Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

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PGSE studies of complex 2. The PGSE measurement of complex **2** (4 mM) was carried out in a $CDCl_3$ solution. The diffusion coefficient was obtained from the PGSE NMR studies and the hydrodynamic radii (r_H) was calculated via the Stokes-Einstein equation (Eq 1, where η = viscosity of the solution).

$$D = \frac{kT}{6\pi\eta r_H} \qquad (1)$$

The viscosity is assumed the same as pure solvent due to the low concentration of complex **2**. The measured average diffusion coefficient is 5.5(5) x 10^{-10} m^2s^{-1} (Figure S1), and corresponding hydrodynamic radii is 6.9(5) Å. The molecular size in solid state also has been calculated according to crystal data of complex **2**. If assuming the molecule is spherical, the radius is 6.78 Å, which is similar with hydrodynamic radii, suggest the morphology of these complexes is the same whatever in solid state and solution.

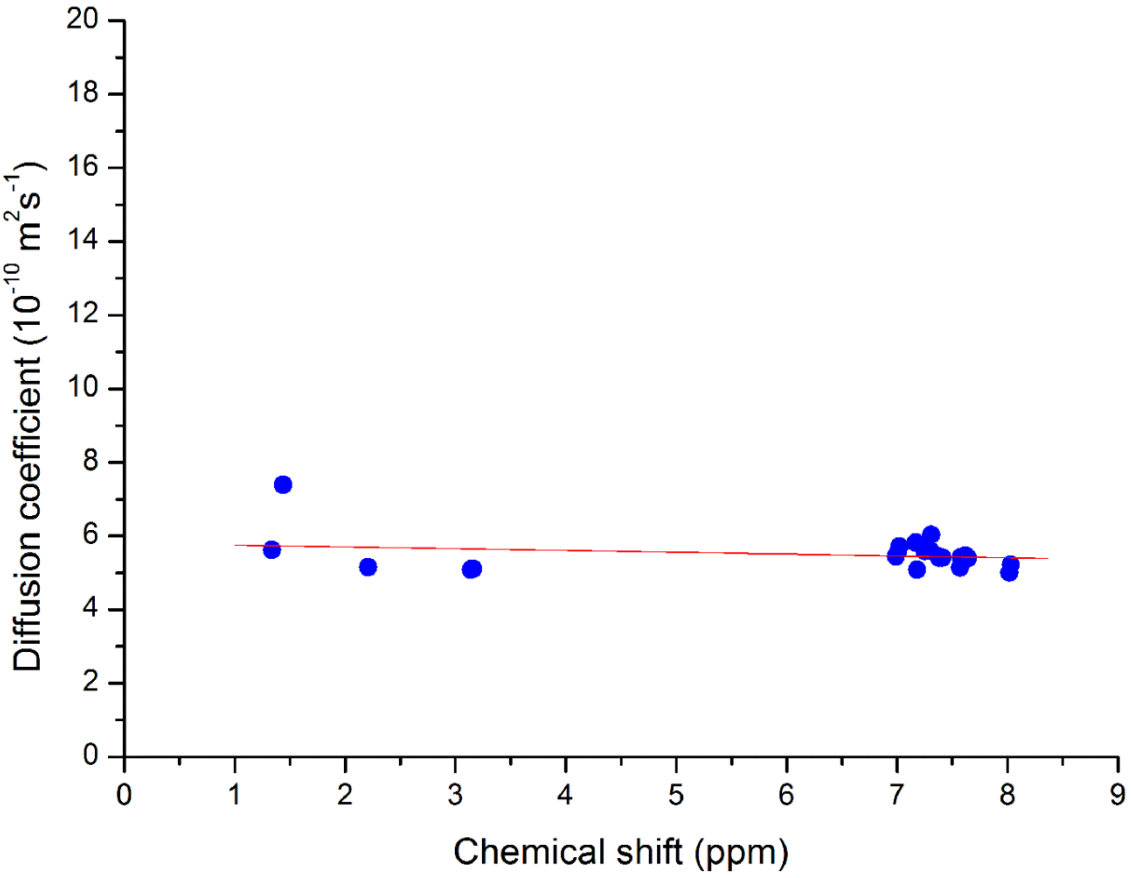

Figure S1. Measured diffusion coefficient of complex **2**

Reaction of complex 2 with BnOH. In the glove box, a mixture of complex **1** (4 mM) and benzyl alcohol (24 mM) in toluend-d_8 was sealed into a J. Young NMR tube and the reaction was monitoring via ^{1}H NMR until it reached equilibrium.

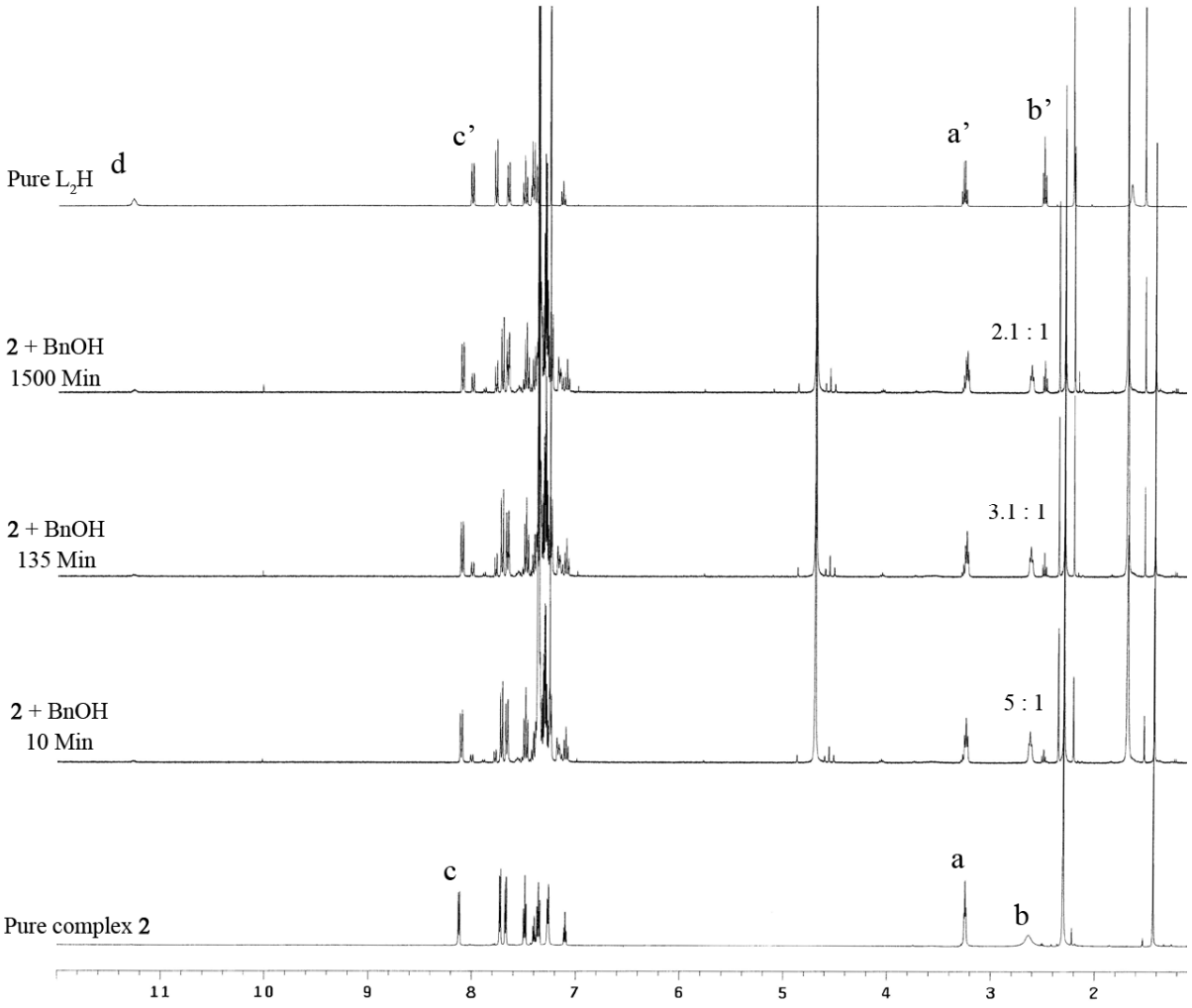

Figure S2. Time dependent NMR spectroscopic studies of reaction of complex **1** with 6 equiv of BnOH in toluene-d_8.

MALDI-TOF Mass spectrometry. MALDI-TOF mass spectrometry experiments have been performed to check the occurrence of transesterification (Figure S4). According to the mass spectrum, transesterification probably occurred during polymerization because the mass difference between peaks is 72 m/z. However, the molecular weight distribution still remains in a small range based on GPC analysis.

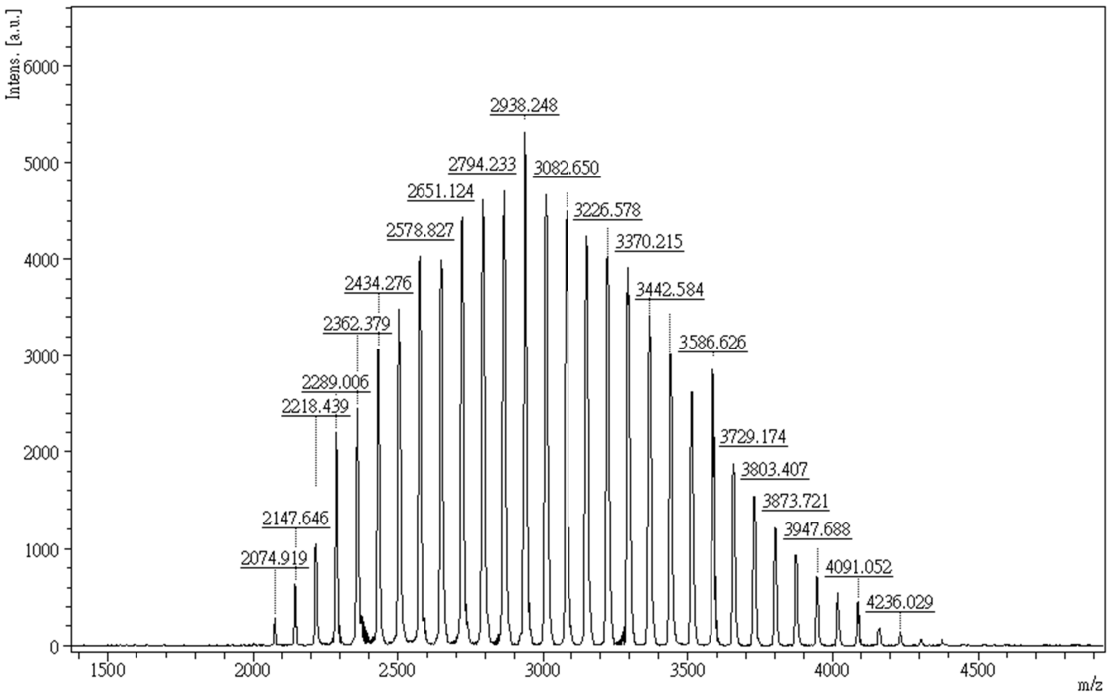

Figure S3. MALDI-TOF-MS spectrum of poly(L-LA) prepared by ROP of L-LA using **1** as an initiator.

Table S1. Crystal data and structure refinement for complexes **2** and **1a**

Identification code	**2**	**1a**
Empirical formula	$C_{54}H_{54}CaN_8O_2$	$C_{51}H_{62}Ca_2N_8O_8$
Formula weight	887.14	995.24
Temperature	114(2) K	114(3) K
Wavelength	0.7107 Å	0.7107 Å
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	$P2_1/n$
Unit cell dimensions	a = 27.021(4) Å b = 13.1464(12) Å c = 17.215(3) Å β = 121.30(2) °.	a = 10.0497(10) Å b = 16.055(3) Å c = 19.540(3) Å β = 92.412(12) °.
Volume	5225.0(13) $Å^3$	3150.0(8) $Å^3$
Z	4	4
Density (calculated)	1.344 mgm^3	1.007 mgm^3
Absorption coefficient	0.375 mm^{-1}	0.228 mm^{-1}
F(000)	2216	986
Crystal size	0.50 x 0.40 x 0.15 mm^3	0.3 x 0.2 x 0.2 mm^3
Theta range for data collection	2.74 to 25.99 °.	2.64 to 26.00 °
Index ranges	-33<=h<=32	-12<=h<=12

	-15<=k<=16 -9<=l<=21	-18<=k<=19 -24<=l<=24
Reflections collected	10664	16062
Independent reflections	5137 [R(int) = 0.0210]	6171 [R(int) = 0.1155]
Completeness to theta = 25.99°	99.90%	99.60%
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.92254	1.00000 and 0.91980
Refinement method	Full-matrix least-squares on F2	Full-matrix least-squares on F2
Data / restraints / parameters	5137 / 0 / 321	6171 / 5 / 327
Goodness-of-fit on F2	1.087	1.027
Final R indices [I>2sigma(I)]	R_1 = 0.0521, wR_2 = 0.1667	R_1 = 0.0987, wR_2 = 0.2263
R indices (all data)	R_1 = 0.0681, wR_2 = 0.1740	R_1 = 0.1743, wR_2 = 0.2538
Largest diff. peak and hole	1.691 and -0.874 $Å^3$	0.517 and -0.355 $Å^3$