

Supporting Information

For

**Electronic Influence of Ligand Substituents on the Rate of
Polymerization of ϵ -Caprolactone by Single-Site Aluminum
Alkoxide Catalysts**

Luis M. Alcazar-Roman, Brendan O'Keefe, Marc A. Hillmyer* and William B. Tolman*

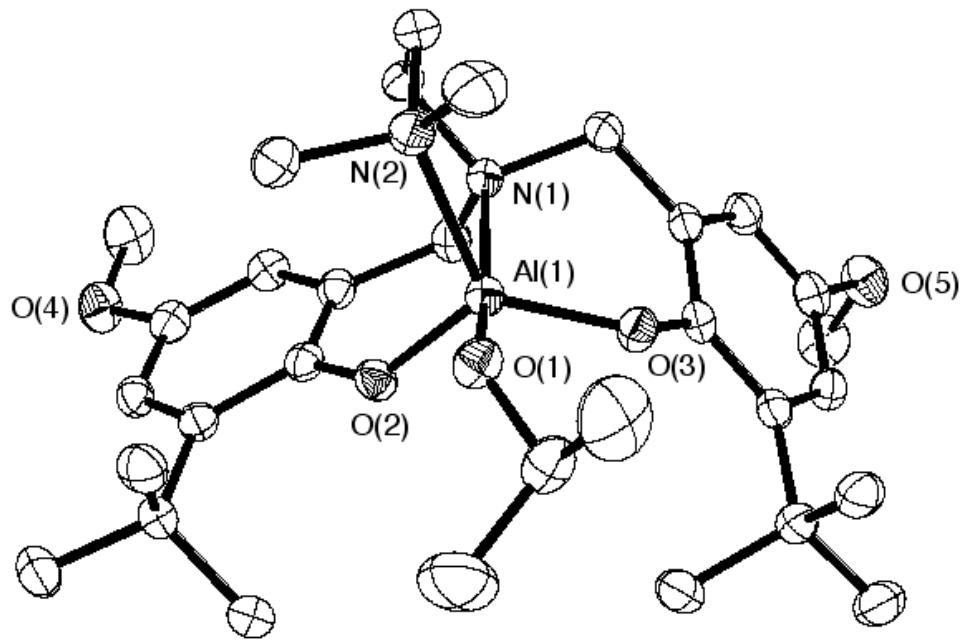


Fig. S1 X-ray structure of **3b**, with all nonhydrogen atoms shown as 50% thermal ellipsoids and hydrogen atoms omitted for clarity.

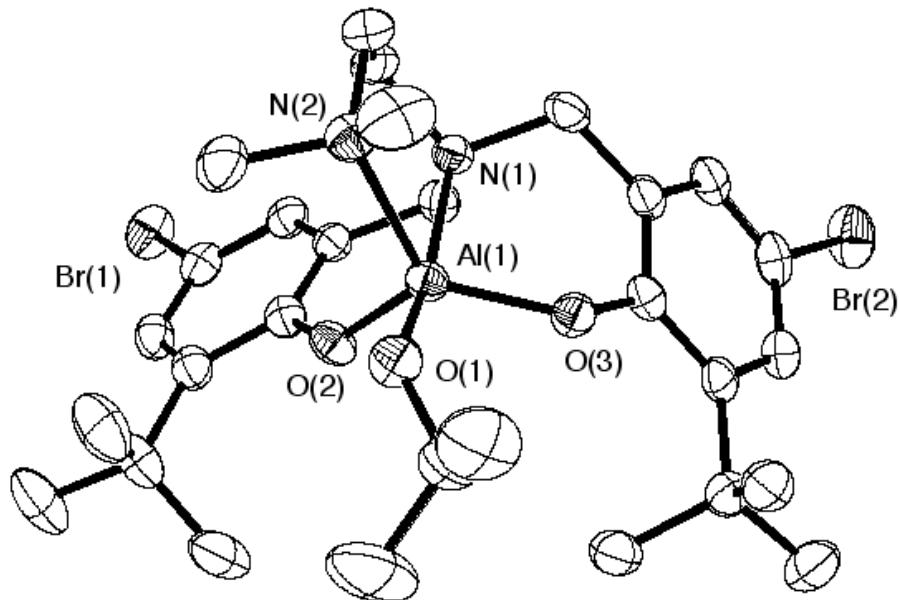


Fig. S2 X-ray structure of **3c**, with all nonhydrogen atoms shown as 50% thermal ellipsoids and hydrogen atoms omitted for clarity.

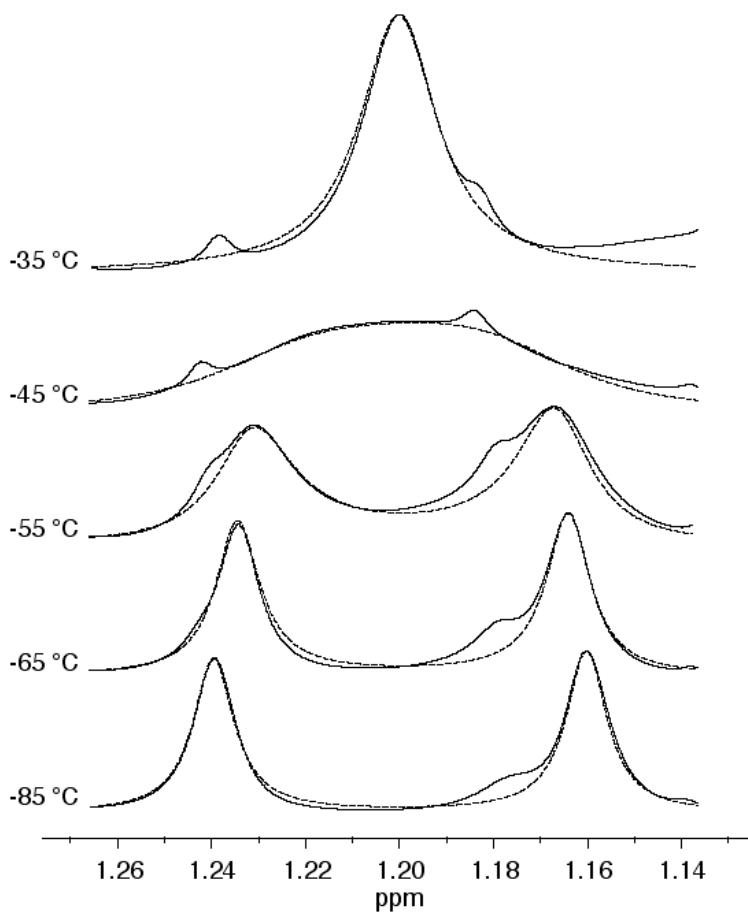


Fig. S3 Line-shape analysis of Variable Temperature ^1H NMR spectra of **3a** showing the coalescence of two tert-butyl peaks. Experimental data (—), simulation (---).

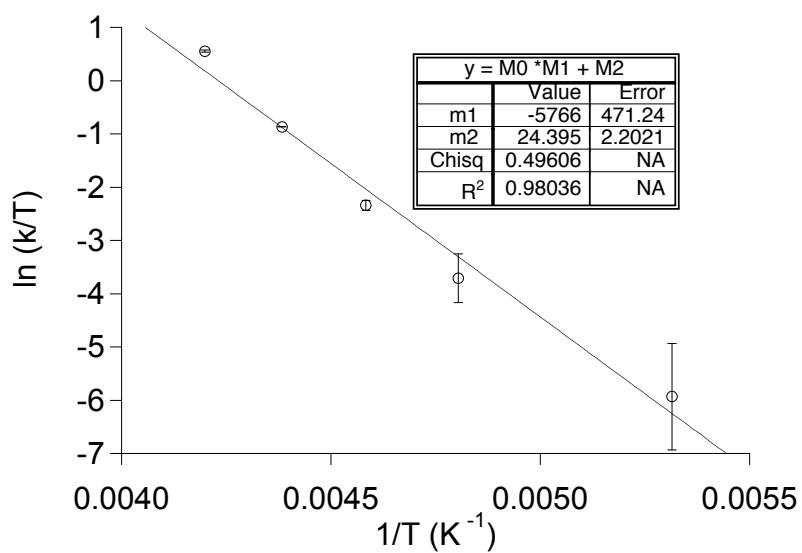


Fig. S4 Eyring plot for the temperature-dependent fluxional process for **3a**.

Table S1. Selected bond lengths (Å) and angles (deg) for (^{t-Bu,OMe}BPBA)Al(O-*i*-Pr) (**3b**)

Al(1)-O(1)	1.7441(11)	Al(1)-O(2)	1.7597(11)
Al(1)-O(3)	1.7694(11)	Al(1)-N(1)	2.1083(13)
Al(1)-N(2)	2.1818(13)		
O(1)-Al(1)-O(2)	100.84(5)	O(1)-Al(1)-O(3)	98.51(5)
O(2)-Al(1)-O(3)	117.33(5)	O(1)-Al(1)-N(2)	85.68(5)
O(3)-Al(1)-N(2)	127.83(5)	O(2)-Al(1)-N(2)	112.67(5)
O(1)-Al(1)-N(1)	164.37(5)	O(3)-Al(1)-N(1)	88.33(5)
O(2)-Al(1)-N(1)	88.26(5)	N(2)-Al(1)-N(1)	79.06(5)

Table S2 Selected bond lengths (Å) and angles (deg) for (^{t-Bu,Br}BPBA)Al(O-*i*-Pr)•1/2(C₇H₈) (**3c** • 1/2 C₇H₈)

Al(1)-O(1)	1.7408(19)	Al(1)-O(2)	1.7642(19)
Al(1)-O(3)	1.7806(19)	Al(1)-N(1)	2.153(2)
Al(1)-N(2)	2.099(2)		
O(1)-Al(1)-O(2)	99.77(9)	O(1)-Al(1)-O(3)	98.13(9)
O(2)-Al(1)-O(3)	119.15(9)	O(1)-Al(1)-N(2)	85.89(9)
O(3)-Al(1)-N(2)	127.88(9)	O(2)-Al(1)-N(2)	111.08(9)
O(1)-Al(1)-N(1)	164.74(9)	O(3)-Al(1)-N(1)	88.27(8)
O(2)-Al(1)-N(1)	89.00(8)	N(2)-Al(1)-N(1)	79.28(9)