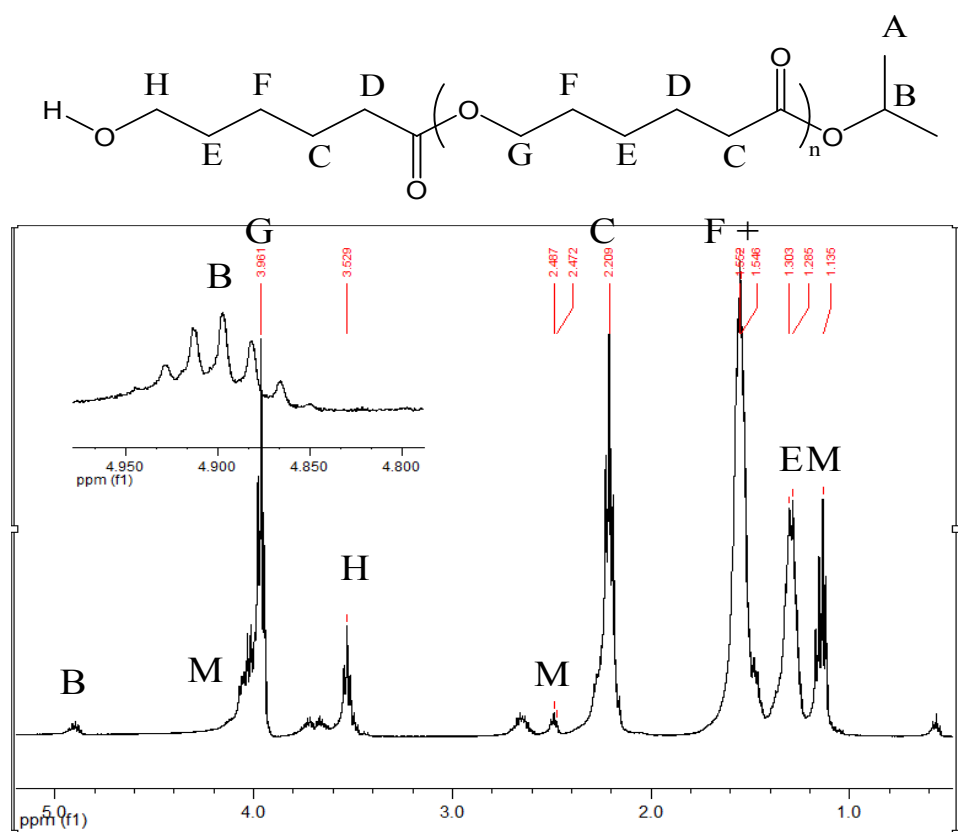


Fig. S14. ¹H NMR spectrum (measured in CDCl₃, 400 MHz) of the polymer isolated from the polymerization of ε-caprolactone initiated with Ti-PADO, (M_0/I_0) = 100, at rt by first dissolving initiator in dry CH₂Cl₂ and stopping the reaction before complete polymerization. Proposed coordination-insertion mechanism.

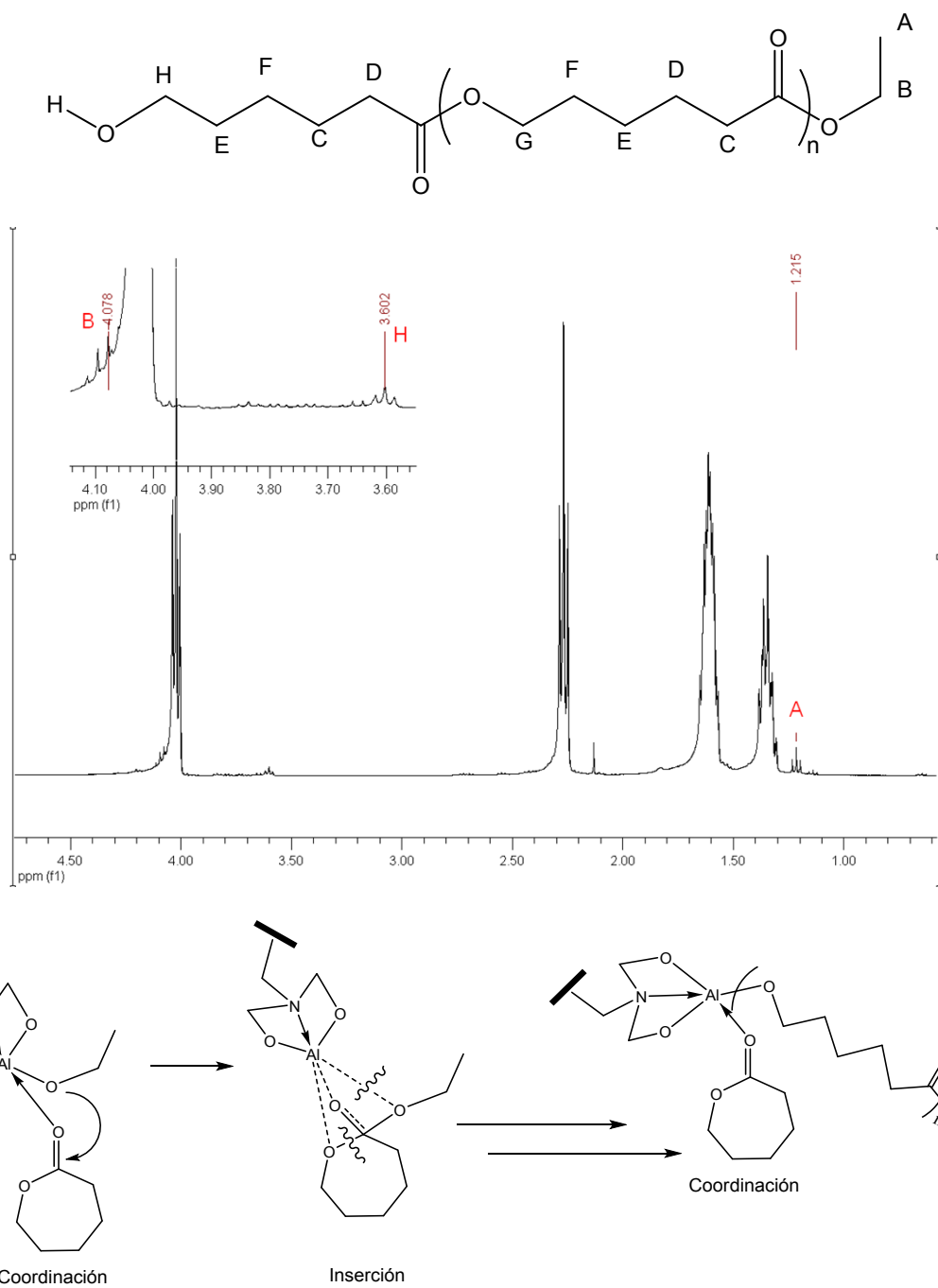


Fig. S15. ^1H NMR spectrum (measured in CDCl_3 , 400 MHz) of the polymer isolated from the polymerization of ϵ -caprolactone initiated with Al-PADO (M_0/I_0) 100) at rt by first dissolving initiator in dry CH_2Cl_2 and stopping the reaction before complete polymerization. Proposed coordination insertion mechanism.

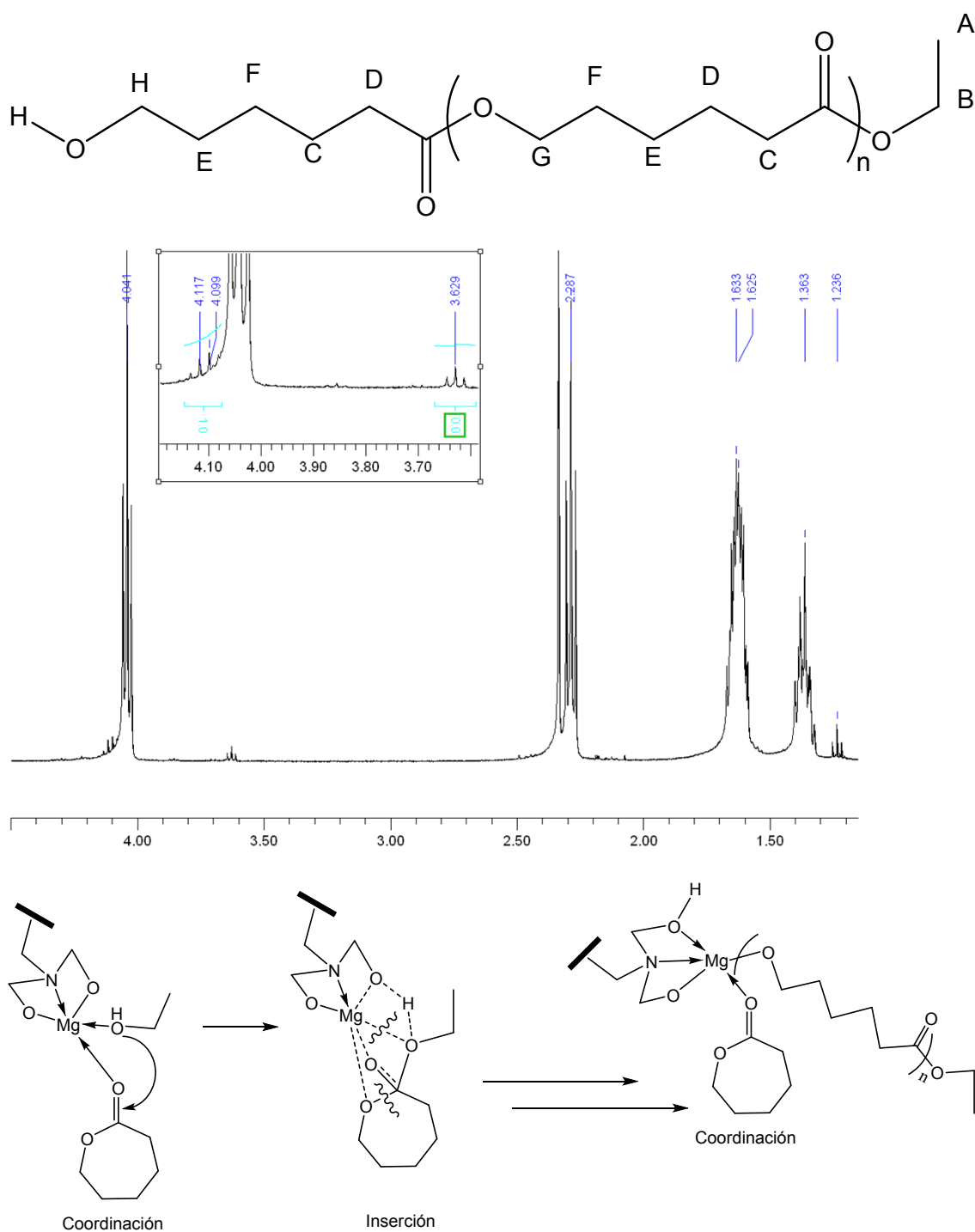


Fig. S16. ¹H NMR spectrum (measured in CDCl₃, 400 MHz) of the polymer isolated from the polymerization of ϵ -caprolactone initiated with Mg-PADO (M_0/I_0) 100) at rt. Proposed coordination insertion mechanism.

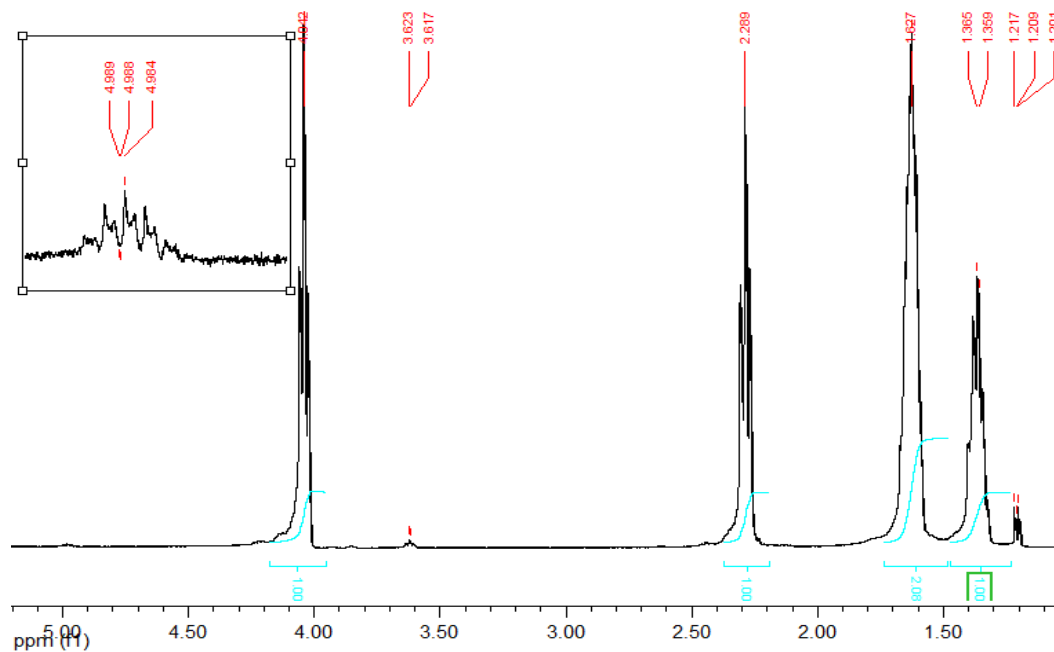


Fig. S17. ^1H NMR spectrum (measured in CDCl_3 , 400 MHz) of the polymer isolated from the polymerization of ϵ -caprolactone initiated with Ti-SBA-15.

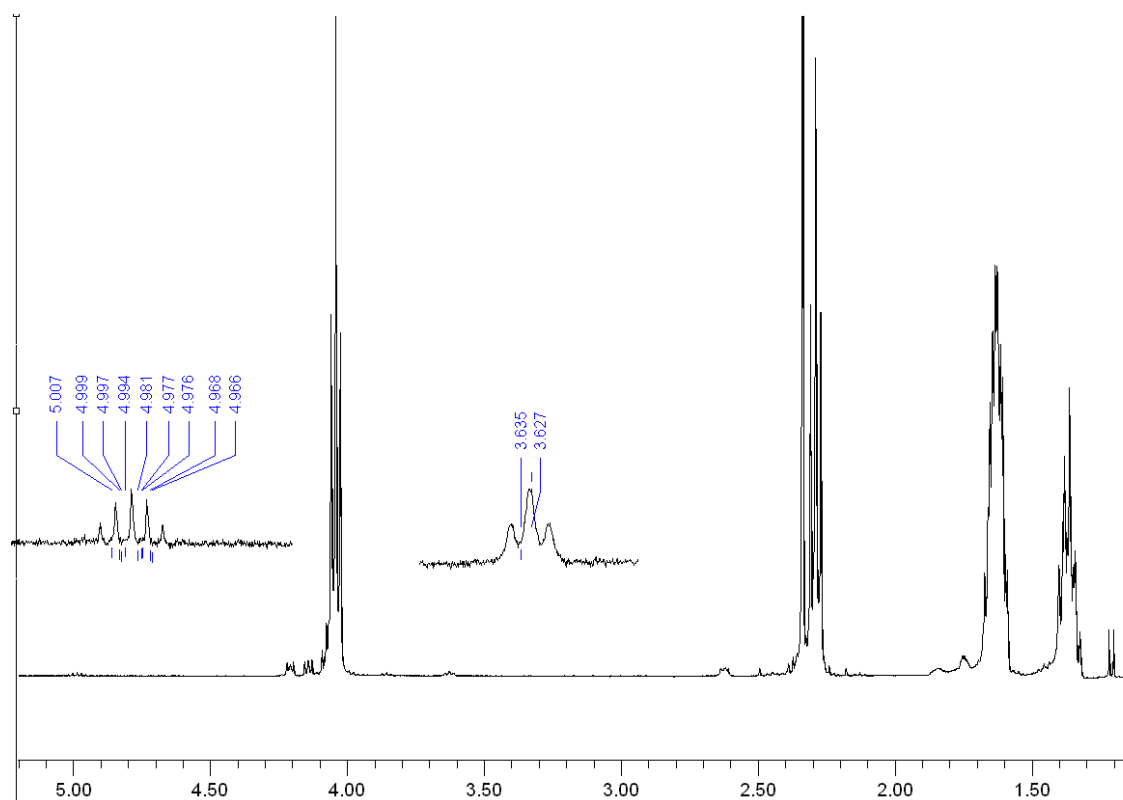


Fig. S18. ^1H NMR spectrum (measured in CDCl_3 , 400 MHz) of the polymer isolated from the polymerization of ϵ -caprolactone initiated with Al-SBA-15.

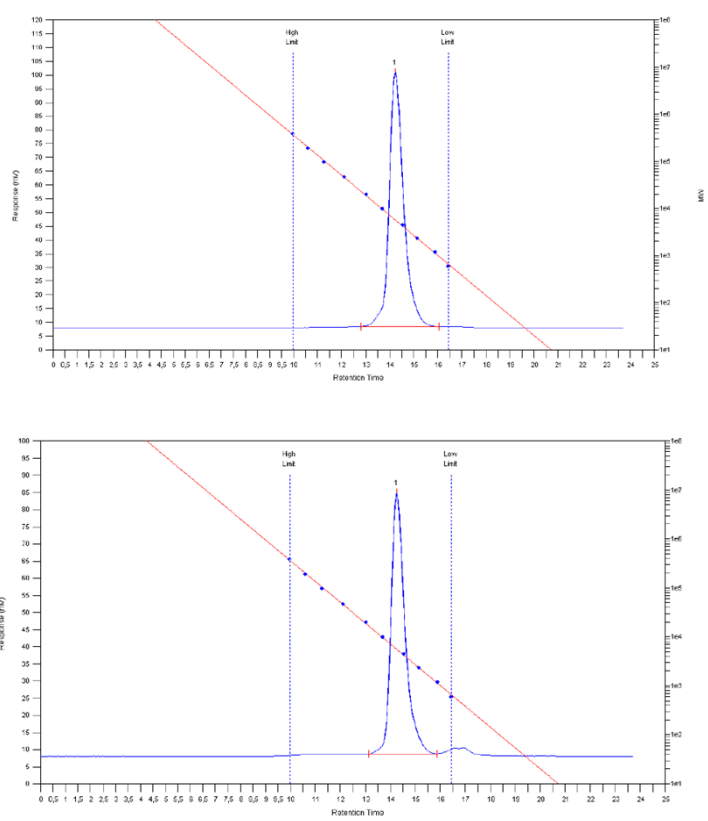


Fig. S19. Gel permeation chromatogram of PCL initiated by a) Zn-PADO-HMDS-SBA-15 and c) Zn-SBA-15.

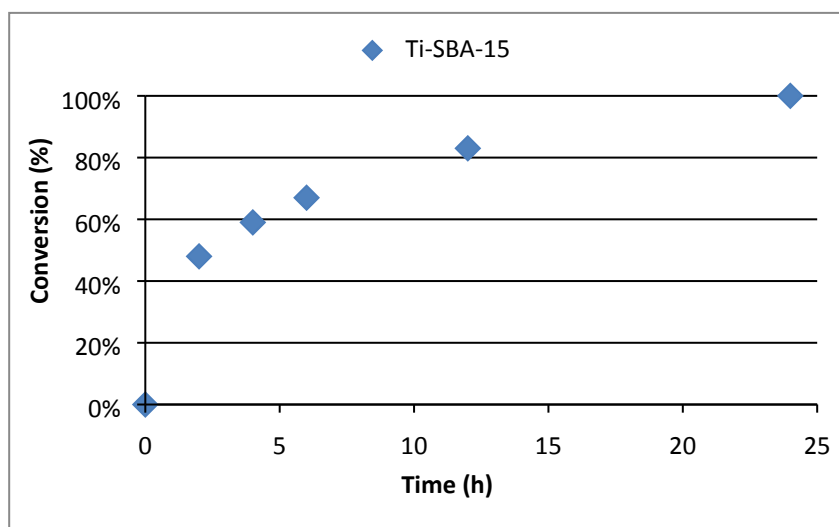


Fig. S20. Plot of conversion as a function of reaction time in ϵ -caprolactone polymerization initiated with Ti-SBA-15 material, at 80°C, with $(M_0/I_0) = 100$.

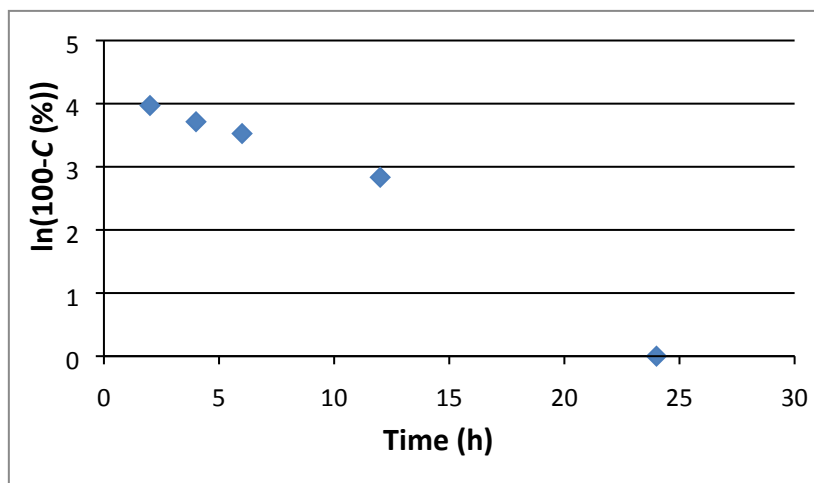


Fig. S21. Plot of $\ln(100-C(\%))$ as a function of time in ϵ -caprolactone polymerization initiated with Ti-SBA-15 material, at 80 °C, with $(M_0/I_0) = 100$. C (%) corresponds to the degree of conversion in percent.

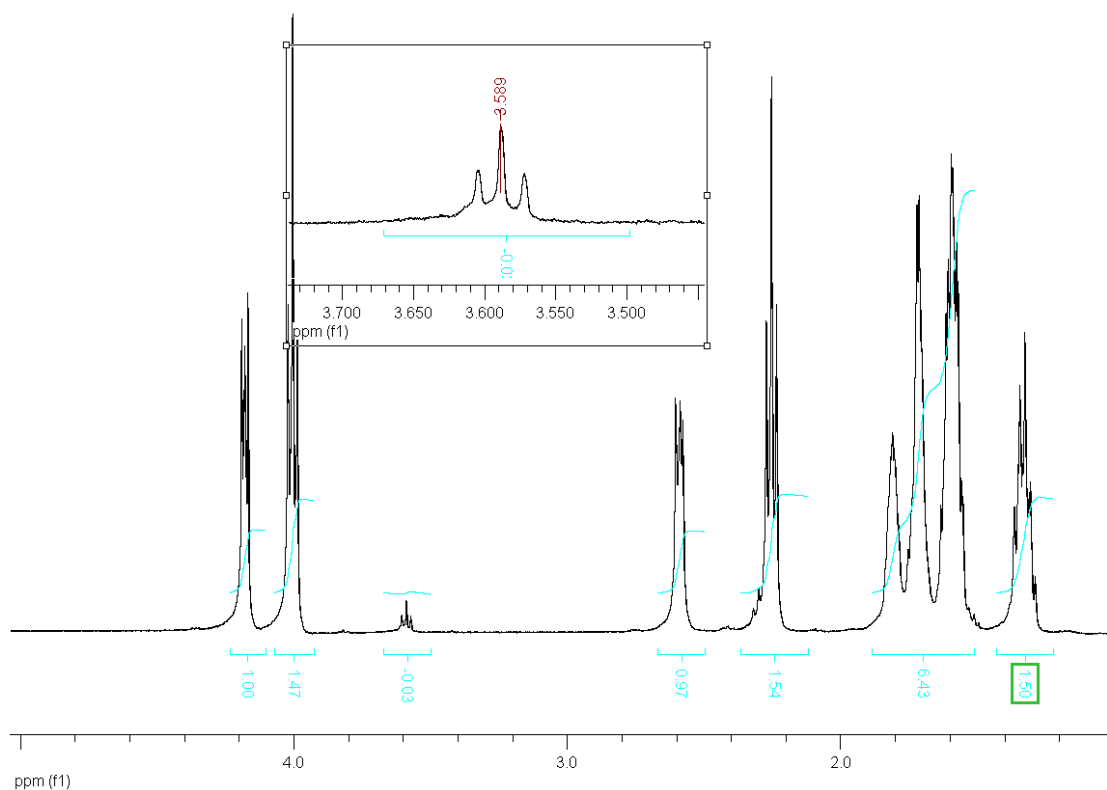


Fig. S22. ^1H NMR spectrum (measured in CDCl_3 , 400 MHz) of the polymer isolated from the polymerization of ϵ -caprolactone initiated with Zn-PADO-HMDS-SBA-15.

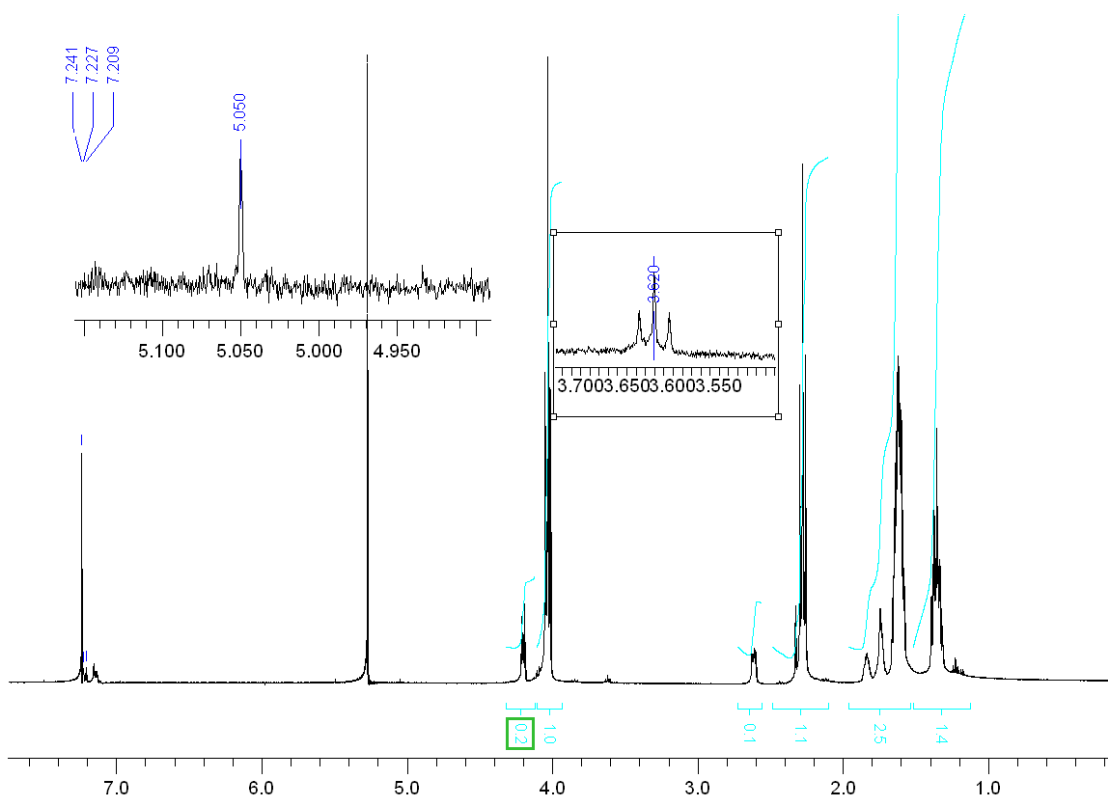


Fig. S23. ¹H NMR spectrum (measured in CDCl₃, 400 MHz) of the polymer isolated from the polymerization of ϵ -caprolactone initiated with Mg-PADO-HMDS-SBA-15 and benzylic alcohol.