

Ring-Opening Polymerization of 3,6-Dimethyl-2,5-Morpholinedione with Discrete Amino-Alkoxy-Bis(phenolate) Yttrium Initiators: Mechanistic Insights

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Supporting Information

Experimental Section.

General considerations. All manipulations were performed under a purified argon atmosphere using standard Schlenk techniques or in a glovebox. Solvents were freshly distilled from Na/K alloy (toluene, pentane, deuterated solvents), Na/benzophenone (THF), CaH₂ (hexane) or Mg (2-propanol) under argon and degassed by three freeze-thaw-vacuum cycles prior to use. Complex **2** was prepared according to published procedures.¹ Monomer **1** was synthesized from ethyl-L-lactate and L-alanine following a published procedure² and purified by recrystallization first from 2-propanol and twice from dry toluene, then sublimed under vacuum at 80 °C, and stored in the glovebox.

Instruments and measurements. NMR spectra of were recorded on Bruker AC 200, AC 300 and AM 500 spectrometers in Teflon valved J. Young NMR tubes (for reactions

¹ (a) Cai, C. X.; Toupet, L.; Lehmann, C. W.; Carpentier, J-F. *J. Organomet. Chem.* **2003**, 683, 131-136. (b) Cai, C. X.; Amgoune, A. Lehmann, C. W.; Carpentier, J-F. *Chem. Commun.* **2004**, 330-331. (c) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J-F. *Chem. Eur. J.* **2006**, 12, 169-179.

² (a) Jörres, V.; Keul, H.; Höcker, H. *Macromol. Chem. Phys.* **1998**, 199, 835-843. (b) Shirahama, H.; Tanaka, A.; Yasuda, H. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, 40, 302-316.

involving sensitive complexes). Chemical shifts are reported in ppm versus TMS and were determined by reference to the residual solvent peaks. MALDI-TOF-MS measurements were performed on a Bruker Daltonics Microflex LT spectrometer equipped with a N₂ 337 nm laser operating in the linear mode. The sample was prepared according to the thin layer method with α -cyano-4-hydroxycinnamic acid as the matrix and a 50:50 v/v solution of acetonitrile and water containing NaCl as the solvent.

Polymerization. In a typical procedure, a Schlenk flask equipped with a magnetic stir bar was charged in the glovebox with a solution of **2** in either toluene or THF, and 3 equivalents of 2-propanol were added (when used). Solid monomer **1** (**1** is sparsely soluble in THF at room temperature and not soluble in toluene below 90 °C) was then added in the appropriate ratio and the Schlenk flask was taken out of the glovebox, and placed in an oil bath at the desired polymerization temperature. After the desired reaction time, volatiles were removed under vacuum and the residue was dried till constant weight. The monomer conversion was determined by ¹H NMR of the crude reaction product in dms-*d*₆ by integration of the OCH-Me resonances of the monomer (δ 5.10 ppm) and the polymer (δ 4.96 ppm).

Figure S1. MALDI-TOF-MS spectrum of the polymer recovered from the ROP of **1** with **3** as the initiator (Run 6, Table 1: $[1]/[Y] = 100$, in toluene at 60 °C, 48h).

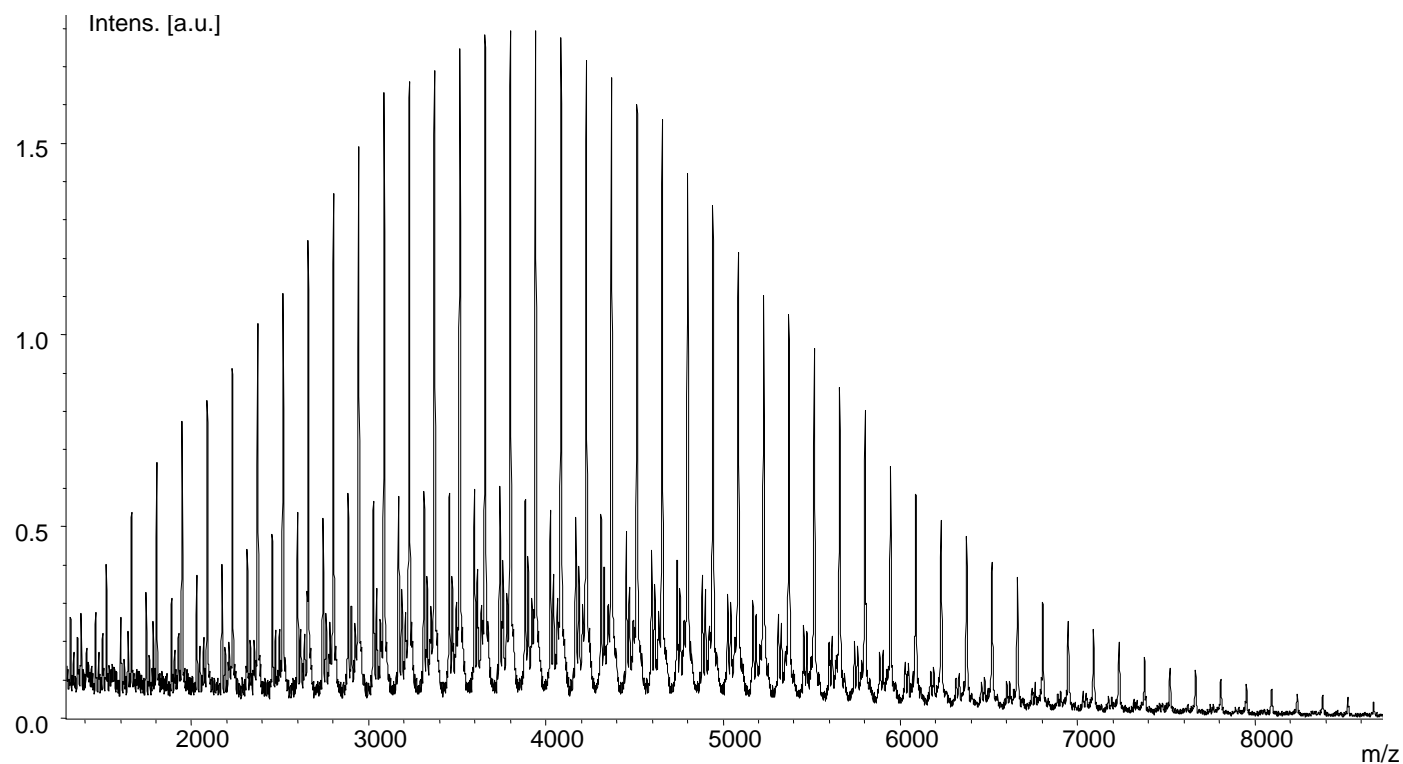


Figure S2. Detail of the MALDI-TOF-MS spectrum of the polymer recovered from the ROP of **1** with **2** as the initiator (Run 2, Table 1: $[1]/[Y] = 25$, in toluene at 60 °C, 24h)

