Macromolecules

Living Ring-Opening Polymerization of Lactones by N-Heterocyclic Olefin/Al(C_6F_5)₃ Lewis Pairs: Structures of Intermediates, Kinetics, and **Mechanism**

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Supporting Information

ABSTRACT: The strong Lewis acid $Al(C_6F_5)_3$, in combination with a strong Lewis base N-heterocyclic olefin (NHO), cooperatively promotes the living ring-opening (co)polymerization of lactones, represented by δ -valerolactone $(\delta$ -VL) and ε -caprolactone (ε -CL) in this study. Medium to high molecular weight linear (co)polyesters (M_w up to 855 kg/ mol) are achieved, and most of them exhibit narrow molecular weight distributions (D as low as 1.02). Detailed investigations



into the structures of key reaction intermediates, kinetics, and polymer structures have led to a polymerization mechanism, in that initiation involves nucleophilic attack of the $Al(C_6F_5)_3$ -activated monomer by NHO to form a structurally characterized zwitterionic, tetrahedral intermediate, followed by its ring-opening to generate active zwitterionic species. In the propagation cycle, this ring-opened zwitterionic species and its homologues attack the incoming monomer activated by $Al(C_6F_5)_3$ to generate the tetrahedral intermediate, followed by the rate-determining ring-opening step to regenerate the zwitterionic species that reenters into the next chain propagation cycles. Owning to the living features and lack of transesterification side reactions possessed uniquely by this Lewis pair polymerization system, well-defined di- and triblock copolymers with narrow molecular weight distributions (D = 1.06 - 1.15) have been successfully synthesized using this method, regardless of the comonomer addition order.

■ INTRODUCTION

As a powerful polymerization technique that combines the ability to produce condensation-type polymers with fast chaingrowth polymerization kinetics, the ring-opening polymerization (ROP) of lactones has been widely utilized to produce the technologically important and environmentally friendly biodegradable and/or biocompatible aliphatic polyesters,¹ such as poly(δ -valerolactone) (PVL) and poly(ϵ -caprolactone) (PCL). Various types of catalysts have been developed for the synthesis of such polyesters, including different metal complexes exhibiting impressive catalytic performance in the ROP of cyclic esters and,^{2,3} more recently, a series of simple, often commercially available but highly effective organocatalysts as well.^{4–12} Among them, N-heterocyclic carbenes (NHCs) are the most successful and widely studied organocatalysts for the ROP of lactones. $^{13-17}$ In the absence of protic initiators, NHCs mediate the zwitterionic ring-opening polymerization (ZROP) of lactones to propagate and cyclize to release macrocycles,^{18,19} and therefore it is difficult to prepare block copolymers. However, by choosing monomers with sufficiently different reactivity, Waymouth et al. succeeded in the copolymerization of ε -CL and δ -VL with an NHC in batch conditions and obtained cyclic gradient copolymers.²⁰ On the other hand, with alcohol as initiator, both linear polyester and block copolymer could be obtained. Although the ZROP of lactones with NHCs

is rapid, polymers with high molecular weights are typically difficult to obtain; for example, the ZROP of ε -CL generates cyclic PCL with number-average molecular weights $M_{\rm n}$ ranging from 41 to 114 kg/mol.²¹

There have been intense investigations into the cooperative (or synergistic) catalytic effects of Lewis acid (LA) and Lewis base (LB) pairs, since the seminal works of Stephan and \hat{L}^{2-32} These Lewis pairs (LPs) have achieved noteworthy Erker. success in many areas of chemistry, such as activation of small molecules,^{33–50} catalytic hydrogenation,^{51–60} and new reactivity/reaction development. $^{61-74}$ In addition, Lewis pair polymerization (LPP)^{75,76} has emerged and began to generate some exciting results on polymerization catalysis. For instance, we employed aluminum LA-based, especially strongly acidic, sterically encumbered alane $Al(C_6F_5)_3$, LPs with several classes of LBs including NHCs and phosphines for the rapid addition polymerization of conjugated polar vinyl monomers or Michael acceptors such as linear methyl methacrylate, cyclic and naturally renewable α -methylene- γ -butyrolactone, and γ -methyl- α -methylene- γ -butyrolactone^{77,78} as well as monomers bearing the C=C-C=N functionality, such as 2-vinylpyridine

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and 2-isopropenyl-2-oxazoline.^{79,80} In such polymerization, the cooperativity of the LA and LB sites of Lewis pairs is essential to achieve an effective polymerization system, which was demonstrated by the borane/phosphine LPs that showed the interacting LPs, and even classical Lewis adducts, can be highly active for the polymerization.⁸¹ This was further nicely demonstrated by Rieger and co-workers, showing the high activity and high degree of control over the polymerization of Michael-type and extended Michael monomer systems by the highly interacting organoaluminum and phosphine LPs.⁸² Extending beyond the commonly employed NHC and phosphine LBs, in 2014, Lu et al. first applied NHOs in the $Al(C_6F_5)_3$ -based LPs for the addition polymerization of (meth)acrylates.^{83,84} The presence of both LA and LB has proven to be crucial for all the cases to achieve the much enhanced polymerization activity and selectivity.

The LPP method has also been extended to the ROP of lactones. In 2012, we attempted the ROP of lactones with several Al(C_6F_5)₃-based LPs and found only P^tBu₃/Al(C_6F_5)₃ LP polymerized ε -CL to PCL at room temperature but with a broad molecular weight distribution of D = 2.76 and a low monomer conversion of only 58% even after 20 h.78 In 2013, Buchmeiser and co-workers reported the bulk polymerization of ε -CL catalyzed by LPs consisting of NHCs and different Lewis acids, yielding PCL with number-average molecular weights (M_n) ranging from 9.0 kg/mol (D = 1.73) to 16.5 kg/ mol (D = 1.69).⁸⁵ Bourissou et al. employed $Zn(C_6F_5)_2$ -based LPs for the controlled ROP of lactide and ε -CL to afford welldefined cyclic polyesters, achieving PLA with M_w = 50.6 kg/mol (D = 1.5) and PCL with $M_w = 18.9$ kg/mol (D = 1.3), respectively.⁸⁶ Most recently, Dove and co-workers revealed that LPs consisting of simple LAs, such as MgI₂ and YCl₃, and LBs, such as 4-(dimethylamino)pyridine (DMAP), can be highly effective for the ROP of lactones, especially the challenging macrolactone.⁸⁷ For the ROP of ε -CL and δ -VL by this system, the highest reported molecular weights of the resulting PCL and PVL were $M_n = 28.7 \text{ kg/mol} (D = 1.33)$ by MgI₂/DMAP and $M_{\rm n} = 13.2$ kg/mol (D = 1.5) by YCl₃/ DMAP. In 2016, Li and co-workers employed the combination of $Zn(C_6F_5)_2$ and different LBs for the ROP of lactide, affording PLA with $M_{\rm p}$ ranging from 2.4 to 28.9 kg/mol.⁸⁸ As shown by the above overview, there are still several undressed key issues in the ROP by LPs. First, the degree of polymerization control needs significant improvement. Second, the molecular weight of the polyester is still limited. Third, detailed mechanistic studies of this polymerization are lacking. To this end, this contribution reports that $NHO/Al(C_6F_5)_3$ LPs promote the living/controlled ROP and copolymerization of δ -VL and ε -CL to produce medium to high molecular weight polyesters with narrow molecular weight distributions. More importantly, this LPP system enabled us to isolate key reaction intermediates and perform kinetic and mechanistic studies, thereby providing the much-needed insights into the LPP mechanism for the ROP of lactones.

EXPERIMENTAL SECTION

Materials, Reagents, and Methods. All syntheses and manipulations of air- and moisture-sensitive materials were carried out in flamed Schlenk-type glassware on a dual-manifold Schlenk line, a high-vacuum line, or an argon-filled glovebox. Toluene, benzene, diethyl ether, THF, and hexane were refluxed over sodium/potassium alloy distilled under a nitrogen atmosphere and then stored over molecular sieves 4 Å. Benzene- d_6 and CD₂Cl₂ was dried over

molecular sieves 4 Å. NMR spectra were recorded on a Varian Inova 300 (300 MHz, ¹H; 75 MHz, ¹³C; 282 MHz, ¹⁹F) or a Bruker Avance II 500 (500 MHz, ¹H; 126 MHz, ¹³C; 471 MHz, ¹⁹F) instrument at room temperature. Chemical shifts for ¹H and ¹³C spectra were referenced to internal solvent resonances and are reported as parts per million relative to SiMe₄, whereas ¹⁹F NMR spectra were referenced to external CFCl₃. ¹H and ¹³C NMR chemical shifts are reported in ppm relative to the residual solvent. Air-sensitive NMR samples were conducted in Teflon valve sealed J. Young-type NMR tubes.

Trimethylaluminum, triethylaluminum, bromopentafluorobenzene, diazabicycloundec-7-ene (DBU), 4-(dimethylamino)pyridine (DMAP), ammonium acetate, and sodium bicarbonate were purchased from J&K. 1,2-Dimethylimidazole and benzil were purchased from Titan. Iodomethane, boron trichloride (1.0 M solution in hexanes), n-BuLi (2.5 M solution in hexanes), and isobutyraldehyde were purchased from Energy Chemical. 1,3-Di-tert-butylimidazol-2-ylidene ^{Bu}NHC) was purchased from TCI. Potassium hydride (30 wt % dispersion in mineral oil) and tris(2,4,6-trimethylphenyl)phosphine (Mes₃P) were purchased from Alfa Aesar. All of the chemicals were used as received unless otherwise specified as follows. Potassium hydride was diluted with hexanes in a glovebox, then mixed, and decanted. This procedure was repeated three times, and the washed KH was finally dried under vacuum. *e*-Caprolactone (*e*-CL, J&K) and δ -valerolactone (δ -VL, Energy Chemical) were dried over CaH₂, distilled under nitrogen, and stored in a glovebox at -35 °C. Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, was prepared according to literature procedures. 89,90 Al(C₆F₅)₃, as a (toluene)_{0.5} adduct, or in its unsolvated form, was prepared by ligand exchange reactions between $B(C_6F_5)_3$ and AlMe₃ or AlEt₃ (for preparation of the unsolvated ³ (Extra caution should be exercised when handling these form). materials, especially the unsolvated $Al(C_6F_5)_3$, due to its thermal and shock sensitivity!) 1,3-Dimethyl-2-methylene-2,3-dihydro-1H-imidazole (NHO2) was prepared according to literature procedures.⁹

Synthesis of 2-Isopropyl-4,5-diphenyl-1H-imidazole. A 250 mL glass vial was charged with NH₄OAc (7.7 g, 99.9 mmol), MeOH (150 mL), and a PTFE stirring bar. The mixture was allowed to cool to 0 °C, and isobutyraldehyde (3.6 g, 49.9 mmol) and benzil (10.5 g, 49.9 mmol) were added. The vial was sealed and submerged in a preheated oil bath at 120 °C for 3 h. The resulting mixture was concentrated under vacuum. The off-white precipitate was collected by filtration, then washed with Et₂O, and dried in a vacuum (8.0 g, 61.0%). ¹H NMR (300 MHz, DMSO-*d*₆): δ 11.92 (s, 1H, NH), 7.48–7.16 (m, 10H, *Ph*), 3.01 (sept, *J* = 7.1 Hz, 1H, CHMe₂), 1.31 (d, *J* = 7.1 Hz, 6H, CHMe₂).

Synthesis of 2-Isopropyl-1,3-dimethyl-4,5-diphenyl-1H-imidazol-3-ium lodide. 2-Isopropyl-4,5-diphenyl-1H-imidazole (8.0 g, 30.5 mmol) and NaHCO₃ (10.2 g, 122.0 mmol) were suspended in dry acetonitrile (150 mL). Methyl iodide (46.5 mL, 747.1 mmol) was added, and the reaction mixture was heated to reflux for 24 h and filtrated while the solution was hot. The resulting mixture was concentrated to half volume under vacuum. A pale yellow solid was collected by filtration, then washed with THF, and dried under vacuum (10.0 g, 78.4%). ¹H NMR (500 MHz, DMSO- d_6): δ 7.52–7.43 (m, 6H, Ph), 7.41–7.39 (m, 4H, Ph), 3.70 (s, 6H, NCH₃), 3.84 (sept, J = 7.2 Hz, 1H, CHMe₂), 1.53 (d, J = 7.2 Hz, 6H, CHMe₂).

Synthesis of 1,3-Dimethyl-4,5-diphenyl-2-(propan-2-ylidene)-2,3dihydro-1H-imidazole (**NHO1**). 2-Isopropyl-1,3-dimethyl-4,5-diphenyl-1H-imidazol-3-ium iodide (5.0 g, 11.9 mmol) was added to a suspension of KH (0.96 g, 23.9 mmol) in THF (100 mL), and the mixture was stirred for 24 h at room temperature under exclusion of light. After filtration and removal of organic solvents *in vacuo*, the desired product was obtained as air-sensitive, red crystals (2.3 g, 66.3%). ¹H NMR (500 MHz, benzene- d_6): δ 7.26–7.23 (m, 4H, *o*-Ph), 7.02–6.99 (m, 4H, *m*-Ph), 6.95–6.92 (m, 2H, *p*-Ph), 2.73 (s, 6H, NCH₃), 1.99 (s, 6H, CMe₂). ¹³C NMR (126 MHz, benzene- d_6): δ 153.5, 132.0, 128.6, 128.4, 128.0, 126.4, 72.0, 38.9, 20.8.

Isolation of Compound 1. To a solution of NHO2 (0.6 g, 5.4 mmol) in 7 mL of benzene was added δ -VL (0.54 g, 5.4 mmol) at room temperature with stirring for 2 h. The off-white precipitate was

obtained by filtration, then washed with benzene $(3 \times 5 \text{ mL})$, and dried *in vacuo* (1.0 g, 87.3%). ¹H NMR (500 MHz, benzene- d_6): δ 5.38 (s, 2H, NCH=), 5.33 (s, 1H, OH), 4.30 (s, 1H, =CH), 3.95 (br, 2H, CH₂OH), 2.82 (s, 6H, NCH₃), 2.68–2.66 (m, 2H, COCH₂), 2.17–2.12 (m, 2H, CH₂), 1.87–1.82 (m, 2H, CH₂). ¹³C NMR (126 MHz, CD₂Cl₂): δ 185.3, 151.2, 118.0, 69.8, 61.5, 40.1, 35.5, 32.6, 22.6.

Isolation of Compound **2**. Compound **2** was isolated as off-white powders in 88.3% yield using the same procedure as described for the isolate of compound **1**. ¹H NMR (500 MHz, benzene-*d*₆): δ 5.38 (s, 2H, NCH=), 4.36 (s, 1H, =CH), 3.80 (q, *J* = 6.0 Hz, 2H, CH₂OH), 3.53 (t, *J* = 6.0 Hz, 1H, OH), 2.86 (s, 6H, NCH₃), 2.65 (t, *J* = 6.7 Hz, 2H, COCH₂), 2.07–2.01 (m, 2H, CH₂), 1.77–1.72 (m, 2H, CH₂), 1.71–1.66 (m, 2H, CH₂). ¹³C NMR (126 MHz, CD₂Cl₂): δ 185.0, 151.2, 118.0, 70.0, 61.9, 41.9, 35.5, 32.9, 27.2, 25.7.

Synthesis of 1-Hydroxynonan-5-one. 1-Hydroxynonan-5-one was prepared according to a modified literature procedure. ⁹⁵ δ -VL (3.0 g, 30.0 mmol) was dissolved in 75 mL of Et₂O under argon. The solution was brought to -78 °C, where a solution of *n*-BuLi (1.6 M in hexane, 18.8 mL, 30.0 mmol) was added dropwise over a 20 min span. The mixture was stirred for 4 h at this temperature and quenched with saturated NH₄Cl(aq). After allowing the solution to warm to room temperature, NaCl was added to saturate the solution. The product was extracted from the aqueous layer with copious amounts of diethyl ether. Pure product (3.2 g, 67.5%) was obtained by distillation under reduced pressure as colorless oil. ¹H NMR (500 MHz, CDCl₃): δ 3.61 (q, *J* = 6.1 Hz, 2H, CH₂OH), 2.44 (t, *J* = 7.1 Hz, 2H, COCH₂), 2.40 (t, *J* = 7.5 Hz, 2H, COCH₂), 2.19–2.17 (m, 1H, OH), 1.68–1.62 (m, 2H, CH₂), 1.59–1.43 (m, 4H, CH₂), 1.39–1.18 (m, 2H, CH₂), 0.89 (t, *J* = 7.4 Hz, 3H, CH₃).

Isolation of Adduct Al(C_6F_5)₃·VL. To a solution of Al(C_6F_5)₃ (0.5 g, 0.95 mmol) in benzene (5 mL) was added δ -VL (94.8 mg, 0.95 mmol) at room temperature with stirring for 5 min. The resulting mixture was concentrated *in vacuo*, and the residue was washed with hexane (20 mL) and then dried *in vacuo* to afford Al(C_6F_5)₃·VL as a white powder (0.57 g, 95.8%). ¹H NMR (500 MHz, benzene- d_6): δ 3.08 (t, J = 5.5 Hz, 2H, OCH₂), 1.60 (t, J = 6.6 Hz, 2H, COCH₂), 0.44–0.32 (m, 4H, CH₂CH₂). ¹⁹F NMR (471 MHz, benzene- d_6): δ –123.72 (dd, $J_{F-F} = 27.4$, 11.9 Hz, 6F, *o*-F), –152.60 (t, $J_{F-F} = 19.8$ Hz, 3F, *p*-F), –160.27 to –162.53 (m, 6F, *m*-F). ¹³C NMR (126 MHz, benzene- d_6): $\delta = 185.3$, 75.2, 28.9, 20.0, 16.0.

Isolation of Adduct Al(C₆F₅)₃·CL. Adduct Al(C₆F₅)₃·CL was isolated as a white powders in 96.2% yield using the same procedure as described for the isolate of the adduct Al(C₆F₅)₃·VL. ¹H NMR (500 MHz, benzene-d₆): δ 3.05–3.03 (m, 2H, OCH₂), 1.69–1.67 (m, 2H, COCH₂), 0.78–0.73 (m, 2H, CH₂), 0.68–0.64 (m, 2H, CH₂), 0.58–0.54 (m, 2H, CH₂). ¹⁹F NMR (471 MHz, benzene-d₆): δ –123.50 (dd, $J_{F-F} = 27.6$, 11.7 Hz, 6F, o-F), -152.55 (t, $J_{F-F} = 19.8$ Hz, 3F, p-F), -161.42 to -161.55 (m, 6F, m-F). ¹³C NMR (126 MHz, benzene-d₆): δ 189.6, 75.1, 33.6, 27.1, 26.3, 20.4.

Isolation of Adduct **NHO2·Al**(C_6F_5)₃. To a solution of Al(C_6F_5)₃ (0.4 g, 0.76 mmol) in 9 mL of benzene was added **NHO2** (83.5 mg, 0.76 mmol) at room temperature with stirring for 1 min. The resulting mixture was concentrated under vacuum to give the white precipitate (**NHO2·Al**(C_6F_5)₃). The solid was collected by filtration, then washed with benzene/hexane (1:4), and dried *in vacuo* (0.29 g, 60.0%). ¹H NMR (500 MHz, benzene- d_6): δ 5.01 (s, 2H, NCH=), 2.15 (s, 6H, NCH₃), 2.01 (br, 2H, CH₂). ¹⁹F NMR (471 MHz, benzene- d_6): δ –122.44 (d, J_{F-F} = 22.3 Hz, 6F, *o*-F), –154.39 (t, J_{F-F} = 19.7 Hz, 3F, *p*-F), –161.89 to –162.03 (m, 6F, *m*-F).

Synthesis and Isolation Zwitterionic, Tetrahedral Intermediate **INT1**. To a solution of Al(C_6F_5)₃ (264.1 mg, 0.5 mmol) in 4 mL of chlorobenzene was added MI (85.1 mg, 0.5 mmol) and **NHO2** (55.1 mg, 0.5 mmol) in hexane at -30 °C with stirring for 5 min. The solid was collected by filtration, then washed with hexane (3 × 5 mL), and dried *in vacuo* to afford **INT1** as a light-yellow powder (279 mg, 69.2%). ¹H NMR (500 MHz, benzene- d_6): δ 5.39 (s, 2H, NCH= CHN), 2.88 (dd, J = 8.9, 3.8 Hz, 1H, OCH), 2.70 (s, 6H, NCH₃), 2.28 (d, J = 15.2 Hz, 1H, CN₂CH₂), 2.17 (d, J = 15.1 Hz, 1H, CN₂CH₂), 2.12–2.06 (m, 1H, CH(CH₃)₂), 1.81 (d, J = 13.8 Hz, 1H, CO₂CH₂CH), 1.51 (d, J = 9.0 Hz, 1H, CO₂CH₂CH), 1.49–1.39

(m, 1H, MeCH), 1.38–1.35 (m, 1H, OCHCH₂), 1.19–1.17 (m, 1H, OCHCH₂), 0.91 (d, J = 6.7 Hz, 3H, CHCH₃), 0.76–0.66 (m, 2H, OCHCH₂CH₂), 0.72 (d, J = 6.7 Hz, 6H, CH(CH₃)₂). This spectrum contains a small amount of hexanes (peaks marked with an asterisk). ¹⁹F NMR (471 MHz, benzene- d_6): δ –121.68 (d, $J_{F-F} = 19.0$, 6F, o-F), –157.44 (t, $J_{F-F} = 19.7$, 3F, p-F), –163.53 to –163.66 (m, 6F, m-F). ¹³C NMR (126 MHz, benzene- d_6): δ 145.6, 120.4, 101.2, 78.8, 51.4, 38.0, 37.6, 34.6, 33.9, 29.7, 27.7, 23.5, 18.2, 16.8 (broad resonances for the C₆F₅ groups due to C–F coupling omitted). This spectrum contains a small amount of chlorobenzene (peaks marked with an asterisk).

Synthesis and Isolation of Ring-Opened, Zwitterionic Intermediate (INT2). To a solution of INT1 (250 mg, 0.3 mmol) in 5 mL of chlorobenzene was added Al(C_6F_5)₃ (163.3 mg, 0.3 mmol) at -35 °C with stirring for 2 h. The resulting mixture was concentrated in vacuo, and the residue was dissolved in 5 mL of benzene. After filtration, the organic solvents were removed; the resulting white solid was then washed with benzene/hexane (1:5) and dried in vacuo (189 mg, 45.8%). ¹H NMR (500 MHz, benzene- d_6) INT2: δ 5.27 (s, 2H, NCH=CHN), 4.77 (d, J = 8.4 Hz, 1H, OH), 4.01 (s, 1H, =CH), 3.91-3.87 (m, 1H, CHOH), 2.56 (s, 6H, NCH₃), 2.25 (dd, J = 13.2, 4.1 Hz, 1H, =COCH₂), 1.85-1.77 (m, 1H, MeCH), 1.65 (dd, J = 13.1, 10.3 Hz, 1H, =COCH₂), 1.44–1.36 (m, 1H, CH(CH₃)₂), 1.44– 1.36 (m, 1H, CH2CHCO), 1.34-1.29 (m, 1H, CH2CHCO), 1.14-1.07 (m, 1H, CH₂CH₂CHCO), 0.84–0.78 (m, 1H, CH₂CH₂CHCO), 0.76 (d, J = 6.5 Hz, 3H, CHCH₃), 0.56 (d, J = 6.9 Hz, 6H, $CH(CH_3)_2$). This spectrum contains a small amount of hexanes (peaks marked with an asterisk). ¹⁹F NMR (471 MHz, benzene- d_6): δ −122.98 (dd, J_{F−F} = 26.5, 11.9 Hz, 12F, *o*-F, Alane), −150.52 (t, J_{F−F} = 19.7 Hz, 3F, p-F, HO·Alane), -154.93 (t, J_{F-F} = 19.6 Hz, 3F, p-F, C= CO·Alane), -160.05 to -160.19 (m, 6F, m-F, HO·Alane), -162.29 to -162.42 (m, 6F, m-F, C=CO·Alane). ¹³C NMR (126 MHz, benzene d_6): δ 170.9, 145.0, 119.6, 91.5, 81.0, 44.9, 34.0, 32.8, 31.6, 29.9, 29.8, 18.8, 17.3, 14.7.

Synthesis and Isolation of NHO1-CL-Al(C_6F_5)₃ (INT3). To a solution of Al(C_6F_5)₃ (0.53 g, 1.0 mmol) in 3 mL of benzene was added ε -CL (0.11 g, 1.0 mmol) and NHO1 (0.29 g, 1.0 mmol) at room temperature with stirring for 30 min. After filtration and removal of the organic solvent *in vacuo*, the solid was washed with hexane $(3 \times$ 5 mL). The desired product was obtained as colorless crystals (0.80 g, 86.1%). ¹H NMR (500 MHz, benzene- d_6): δ 6.94–6.86 (m, 10H, Ph), 3.86 (t, J = 12.0 Hz, 1H, OCH₂), 3.30–3.28 (m, 1H, OCH₂), 3.28 (s, 6H, NMe), 2.25-2.21 (m, 1H, COCH₂), 2.15-2.10 (m, 1H, COCH₂), 1.50-1.45 (m, 2H, CH₂), 1.42 (s, 3H, Me), 1.34-1.28 (m, 1H, CH₂), 1.21-1.13 (m, 2H, CH₂), 1.09 (s, 3H, Me), 1.06-1.01 (m, 1H, CH₂). ¹⁹F NMR (471 MHz, benzene- d_6): δ –121.44 (d, J_{F-F} = 26.9 Hz, 6F, o-F), -156.14 (t, $J_{F-F} = 19.9$ Hz, 3F, p-F), -162.97 to -163.10 (m, 6F, m-F). ¹³C NMR (126 MHz, methylene chloride- d_2): δ 152.4, 132.9, 130.9, 130.0, 128.9, 128.3, 126.3, 107.2, 63.0, 38.8, 37.8, 31.4, 30.2, 27.6, 27.2, 25.2 (broad resonances for the C_6F_5 groups due to C-F coupling omitted).

X-ray Crystallographic Analysis of Compound 1, $Al(C_{6}F_{5})$; CL, and INT3. Single crystals were quickly covered with a layer of Paratone-N oil (Exxon, dried and degassed at 120 $^\circ\text{C}/10^{-6}$ Torr for 24 h) after decanting the mother liquor. A crystal was then mounted on a thin glass fiber and transferred into the cold nitrogen stream of a Bruker APEX-II CCD diffractometer. The structures were solved by direct methods and refined using the Bruker SHELXTL program library by full-matrix least-squares on F^2 for all reflections (SHELXTL, Version 6.12; Bruker Analytical X-ray Solutions: Madison, WI, 2001). The structure was refined by full-matrix least-squares on F^2 for all reflections. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were included in the structure factor calculations at idealized positions. Selected crystallographic data for compound 1: C11H18N2O2, triclinic, space group P-1, a = 7.5941(13) Å, b = 8.6701(15) Å, c = 9.0386(16) Å, $\alpha =$ 86.210(3)°, $\beta = 77.541(3)°$, $\gamma = 76.473(3)°$, $V = 564.91(17) Å^3$, Z = 2, $D_{\text{calcd}} = 1.248 \text{ mg/m}^3$, GOF = 1.036, R1 = 0.0562 [I > $2\sigma(I)$], wR2 = 0.1472 (all data). Selected crystallographic data for $Al(C_6F_5)_3$ ·CL: $C_{24}H_{10}AlF_{15}O_2$, orthorhombic, space group *Pbca*, a = 18.8274(7) Å, b

= 12.7040(5) Å, *c* = 19.8612(7) Å, $\alpha = \beta = \gamma = 90^{\circ}$, *V* = 4750.5(3) Å³, *Z* = 8, $D_{calcd} = 1.791 \text{ mg/m}^3$, GOF = 1.062, R1 = 0.0387 [*I* > 2 σ (*I*)], *w*R2 = 0.0981 (all data). Selected crystallographic data for **INT3**: C_{52.5}H₄₃AlClF₁₅N₂O₂, triclinic, space group *P*-1, *a* = 10.9044(8) Å, *b* = 12.1572(9) Å, *c* = 20.2479(15) Å, $\alpha = 79.430(2)^{\circ}$, $\beta = 84.882(2)^{\circ}$, $\gamma =$ 77.124(2)°, *V* = 2569.0(3) Å³, *Z* = 2, $D_{calcd} = 1.398 \text{ mg/m}^3$, GOF = 1.049, R1 = 0.0716 [*I* > 2 σ (*I*)], *w*R2 = 0.2461 (all data). Crystallographic data for the structure of compound 1 (CCDC 1513721), Al(C₆F₅)₃·CL (CCDC 1513741), and **INT3** (CCDC 1513717) have been deposited in the Supporting Information.

General Polymerization Procedures. Polymerizations were performed either in 25 mL flame-dried Schlenk flasks interfaced to the dual-manifold Schlenk line for runs using external temperature bath or in 30 mL glass reactors inside the glovebox for ambient temperature (ca. 25 °C) runs. In a typical polymerization procedure, a predetermined amount of Al(C_6F_5)₃·(toluene)_{0.5} was first dissolved in monomer (456 μ L for δ -VL or 529 μ L for ϵ -CL, 200 equiv relative to the LB) and toluene inside a glovebox. The polymerization was started by rapid addition of a solution of a LB (1 equiv of an NHO) in 1.0 mL of toluene via a gastight syringe to the above mixture containing the LA and monomer under vigorous stirring. The amount of the monomer was fixed for all polymerization. After the measured time interval, a 0.2 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 4 mL vial containing 0.6 mL of undried "wet" CDCl₃ stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by ¹H NMR to obtain the percent monomer conversion data. After the polymerization reaction mixture was stirred for the stated reaction time, then the polymer was immediately precipitated into 200 mL of hexane, stirred for 1 h, filtered, washed with hexane, and dried in a vacuum oven at 50 °C overnight to a constant weight.

Polymerization Kinetics. Kinetic experiments were carried out in a stirred glass reactor at ambient temperature (ca. 25 °C) inside an argon-filled glovebox using the polymerization procedure already described above, with the $[Al(C_6F_5)_3]/[NHO2]$ ratio fixed at 2:1, [ε -CL]₀ was fixed at 1.0 M, where NHO2 = 1.25, 2.5, 5.0, 10.0 mM and $[Al(C_{6}F_{5})_{3}] = 2.5, 5.0, 10.0, 20.0 \text{ mM in 5 mL mixture solutions. At}$ appropriate time intervals, 0.2 mL aliquots were withdrawn from the reaction mixture using syringe and quickly quenched into 4 mL septum-sealed vials containing 0.6 mL of undried "wet" CDCl₂ mixed with 250 ppm BHT-H. The quenched aliquots were analyzed by ¹H NMR for determining the ratio of $[\varepsilon$ -CL]_t at a given time t to $[\varepsilon$ -CL]₀, $[\varepsilon$ -CL]_i: $[\varepsilon$ -CL]₀. Apparent rate constants (k_{app}) were extracted from the slopes of the best fit lines to the plots of $[\hat{\epsilon}$ -CL]_{*i*} $[\epsilon$ -CL]₀ vs time. Another set of kinetic experiments were carried out to determine the kinetic order with respect to [NHO2]. In these experiments, with $[Al(C_6F_5)_3]/[NHO2]$ ratios of 5:4, 4:3, 3:2, and 2:1, $[\varepsilon$ -CL]₀ was fixed at 1.0 M for all polymerization, where NHO2 = 10, 7.5, 5.0, 2.5 mM and $[Al(C_6F_5)_3] = 12.5, 10, 7.5, 5 \text{ mM}$ in 5 mL mixture solutions. The rest of the procedure was same as the described above.

Polymer Characterizations. The weight-average molar masses (M_w) and molar mass distributions (M_w/M_n) of the polymer samples were determined by gel permeation chromatography (GPC) with a multiangle light scattering detector at 35 °C. THF (HPLC grade) was used as an eluent with a flow rate of 1 mL/min. The differential refractive index (DRI) increment (dn/dc) value of 0.084 mL/g was used for PVL and 0.076 for PCL. Chromatograms were processed with Waters Breeze2 software.

The isolated low-MW polymer samples were analyzed by matrixassisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS); the experiment was performed on a BrukerAutoflex III mass spectrometer in linear, positive ion mode. The matrix was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propylidene]malonitrile (DCTB), and the solvent was THF.

RESULTS AND DISCUSSION

Characteristics of the ROP of Lactones by NHO/ Al(C_6F_5)₃ LPs. As NHCs alone have been shown to be effective for the ROP of lactones producing cyclic polyesters,^{21,96–98} and also for the chain-growth addition polymerization of Michael acceptors,⁹⁹ we initially probed the LPP approach by examining the cooperative effects of NHC and other common LBs on the Al(C_6F_5)_3-based LPs for the ROP of ε -CL in a fixed 400/1/2 ε -CL/LB/Al(C_6F_5)_3 ratio (Table S1 and Scheme S1). Based on the results of this initial screening, the NHO/Al(C_6F_5)_3 pair stood out as the most active and effective LP for the ROP of ε -CL (Scheme 1), thanks to the higher nucleophilicity of NHO





(due to the highly polarized double bond that places a partial negative charge on the exocyclic carbon) relative to other LBs investigated (NHCs, phosphines, etc.). Thus, quantitative monomer conversion was achieved with the NHO/Al(C_6F_5)₃ LP (18 h for **NHO1** and 3.5 h for **NHO2**), while much lower and incomplete monomer conversions (17.0–56.2%) were observed, even after 24 h with the other LB/Al(C_6F_5)₃ LPs.

Encouraged by these promising initial results, we investigated the ROP of lactones by NHO/Al(C_6F_5)₃ LPs in more detail. At the outset, we performed a series of control experiments and found that $Al(C_6F_5)_3$ itself only produced a trace amount of polymer products for the ROP of both ε -CL and δ -VL up to 24 h at ambient temperature (Table 1, runs 1 and 2). Without $Al(C_6F_5)_3$, NHO1 alone yielded a trace amount of PCL but effectively polymerized δ -VL, achieving 93.8% δ -VL conversion after 24 h (Table 1, runs 3-5). On the other hand, NHO2 alone is completely ineffective for the ROP of either ε -CL or δ -VL, and no polymer products were obtained for up to 24 h at room temperature (Table 1, runs 6 and 7). Noteworthy here is that although NHO1 alone is effective for the ROP of δ -VL, the resulting polymers with different [VL]/[NHO1] ratios all exhibited a bimodal molecular weight distribution (Table 1, runs 3 and 4). Most recently, Dove and co-workers used the alcohol initiator in addition to an NHO, 2-isopropylidene-1,3,4,5-tetramethylimidazoline, the combined system of which rapidly converted δ -VL (500 equiv) into PVL but with relatively low molecular weight of $M_n = 11.4$ kg/mol and broad molecular weight distribution of D = 3.29. In the absence of the alcohol initiator, this NHO alone produced PVL with even higher D value of 4.26.12 In contrast, after introducing $Al(C_6F_5)_3$ into the NHO1 system, the M_w value of the resulting PVL increased linearly from 29.5 to 45.6 to 69.2 kg/mol as the monomer-to-LP ratio increased from 100 to 200 to 400 (Table 1, runs 8-10). However, the D value was still relatively broad (1.74–1.77). More pronounced synergetic effects rendered by the NHO1/Al(C_6F_5)₃ system were observed for the ROP of ε -CL. Thus, the monomer conversion was drastically enhanced from essentially zero in the absence of $Al(C_6F_5)_3$ to 100% in the presence of $Al(C_6F_5)_3$. With increasing the monomer-to-LP ratio from 100 to 200 to 400, the $M_{\rm w}$ value of the corresponding PCL increased linearly from 33.9 to 65.2 to 103 kg/mol while the D value remained in a narrow range of 1.27–1.43 (Table 1, runs 11–13). The relatively broad molecular weight distribution for both PVL and PCL is presumably related to the existence of different active species in

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run no.	LA (equiv)	LB	М	time (h)	conv ^b (%)	$M_{\rm w}^{\ c}$ (kg/mol)	$M_{\rm n}^{\ c} \ ({\rm kg/mol})$	Đ	$I^{*^{d}}(\%)$
1	2		400VL	24	trace				
2	2		400CL	24	trace				
3	0	NHO1	200VL	8	93.8	32.5	30.0	1.08	
						78.2	71.7	1.09	
4	0	NHO1	400VL	24	93.8	34.2	32.3	1.06	
						82.0	75.2	1.09	
5	0	NHO1	400CL	24	trace				
6	0	NHO2	400VL	24	0				
7	0	NHO2	400CL	24	0				
8	2	NHO1	100VL	6	92.3	29.5	17.0	1.74	56
9	2	NHO1	200VL	12	91.2	45.6	25.8	1.77	72
10	2	NHO1	400VL	24	93.7	69.2	39.1	1.77	97
11	2	NHO1	100CL	6	100	33.9	23.7	1.43	49
12	2	NHO1	200CL	12	100	65.2	51.3	1.27	45
13	2	NHO1	400CL	18	100	103	78.0	1.32	59
14	2	NHO2	100VL	1.25	93.2	13.0	12.0	1.08	78
15	2	NHO2	200VL	2.5	94.4	19.6	18.5	1.06	102
16	2	NHO2	400VL	5	93.9	39.7	34.5	1.15	110
17	2	NHO2	800VL	10	94.1	64.6	59.3	1.09	127
18	2	NHO2	100CL	1	100	14.7	14.3	1.03	81
19	2	NHO2	200CL	2	100	22.8	21.5	1.06	106
20	2	NHO2	400CL	3.5	100	52.6	51.6	1.02	89
21	2	NHO2	800CL	6	100	102	96.2	1.06	95
22	2	NHO2	1600CL	12	100	306	223	1.37	82
23	2	NHO2	3200CL	24	100	855	525	1.63	70

^{*a*}Carried out at ambient temperature (~25 °C) in toluene (Tol), where $[\epsilon$ -CL]₀ = 1.0 M and LA = Al(C₆F₅)₃·(Tol)_{0.5}. ^{*b*}Monomer conversions measured by ¹H NMR. ^{*c*}Absolute molecular weight (M_w) measured by GPC using a light scattering detector. Number-average molecular weight (M_n) is calculated from M_w/D . ^{*d*}Initiator efficiency (I^*) = $M_n(\text{calcd})/M_n(\text{exptl})$, where $M_n(\text{calcd}) = MW(M) \times [M]/[I] \times \text{conversion}$ (%) + MW(chain-end groups).

the NHO1/Al(C_6F_5)₃ LP system as NHO1 itself is also active for the polymerization of lactones (*vide supra*).

To avoid the background polymerization initiated by NHO itself, NHO2 was chosen as the more desired LB in the LPP of lactones as the above control experiments showed that it is inactive by itself for the ROP of lactones. Gratifyingly, the NHO2/Al(C_6F_5)₃ LP system promoted rapid and controlled ROP of lactones, yielding polymers with narrow molecular weight distributions. Runs 14-17 (Table 1) summarized selected ROP results of δ -VL by NHO2/Al(C₆F₅)₃ in toluene at room temperature. Relative to the NHO1/Al(C_6F_5)₃ system, the polymerization activity of NHO2/Al(C_6F_5)₃ was 4.8 times higher (Table 1, run 15 vs run 9) and also produced PVL with much lower D values (1.06–1.15). When switching from δ -VL to ε -CL (Table 1, runs 18–23), NHO2/Al(C₆F₅)₃ exhibited significantly enhanced polymerization activity by 6-fold (Table 1, run 19 vs run 12), compared with NHO1/Al(C_6F_5)₃, achieved quantitative monomer conversion for all ratios examined, and produced PCL with very low D values of 1.02-1.06 for $[\varepsilon-CL]/[LP] = 100-800$. Even with a high monomer to LP ratio of 3200, quantitative ε -CL conversion was still achieved and produced PCL with a high M_w of 855 kg/ mol (Table 1, run 23).

Three lines of key evidence summarized below clearly revealed the living characteristics of the ROP of lactones by NHO2/Al(C_6F_5)₃. First, the M_n value of PVL or PCL produced by NHO2/Al(C_6F_5)₃ increased linearly ($R^2 = 0.998$ and 0.995) with an increase in $[M]_0/[NHO2]_0/[Al(C_6F_5)_3]_0$ ratio from 100:1:2 to 800:1:2 (Figure S25), while the *D* value remained narrow (from 1.02 to 1.15). Second, a plot of the

PCL $M_{\rm p}$ vs monomer conversion at a fixed $[\varepsilon$ -CL]₀/[**NHO2**]₀/ $[Al(C_6F_5)_3]_0$ ratio of 800:1:2 also gave a straight line $(R^2 =$ 0.993), which was coupled with the small D values (Figure S26). Third, chain extension experiments were also carried out to provide more direct evidence for the living characteristics of the polymerization. The PCL with $M_{\rm w}$ = 22.8 kg/mol and D = 1.06 was first prepared by polymerizing 200 equiv of ε -CL to completion without quenching. The polymerization was resumed by addition of another 200 equiv of ε -CL, affording the resulting PCL with M_w = 58.6 kg/mol and D = 1.07 (Table S2, run 1). It is also noted that the corresponding initiator efficiency (I^* %) obtained from the polymerization by NHO2/ $Al(C_6F_5)_3$ was significantly higher compared to that obtained by NHO1/Al(C_6F_5)₃; for example, the *I**% for the ROP of ε -CL in a 200/1/2 ε -CL/LB/Al(C₆F₅)₃ ratio was increased from 45% for NHO1 to 106% for NHO2.

Characterization of Key Intermediates. To gain more insights into this living/controlled polymerization by NHO2/ Al(C₆F₅)₃, we endeavored to isolate and characterize the key intermediates of the reaction. NHO2 alone is inactive for the polymerization of both δ -VL and ε -CL, but it forms cleanly stable compounds 1 (NHO2-VL) and 2 (NHO2-CL) with δ -VL or ε -CL at room temperature, respectively. They were readily characterized by NMR spectra (see Experimental Section and Figures S3–S6) to be ring-opened products, and the molecular structure of 1 was also confirmed by single crystal X-ray diffraction analysis (Figure 1). From the X-ray diffraction data, the distance for C(5)–C(6) is 1.423(3) Å and that for C(6)–C(7) is 1.390(3) Å, which is somewhat between a typical C–C single bond (~1.53 Å) and C=C double bond (~1.32



Figure 1. X-ray crystal structure of compound 1. Ellipsoids are drawn at 50% probability.

Å). It is noted that only one hydrogen atom was found on C(6); while the distance for C(7)–O(1) is 1.269(2) Å, between a C-O single bond (1.41-1.44 Å) and C=O double bond (1.19-1.23 Å), no hydrogen atom was found on O(1). On the other hand, the terminal O(2) carries a hydrogen atom, transferred from the original exocyclic methylene unit of NHO2. Overall, the spectroscopic analysis and X-ray diffraction data confirmed the structure of the ring-opened, H-transferred product 1, which is best represented as resonance contributors 1a and 1b (Scheme 2). The clean formation of 1 upon mixing **NHO2** with δ -VL can be rationalized via fundamental steps involving initial nucleophilic attack of the δ -VL carbonyl group by NHO2, followed by the ring-opening of the lactone to form a zwitterionic intermediate, in which the acidic H atom on the exocyclic methylene unit of NHO2 is subsequently transferred to the terminal alkoxy anion (or oxyanion) to generate compound 1.

Isolation, characterization, and reactivity check of compound 1 proved instructive for a mechanistic understanding of this LPP system. Ring-opened product 1 itself does not initiate the polymerization since it is not nucleophilic enough to attack monomer. In fact, the formation of ring-opened product 1 was proposed as a possible deactivation pathway in the ROP of lactones by NHO.¹² However, addition of 2 equiv of $Al(C_6F_5)_3$ to 1 rendered a highly active ROP system, consuming all of the monomer in 1 h, which is even considerably more active (by >3×) than the system with direct mixing of NHO2/Al(C_6F_5)₃ in a 1:2 ratio. These results implied that the formation of ringopened product 1 is a prerequisite for the formation of active species in such ROP by LPs. There are two possible oxygen sites in compound 1 that could initiate the polymerization in the presence of $Al(C_6F_5)_3$: one is from the enol-form oxyanion,¹⁰⁰ and the other one is from the terminal hydroxy

group.¹⁰¹ To determine whether the terminal hydroxy group initiates the polymerization or not, 1-hydroxynonan-5-one (Figure S7) with a terminal hydroxy group was chosen as a model compound to test its catalytic performance. The addition of 1 or 2 equiv of $Al(C_6F_5)_3$ to the model compound yielded only negligible monomer conversion in 1 h, in contrast to the quantitative monomer conversion achieved by the compound $1/2Al(C_6F_5)_3$ system under the same condition. This observation provided strong evidence that the enol-form oxyanion in compound 1 plays an important role in initiating the polymerization. It is also noted that 2 equiv of $Al(C_6F_5)_3$ is required for the enhanced polymerization activity such that 1 equiv of $Al(C_6F_5)_3$ is utilized for the activation of the monomer, while the other equiv is reacted with compound 1 to generate the zwitterionic enolaluminate active species as shown in Scheme 2. The evidence for the activation of monomer by $Al(C_6F_5)_3$ was confirmed by the crystal structure of adduct $Al(C_6F_5)_3$ ·CL (Figure 2). As revealed from the X-ray diffraction



Figure 2. X-ray crystal structure of adduct $Al(C_6F_5)_3$ ·CL. Hydrogen atoms are omitted for clarity, and ellipsoids are drawn at 50% probability.

data, a coordinated bond is formed between Al(1) and O(1) (1.8327(13) Å). The distance for C(1)–O(1) (1.252(2) Å) and C(1)–O(2) (1.294(2) Å) is between a C–O single bond (1.41–1.44 Å) and a C=O double bond (1.19–1.23 Å).

Next, in situ NMR reaction of NHO2 and adduct $Al(C_6F_5)_3$. CL was carried out to investigate the synergetic effects of NHO2 and $Al(C_6F_5)_3$; a complicated NMR spectrum was obtained. Replacing ε -CL with menthide (MI), a clean, zwitterionic, tetrahedral intermediate INT1 is generated





Scheme 3. Formation of Intermediate INT1 and Ring-Opened Intermediate INT2

(Scheme 3). Adding another equiv of $Al(C_6F_5)_3$, a ring-opened, zwitterionic intermediate INT2 was formed (Scheme 3). The formation of INT2 can be reasoned by following the similar ring-opening, proton transfer, and enolaluminate formation reaction sequences as outlined in Scheme 2, followed by the terminal hydroxyl group coordinated to $Al(C_6F_5)_3$. INT1 (Figures S16–S18) and INT2 (Figures S19–S21) have been successfully isolated and characterized. INT2 could polymerize 99.1% of ε -CL (400 equiv) into PCL in 10 h, which clearly indicated both INT1 and INT2 are the key intermediates for the ROP of ε -CL. Attempts to get the crystal structures of INT1 and INT2 were not successful.

Switching the NHO2 to NHO1 enabled us to generate the corresponding clean, zwitterionic, tetrahedral intermediate (INT3) from the *in situ* NMR reaction of NHO1, $Al(C_6F_5)_3$, and ε -CL (Scheme 4). More importantly, we have successfully

Scheme 4. Formation of Intermediate INT3



isolated and characterized **INT3** both spectroscopically by NMR and structurally by X-ray diffraction analysis (Figure 3). The diffraction data revealed the formation of a single bond between C(7) and C(8) [1.534(4) Å], from the previous C=C double bond, and between C(7) and C(1) [1.578(4) Å], for the newly formed σ bond between **NHO1** and ε -CL. It is also noted the newly formed C–O single bond between C(1) and O(1) (1.381(3) Å) in **INT3** from the previous C=O carbonyl



Figure 3. X-ray crystal structure of zwitterionic, tetrahedral intermediate INT3. Solvent molecules and hydrogen atoms are omitted for clarity, and ellipsoids are drawn at 50% probability.

bond, which indicated the activation of the C-O bond. Previously, Waymouth et al. predicted the formation of such a zwitterionic tetrahedral intermediate in the NHC mediated ZROP of lactones with the aid of computational studies,^{102,103} but the isolation and/or characterization of such a tetrahedral intermediate was not accomplished until this work. The sufficient stability of INT3 that enabled our isolation, and characterization can be ascribed to the stabilization of $Al(C_6F_5)_3$ on the oxyanion. **INT3** itself only converted 9.3% of ε -CL into PCL in 14 h. However, adding 1 equiv of $Al(C_6F_5)_3$ to the isolated INT3 enhanced the polymerization activity drastically, thus achieving 100% monomer conversion in 8 h. These results indicated that INT3 is an active intermediate for the ROP of ε -CL, which can be ring-opened to form the zwitterionic species that attacks the incoming $Al(C_6F_5)_3$ -activated monomer to proceed the polymerization (vide infra). The ¹⁹F NMR spectrum of INT3 (Figure S23) closely resembled that of INT1 (Figure S17); therefore, the structure of zwitterionic tetrahedral INT1 was also indirectly verified by its analogue INT3.

Kinetics and Mechanism of Polymerization. To continue the investigation of the mechanistic aspects of the polymerization, we next examined the kinetics of the ROP of ε -CL by the NHO2/Al(C₆F₅)₃ system. The kinetic experiments employed [CL]₀/[NHO2]₀ with varied ratio of 100, 200, 400, and 800 and a fixed [Al(C₆F₅)₃]₀/[NHO2]₀ ratio of 2:1. As can be seen from the representative kinetic plots of $[\varepsilon$ -CL]_t/[ε -CL]₀ vs time, the polymerization clearly followed zero-order kinetics with respect to [ε -CL] concentration for all the ratios employed. Since the [Al(C₆F₅)₃]/[NHO2] ratio was kept at 2:1, the combined kinetic order of [Al(C₆F₅)₃] and [NHO2] can be obtained from the double-logarithm plot (Figure 4) of the apparent rate constants (K_{app}) obtained from the slopes of the best-fit lines to the plots of [ε -CL]_t/[ε -CL]₀ vs time as a



Figure 4. Zero-order kinetic plots for ROP of ε -CL by NHO2/ Al(C₆F₅)₃ in toluene at 25 °C: [ε -CL]₀ = 1.0 M; [Alane]₀ = 2[NHO2]₀; [NHO2]₀ = 0.01 (\triangle), 0.005 (\blacktriangle), 0.0025 (\square), 0.00125 M (\blacksquare). Inset: plot of ln(k_{app}) vs ln[NHO2].

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function of ln[**NHO2**], which was fit to a straight line ($R^2 = 0.999$) with a slope of 0.991. Thus, the combined kinetic order with respect to the [**NHO2**]/[Al(C₆F₅)₃] LP, given by the slopes of ~1, reveals that the propagation is first-order in the concentration of the LP.

In the second set of kinetic experiments, with a fixed amount of $[\varepsilon$ -CL]₀, the $[Al(C_6F_5)_3]/[NHO2]$ ratio was varied at 5:4, 4:3, 3:2, and 2:1 such that at each ratio there was 1 equiv of $Al(C_6F_5)_3$ left to activate the monomer upon formation of the active intermediate that consumes equimolar NHO2 and $Al(C_6F_5)_3$. The same zero-order dependence was observed for all the ratios investigated in this study. A double-logarithm plot (Figure 5) of the apparent rate constants (k_{app}), obtained



Figure 5. Zero-order kinetic plots for ROP of ε -CL by NHO2/ Al(C₆F₅)₃ in toluene at 25 °C: [ε -CL]₀ = 1.0 M; [NHO2]₀ = 0.01 (\triangle), 0.0075 (\blacktriangle), 0.005 (\square), and 0.0025 M (\blacksquare); [Al(C₆F₅)₃]₀ = 0.0125 (\triangle), 0.01 (\bigstar), 0.0075 (\square), and 0.005 M (\blacksquare). Inset: plot of ln(k_{app}) vs ln[NHO2].

from the slopes of the best-fit lines to the plots of $[e-CL]_t/[e-CL]_0$ vs time, as a function of $\ln[NHO2]$ was fit to a straight line ($R^2 = 0.996$) with a slope of 0.963, revealing that the

propagation is first order in [NHO2] concentration. In combination with the first set of kinetic results, the propagation is zero-order dependence on $[Al(C_6F_5)_3]$ concentration, which thus highlighted that the rate-determining step for the ROP of ε -CL catalyzed by NHO2/Al(C₆F₅)₃ is only dependent on the concentration of [NHO2], not on $[Al(C_6F_5)_3]$ and $[\varepsilon$ -CL].

Overall, the above kinetic results, coupled with mechanistic insights obtained through monitoring the polymerization and identification or characterization of the reaction intermediates (vide supra), led to a proposed polymerization mechanism for the ROP of lactones by the $[NHO2]/[Al(C_6F_5)_3]$ LP (Scheme 5). In this mechanism, initiation involves nucleophilic attack of $Al(C_6F_5)_3$ -activated monomer by NHO2 to form zwitterionic, tetrahedral intermediate INT4, followed by its ring-opening to generate active zwitterionic enolaluminate species INT5. In the propagation cycle, INT5 and its homologues INT6 attack the incoming $Al(C_6F_5)_3$ -activated monomer to generate zwitterionic, tetrahedral intermediate INT7, which is then ring-opened to re-form INT6, entering into the next chain propagation catalytic cycle. Kinetic studies indicated that the ratedetermining step is only dependent on the concentration of [NHO2]. As shown in Scheme 5, only the ring-opening of INT7 to regenerate INT6 does not rely on the concentration of $[Al(C_6F_5)_3]$ and [monomer], and therefore this ring-opening process is the rate-determining step and also required for each propagation cycle during the polymerization.

The low-MW oligomer produced by the NHO2/Al(C_6F_5)₃ system was analyzed by MALDI-TOF mass spectroscopy. The results clearly showed one series of molecular mass ions (Figures 6 and 7). A plot of m/z values of this series vs the number of monomer repeat units (*n*) yielded a straight line with a slope of 100.12 (mass of δ -VL) or 114 (mass of ε -CL) and intercept of 211 or 225 corresponding to the sum of NHO2, monomer (δ -VL or ε -CL) and H moieties, respectively, indicating PVL or PCL produced in the polymerization is a *linear polymer*. The imdazolium enol-form chain-end group formed by the NHO2 and monomer is consistent with

Scheme 5. Proposed Mechanism for ROP of δ -VL or ε -CL by NHO2/Al(C₆F₅)₃ Lewis Pairs



Article



Figure 6. MALDI-TOF MS analysis for the resulting PVL produced by $NHO2/Al(C_6F_5)_3$ in toluene at room temperature.





that proposed in the mechanism (Scheme 5). Furthermore, such imdazolium enol-form chain-end was also confirmed by ¹H NMR spectra (Figure S27), as evidenced by the resonances at δ 5.47 [NCH=CHN], 4.37 [OC=CH], and 2.94 ppm [NCH₃], which are similar to those observed in compound 1 (δ 5.38 [NCH=CHN], 4.30 [OC=CH], and 2.82 ppm [NCH₃]) and in compound 2 (δ 5.38 [NCH=CHN], 4.36 [OC=CH], and 2.86 ppm [NCH₃]), respectively.

Random and Block Copolymerizations. The living features of this ROP by LPs, as demonstrated by the above-described chain-extension experiments and mechanistic studies, also enabled the synthesis of the well-defined block copolymers. When both monomers were added at the same time, copolymerization of δ -VL and ε -CL produced randomly sequenced copolymers (Table S2, run 2). As indicated by

quantitative ¹³C NMR spectra (Figure 8C), the equal integral of each type of methylene resonance within the copolymer [VL–*CL* (0.23), CL–*CL* (0.27), VL–*VL* (0.25), CL–*VL* (0.25)] is characteristic of a random copolymer. On the other hand, sequential block copolymerization by polymerizing ε -CL first with [ε -CL]₀/[**NHO2**]₀/[Al(C₆F₅)₃]₀ = 200/1/2 without quenching, followed by addition of another 200 equiv of δ -VL, afforded successfully linear diblock copolymer PCL-*b*-PVL (Table S2, run 3). As shown in ¹³C NMR spectra (Figure 8d), the methylene signals for the resulting PCL-*b*-PVL have two equal integrals, corresponding to the homodyads CL–*CL* and VL–*VL*, and no resonances for the heterodyads VL–*CL* and CL–*VL*. This implies the formation of the well-defined diblock copolymer, with no occurrence of transesterification side reactions, which is rather difficult to achieve as commonly



Figure 8. ¹³C NMR spectra (a) PCL, (b) PVL, (c) linear random PCL-*co*-PVL, and (d) linear diblock PCL-*b*-PVL, all produced by NHO2/ Al(C_6F_5)₃ in toluene at room temperature. CL-VL denotes the methylene signal of the δ -VL unit is connected to a CL.

random copolymers with broad dispersities were obtained, $^{104-113}$ due to inter- and intramolecular transesterification side reactions.

GPC traces (Figure 9a) provided further evidence for the well-defined block copolymer formation with NHO2/Al-



Figure 9. (a) GPC traces for PCL (black), PCL-*b*-PVL (red), and PCL-*b*-PVL-*b*-PCL (blue). (b) GPC traces for PVL (black) and PVL-*b*-PCL (red) produced by $NHO2/Al(C_6F_5)_3$ in toluene at room temperature.

 $(C_6F_5)_3$ in toluene at room temperature. As can be seen from Figure 9a, the GPC trace for the PCL produced during the first ROP shifted to a higher molecular weight region with low dispersity value of D = 1.06-1.09, while the M_w values increased from 22.8 kg/mol (black trace) for the homopolymer PCL to 44.6 kg/mol (red trace) for the diblock PCL-*b*-PVL produced. In addition, we employed δ -VL as the primary monomer and ε -CL as the subsequent monomer for the copolymerization and obtained similar results (Figure 9b and Table S2, run 4). Worth noting here is the possibility of the rapidly exchanging Al $(C_6F_5)_3$ moiety between the two terminal alkoxy and alcohol sites (cf. INT6 in Scheme 5), which would lead to a possible triblock copolymer structure. The validation of this possibility requires extensive future studies that are underway. On the other hand, through the conventional sequential monomer addition method for triblock copolymers, copolymer PCL-*b*-PVL-*b*-PCL was also successfully prepared with a M_w value of 72.1 kg/mol (Figure 9a, blue trace) and a *D* value of 1.15 (Table S2, run 5). Therefore, the NHO2/Al(C₆F₅)₃ LP successfully prevented any transesterification side reaction and yield well-defined block copolymers, regardless of the monomer addition order.

CONCLUSIONS

Although LPP has been extended to include several classes of monomers, this work reveals the first LPP system for the living ROP of lactones and also reports the first comprehensive mechanistic study of such polymerization including examination of polymerization characteristics, isolation and structural characterization of key reaction intermediates, polymerization kinetics, and analysis of resulting polymer chain structures.

Using NHO/Al(C_6F_5)₃ LPs for the ROP of lactones including δ -VL and ε -CL in this study, we showed that while the individual LA or LB exhibited none to negligible activity for the polymerization or produced polymer products with bimodal molecular weight distributions, a combination of the two in the form of a LP mediates the living/controlled ROP of lactones to produce high molecular weight linear (co)polyesters with M_w up to 855 kg/mol and narrow molecular weight distributions, highlighting the unique cooperative and synergistic effects of the LP in the polymerization. The livingness of the ROP has been confirmed with multiple protocols, including observations of the linear increase of the polymer $M_{\rm p}$ vs time or conversion and monomer-to-LP ratio while maintaining low D values (from 1.02 to 1.15), no induction or chain termination events by kinetics, successful chain extension experiments, and the synthesis of the well-defined di- and triblock copolymers with narrow molecular weight distribution (D = 1.06 - 1.15), regardless of the comonomer addition order and without transesterification side reactions.

Several key intermediates directly relevant to the ROP have been successfully isolated and characterized spectroscopically and structurally, including LA–monomer adduct (i.e., activated monomer) Al(C_6F_5)₃·CL, the LB-monomer reaction product (i.e., ring-opened intermediate) NHO2-VL (1), and zwitterionic, tetrahedral intermediate (i.e., pre-ring-opening species) **NHO1**-Al(C_6F_5)₃-CL (**INT3**). The results obtained from the polymerization kinetics revealed that ROP of lactones catalyzed by NHO2/Al(C_6F_5)₃ is zero-order with respect to both monomer and $Al(C_6F_5)_3$ concentrations but first-order to NHO2 concentration. Taken in total, the polymerization is proposed to proceed with initiation involving nucleophilic attack of the Al(C_6F_5)₃-activated monomer by NHO to form the zwitterionic, tetrahedral intermediates, followed by its ringopening to generate zwitterionic enolaluminate active species. In the propagation cycle, this ring-opened zwitterionic species and its homologues attack the incoming monomer activated by $Al(C_6F_5)_3$ to generate the tetrahedral intermediate, followed by the rate-determining ring-opening step to regenerate the zwitterionic species, thus re-entering into the next chain propagation cycle. NMR and MALDI-TOF MS analyses of the obtained low molecular weight oligomers confirmed the resulting linear polymer structure with predicted chain-end groups.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.6b02398.

NMR spectra, crystal data, bond lengths and angles, and further tabular data (PDF)

Crystallographic data for the structure of compound 1 (CIF)

Crystallographic data for the structure of $Al(C_6F_5)_3$ ·CL (CIF)

Crystallographic data for the structure of INT3 (CIF)

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Notes

The authors declare no competing financial interest.

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