Polymerization of 2,2′-Dimethyltrimethylene Carbonate by Lutetium Complexes Bearing Amino-Phosphine Ligands

Bo Liu,[1,2] Dongmei Cui[1]

[1]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China*
[2]*Graduate School of the Chinese Academy of Sciences, Beijing 100039, China*

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ABSTRACT: A series of lutetium alkyl, amino, and guanidinato complexes based upon an amino-phosphine ligand framework had been prepared. These complexes were applied to initiate ring-opening polymerization of 2,2′-dimethyltrimethylene carbonate (DTC). The type of the initiator significantly influenced the catalytic activity of these complexes in a trend as follows: alkyl ≈ guanidinate > amide, whereas the complexes with flexible backbone between P and N atoms within the ligand exhibited higher activity than those with rigid backbone. The isolated PDTC had bimodal-mode molecular weight distribution. The molecular weights of each fraction increased linearly with the conversion, indicating that there might be two active species. This had been confirmed by analyses of oligomeric DTC living species and oligomer with NMR technique as the metal-alkoxide and the four-membered metallocyclic lactate. Kinetic investigation displayed that the polymerization rate was the first order with the monomer concentration. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 112: 3110–3118, 2009

Key words: polycarbonates; catalysts; amino-phosphine; lutetium complex

INTRODUCTION

Aliphatic polyesters and polycarbonates as well as their copolymers have been widely used in medicine, pharmaceutics, and tissue engineering such as medium for controlled release of drug, scaffold, and delivery of antibody and gene because of their biocompatibility, biodegradability, and low toxicity of the degraded products.[1–8] Ring-opening polymerization (ROP) of cyclic monomers, as the most efficient manner to obtain homo or copolyester with predicted molecular weight and narrow molecular weight distribution, has attracted much attention during the past decades. The ROP of cyclic carbonate has been investigated using various metal catalysts based on main group[9–11] and transition[12–15] metals and some lanthanide elements.[16–23] In some cases, the gel permeation chromatography (GPC) curves of the resultant polycarbonates are bimodal even though each with narrow distribution[10,15] no unambiguous mechanism was given. Thus, to develop new catalyst systems for such polymerization and to further investigate the mechanism are obviously attractive. Our group has successfully isolated several rare earth metal bis(alkyl) complexes bearing amino-phosphine ligand, which exhibited unique chemistry of C—H activation.[24,25] Here, we report the preparation of lutetium amino and guanidinato counterparts of these complexes and their catalytic behavior toward the ROP of 2,2′-dimethyltrimethylene carbonate (DTC). Moreover, the postulated mechanism for the formation of bimodal polymers via monitoring the oligomeric DTC living species with nuclear magnetic resonance (NMR) technique will also be discussed.

Correspondence to: D. Cui (dmcui@ciac.jl.cn).
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EXPERIMENTAL

General methods

All reactions were carried out under dry and oxygen-free argon atmosphere by using Schlenk technique or in a glovebox. Solvents were purified by a MBRAUN SPS system. All starting materials were purchased from Aldrich or Fluka, and distilled before use. Syntheses of complexes **1,** $L^fLu(CH_2Si(CH_3)_3)_2(THF)$ (L^f = (2,6-$C_6H_3(CH_3)_2$)$NCH(C_6H_5)CH_2P(C_6H_5)_2$),[24] and **2,** $L^rLu(CH_2SiMe_3)_2(THF)$ (L^r = (2,6-$C_6H_3(CH_3)_2$)$NCH_2C_6H_4P(C_6H_5)_2$),[25] and DTC[26] were according to the literatures.

Instruments and measurements

Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox. ^{1}H and ^{13}C NMR spectra were recorded at 25°C on a Bruker AV300 (FT, 300 MHz for ^{1}H) or AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by the ^{1}H-^{1}H (COSY) and ^{1}H-^{13}C (HMQC) experiments when necessary. Crystals for X-ray analysis were obtained as described in the Experimental section. The crystals were manipulated in a glovebox. Data collections were performed at −86.5°C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The number-average molecular weight (M_n) and molecular weight distribution (PDI) of the polymer were measured by means of GPC on TOSOH HLC-8220 GPC (Column: Super HZM-H×3) at 40°C using THF as eluent (the flowing rate is 0.35 mL/min) against polystyrene standards. Differential scanning calorimetry analyses were determined at a heating rate of 10°C/min on a Perkin Elmer Pyris 1. Elemental analyses were performed at the National Analytical Research Centre of Changchun Institute of Applied Chemistry.

Lutetium bis(amino) complexes 3 and 4

2,6-Diisopropylaniline (0.05 g, 0.28 mmol) in toluene (1 mL) was added to a toluene solution (4 mL) of complex **1** (0.11 g, 0.13 mmol). The reaction mixture remained stirred for 12 h at room temperature. Removal of the volatiles afforded oily residue, which was dissolved with hexane (1 mL) and then cooled to −30°C to generate crystals of complex **3**, $L^fLu(NHC_6H_3i\text{-}Pr_2\text{-}2,6)_2$ (THF) (0.09 g, Yield: 66%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C): δ = 1.05 (broad, 4H, THF), 1.44 (d, ^3J(H,H) = 6.4 Hz, 24H, —NHC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 2.47 (s, 6H, —NCH(CH_3)$_2$), 3.31 (multi, 4H, —NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 3.56 (broad, 4H, THF, 2H, PCH_2CH), 4.70 (s, 2H, —NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 5.13 (s, 1H, PCH$_2$CH), 6.73 (t, ^3J(H,H) = 7.2 Hz, 1H, *p*-NC$_6H_3$(CH$_3$)$_2$), 6.86 (d, ^3J(H, H) = 7.6 Hz, 2H, *m*-NC$_6H_3$(CH$_3$)$_2$), 6.95 (t, ^3J(H,H) = 7.6 Hz, 2H, *p*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.08 (multi, 4H, *o*-P(C$_6H_5$)$_2$, 2H, *p*-P(C$_6H_5$)$_2$, 1H, *p*-CH(C$_6H_5$)N), 7.14 (t, ^3J(H,H) = 7.2 Hz, 2H, *m*-CH(C$_6H_5$)N), 7.24 (d, ^3J(H,H) = 7.2 Hz, 2H, *m*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.25 (d, ^3J(H,H) = 7.6 Hz, 2H, *m*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.73 (d, ^3J(H,H) = 7.2 Hz, 2H, *o*-CH(C$_6H_5$)N), 7.78 ppm (t, ^3J(H,H) = 7.2 Hz, 4H, *m*-P(C$_6H_5$)$_2$). ^{13}C NMR (100 MHz, [D$_6$]benzene, 25°C): δ = 21.54 (s, 2C, —NC$_6$H$_3$(CH_3)$_2$), 24.55 (s, 8C, —NHC$_6$H$_3$ (CH(CH_3)$_2$)$_2$), 25.51 (s, 2C, THF), 30.21 (s, 1C, PCH2CH), 30.46 (s, 4C, —NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 72.98 (s, 2C, THF), 86.35 (d, ^1J(C,P) = 31 Hz, 1C, PCH$_2$CH), 116.74 (s, 2C, *p*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 123.49 (s, 1C, *p*-NC$_6H_3$(CH$_3$)$_2$), 123.76 (s, 4C, *m*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 129.03 (s, 2C, *p*-P(C$_6H_5$)$_2$), 129.13 (d, ^2J(C,P) = 8.2 Hz, 4C, *o*-P(C$_6H_5$)$_2$), 129.68 (s, 2C, *m*-NC$_6H_3$(CH$_3$)$_2$), 133.71 (d, ^3J(C,P) = 13 Hz, 4C, *m*-P(C$_6H_5$)$_2$), 134.59 (s, 1C, *p*-CHC$_6H_5$), 135.00 (s, 2C, *m*-CHC$_6H_5$), 135.25 (d, ^1J(C,N) = 19.5 Hz, 2C, *ipso*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 137.06 (d, ^1J(C,P) = 26 Hz, 2C, *ipso*-P(C$_6H_5$)$_2$), 137.19 (s, 4C, *o*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 143.55 (s, 2C, *o*-CHC$_6H_5$), 148.89 (s, 1C, *ipso*-NC$_6H_3$(CH$_3$)$_2$), 152.86 (s, 2C, *o*-NC$_6H_3$(CH$_3$)$_2$), 175.02 ppm (s, 1C, *ipso*-CHC$_6H_5$). Anal. Calcd for C$_{56}$H$_{71}$N$_3$OPLu: C, 66.72; H, 7.10; N, 4.17. Found: C, 66.69; H, 7.10; N, 4.15.

Following the same procedure, treatment of complex **2** with 2,6-diisopropylaniline gave complex **4**, $L^rLu(NHC_6H_3i\text{-}Pr_2\text{-}2,6)_2$ (THF) (Yield: 68%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C): δ = 1.01 (broad, 4H, THF), 1.36 (d, ^3J(H,H) = 6.8 Hz, 24H, —NHC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 2.34 (s, 6H, —NC$_6$H$_3$(CH_3)$_2$), 3.42 (multi, 4H, —NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 3.61 (broad, 4H, THF), 4.70 (s, 2H, —NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 4.71 (s, 2H, —CH_2N), 6.75 (multi, 1H, *p*-NC$_6H_3$(CH$_3$)$_2$), 6.96–7.00 (multi, 2H, *m*-NC$_6H_3$(CH$_3$)$_2$, 4H, *o*-P(C$_6H_5$)$_2$, 2H, *p*-P(C$_6H_5$)$_2$, 1H, *o*-PC$_6H_4$N, 1H, *p*-PC$_6H_4$N), 7.01 (t, ^3J(H,H) = 7.2 Hz, 2H, *p*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.22 (multi, 1H, *o*-CH$_2$C$_6H_4$P), 7.24 (d, ^3J(H,H) = 7.2 Hz, 2H, *m*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.26 (d, ^3J(H,H) = 7.2 Hz, 2H, *m*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.30 (t, ^3J(H,H) = 6.8 Hz, 1H, *m*-PC$_6H_4$N), 7.61 ppm (t, ^3J(H,H) = 7.2 Hz, 4H, *m*-P(C$_6H_5$)$_2$). ^{13}C NMR (100 MHz, [D$_6$]benzene, 25°C): δ = 20.55 (s, 2C, —NC$_6$H$_3$(CH_3)$_2$), 24.74 (s, 8C, —NHC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 25.48 (s, 2C, THF), 30.02 (s, 4C, —NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 57.53 (d, ^3J(C,P) = 14 Hz, 1C, —NCH$_2$C$_6$H$_4$P), 72.44 (s, 2C, THF), 116.35 (s, 2C, *p*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 123.41 (s, 1C, *p*-NC$_6H_3$(CH$_3$)$_2$), 123.67 (s, 4C, *m*-NHC$_6H_3$ (CH(CH$_3$)$_2$)$_2$), 127.51 (d, ^2J(C,P) = 2.8 Hz, 1C, *o*-PC$_6H_4$N), 129.32 (s, 2C, *p*-P(C$_6H_5$)$_2$), 129.43 (d, ^2J(C,P) = 8.2 Hz, 4C, *o*-P(C$_6H_5$)$_2$), 129.72 (d, ^3J(C,P) = 6.8 Hz, 1C, *m*-PC$_6H_4$N), 130.39 (s, 2C, *m*-NC$_6H_3$(CH$_3$)$_2$), 130.65 (s, 1C, *p*-PC$_6H_4$N), 132.24 (d, ^3J(C,P) = 7 Hz, 4C, *m*-P(C$_6H_5$)$_2$), 134.32 (s, 1C, *o*-CH$_2$C$_6H_4$P), 134.62 (s, 1C, *ipso*-PC$_6H_4$N), 135.25 (d, ^1J(C,N) = 19.5 Hz, 2C, *ipso*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 135.40 (d, ^1J(C,P) = 15 Hz, 2C, *ipso*-P(C$_6H_5$)$_2$), 137.16 (s, 4C, *o*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 149.93 (d, ^2J(C,P) = 17.5 Hz, 1C, *ipso*-CH$_2$C$_6$H$_4$P), 153.37 (s, 1C, *ipso*-NC$_6H_3$(CH$_3$)$_2$), 155.09 ppm (s, 2C, *o*-NC$_6H_3$(CH$_3$)$_2$). Anal. Calcd for C$_{55}$H$_{69}$N$_3$OPLu: C, 66.45; H, 6.99; N, 4.23. Found: C, 66.21; H, 6.88; N, 4.19.

Lutetium guanidinato complexes 5 and 6

N,*N*′-Diisopropylcarbodiimide (DIPCDI) (0.02 g, 0.16 mmol) in toluene (1 mL) was added to a toluene solution (4 mL) of complex **3** (0.08 g, 0.08 mmol). The reaction mixture was kept stirring for 12 h at room

temperature. Removal of the volatiles afforded oily residue, which was dissolved with hexane (1 mL) and then cooled to −30°C to generate crystals of complex **5**, $L^fLu(N(i\text{-}Pr)C(NHC_6H_3i\text{-}Pr_2\text{-}2,6)N(i\text{-}Pr))_2$ (0.05 g, Yield: 57%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C): δ = 1.24 (d, ^3J(H,H) = 6.4 Hz, 12H, CNCH(CH_3)$_2$), 1.31 (d, ^3J(H,H) = 6.4 Hz, 12H, CNCH(CH_3)$_2$), 1.40 (d, ^3J(H,H) = 6.8 Hz, 24H, NC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 2.09 (s, 6H, NC$_6$H$_3$(CH_3)$_2$), 2.82 (s, 2H, PCH_2CHN), 3.65 (multi, 1H, PCH$_2$C*H*N), 3.82 (multi, 4H, NC$_6$H$_3$(C*H*(CH$_3$)$_2$)$_2$, 4H, CNC*H*(CH$_3$)$_2$), 5.60 (s, 2H, N*H*C$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 6.88 (t, ^3J(H,H) = 7.2 Hz, 1H, *p*-NC$_6H_3$(CH$_3$)$_2$), 6.97 (d, ^3J(H,H) = 7.6 Hz, 2H, *m*-NC$_6H_3$(CH$_3$)$_2$), 7.09 (multi, 2H, *p*-NC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.14 (multi, 2H, *p*-P(C$_6H_5$)$_2$, 2H, *o*-CHC$_6H_5$), 7.19 (d, ^3J(H,H) = 6.8 Hz, 4H, *o*-P(C$_6H_5$)$_2$), 7.22 (td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 2.8 Hz, 4H, *m*-NC$_6H_3$(CH(CH$_3$)$_2$)$_2$), 7.44 (t, ^3J(H,H) = 6.8 Hz, 2H, *m*-CHC$_6H_5$), 7.49 (t, ^3J(H,H) = 7.2 Hz, 2H, *m*-P(C$_6H_5$)$_2$), 7.53 (t, ^3J(H,H) = 7.2 Hz, 2H, *m*-P(C$_6H_5$)$_2$), 8.15 ppm (t, ^3J(H,H) = 8.0 Hz, 1H, *p*-CHC$_6H_5$). ^{13}C NMR (100 MHz, [D$_6$]benzene, 25°C): δ = 19.66 (s, 2C, NC$_6$H$_3$(*C*H$_3$)$_2$), 22.15 (s, 1C, PCH$_2$CHN), 24.32, 24.68 (s, 8C, NHC$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 26.57, 26.78 (s, 8C, CNCH(*C*H$_3$)$_2$), 28.93 (s, 4C, NHC$_6$H$_3$(*C*H(CH$_3$)$_2$)$_2$), 38.09 (s, 1C, PCH$_2$*C*HN), 38.26 (d, ^1J(C,P) = 28 Hz, 1C, P*C*H$_2$CH), 45.74 (s, 4C, CNCH(CH$_3$)$_2$), 122.47 (s, 1C, *p*-N*C*$_6$H$_3$(CH$_3$)$_2$), 123.26 (s, 2C, *p*-P(C$_6H_5$)$_2$), 127.56 (s, 2C, *p*-NC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 127.84 (s, 2C, *o*-CHC$_6H_5$), 128.51 (overlap, 4C, *m*-NC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 129.15 (d, ^2J(C,P) = 9 Hz, 4C, *o*-P(C$_6H_5$)$_2$), 129.39 (s, 2C, *m*-CHC$_6H_5$), 129.77 (s, 2C, *m*-NC$_6$H$_3$(CH$_3$)$_2$), 132.80 (d, ^1J(C,N) = 10 Hz, 2C, *ipso*-NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 133.50, 134.06 (d, ^3J(C,P) = 19 Hz, 4C, *m*-P(C$_6H_5$)$_2$), 136.16 (d, ^1J(C,P) = 16 Hz, 2C, *ipso*-P(C$_6H_5$)$_2$), 137.85 (s, 4C, *o*-NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 144.83, 145.35 (s, 2C, *o*-CHC$_6H_5$), 148.80 (s, 1C, *ipso*-NC$_6$H$_3$(CH$_3$)$_2$), 152.00 (s, 2C, *o*-NC$_6$H$_3$(CH$_3$)$_2$), 160.67 (s, 1C, *ipso*-CHC$_6H_5$), 161.42 ppm (s, 2C, NCN). Anal. Calcd for $C_{70}H_{99}N_7PLu$: C, 67.55; H, 8.02; N, 7.88. Found: C, 67.10; H, 8.05; N, 7.32.

Under the same conditions, reaction of complex **4** with DIPCDI gave complex **6**, $L^rLu(N(i\text{-}Pr)C(NHC_6H_3i\text{-}Pr_2\text{-}2,6)N(i\text{-}Pr))_2$ (Yield: 60%), as colorless crystals. ^{1}H NMR (400 MHz, [D$_6$]benzene, 25°C): δ = 1.23 (d, ^3J(H,H) = 6.0 Hz, 24H, NCH(CH_3)$_2$), 1.33 (d, ^3J(H,H) = 6.8 Hz, 24H, NHC$_6$H$_3$(CH(CH_3)$_2$)$_2$), 2.68 (s, 6H, NC$_6$H$_3$(CH_3)$_2$), 3.71 (multi, 4H, NC*H*(CH$_3$)$_2$, 4H, NHC$_6$H$_3$(C*H*(CH$_3$)$_2$)$_2$), 5.61 (s, 2H, N*H*C$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 5.74 (s, 2H, NCH_2C$_6$H$_4$P), 6.84 (t, ^3J(H,H) = 7.2 Hz, 1H, *p*-NC$_6H_3$(CH$_3$)$_2$), 6.98 (t, ^3J(H,H) = 7.2 Hz, 1H, *m*-PC$_6H_4$C), 7.14 (t, ^3J(H,H) = 7.6 Hz, 1H, *p*-PC$_6H_4$C), 7.20 (multi, 2H, *m*-NC$_6H_3$(CH$_3$)$_2$, 2H, *p*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$, 4H, *m*-NHC$_6H_3$(CH(CH$_3$)$_2$)$_2$, 4H, *o*-P(C$_6H_5$)$_2$, 2H, *p*-P(C$_6H_5$)$_2$), 7.25 (d, ^3J(H,H) = 6.8 Hz, 1H, *o*-CC$_6H_4$P), 7.61 (td, ^3J(H,H) = 7.2 Hz, ^4J(H,H) = 1.6 Hz, 4H, *m*-P(C$_6H_5$)$_2$), 7.69 ppm (multi, 1H, *o*-PC$_6H_4$C). ^{13}C NMR (100 MHz, [D$_6$]benzene, 25°C): δ = 22.79 (s, 2C, NC$_6$H$_3$(*C*H$_3$)$_2$), 24.25 (s, 8C, NHC$_6$H$_3$(CH(*C*H$_3$)$_2$)$_2$), 26.55 (s, 8C, NCH(*C*H$_3$)$_2$), 28.97 (s, 4C, NHC$_6$H$_3$(*C*H(CH$_3$)$_2$)$_2$), 45.90 (s, 4C, NCH(CH$_3$)$_2$), 50.24 (d, ^3J(C,P) = 28 Hz, 1C, NCH$_2$C$_6$H$_4$P), 117.81 (s, 1C, *p*-NC$_6$H$_3$(CH$_3$)$_2$), 124.15 (s, 2C, *p*-NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 126.42 (s, 1C, *m*-PC$_6$H$_4$C), 127.98 (s, 1C, *o*-PC$_6$H$_4$C), 128.50 (overlap, 4C, *o*-P(C$_6H_5$)$_2$, 4C, *m*-NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$,), 129.00 (s, 1C, *o*-CC$_6$H$_4$P), 129.21 (s, 2C, *p*-P(C$_6H_5$)$_2$), 129.47 (s, 1C, *p*-PC$_6$H$_4$C), 129.77 (s, 1C, *ipso*-CC$_6$H$_4$P), 130.55 (s, 2C, *m*-NC$_6$H$_3$(CH$_3$)$_2$), 133.32 (s, 2C, *ipso*-NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 135.01 (d, ^3J(C,P) = 19 Hz, 4C, *m*-P(C$_6H_5$)$_2$), 136.56 (s, 1C, *ipso*-NC$_6$H$_3$(CH$_3$)$_2$), 138.11 (d, ^1J(C,P) = 11 Hz, 1C, *ipso*-PC$_6$H$_4$C), 150.57 (d, ^1J(C,P) = 21 Hz, 2C, *ipso*-P(C$_6H_5$)$_2$), 146.21 (s, 4C, *o*-NHC$_6$H$_3$(CH(CH$_3$)$_2$)$_2$), 155.20 (s, 2C, *o*-NC$_6$H$_3$(CH$_3$)$_2$), 161.32 ppm (s, 2C, NCN). Anal. Calcd for $C_{69}H_{97}N_7PLu$: C, 67.35; H, 7.94; N, 7.97. Found: C, 67.34; H, 7.96; N, 7.97.

Polymerization of DTC

A typical polymerization is carried out in a 25-mL flask equipped with a magnetic stir bar in a glovebox. A solution of DTC (0.65 g, 5 mmol) in toluene (9 mL) was added to a toluene solution of complex **1** (1 mL, 0.02 mol/L, 0.02 mmol). The reaction solution became viscous after stirring for 30 min at 25°C. The polymerization was quenched by adding 1 mL of 5% HCl/EtOH. The polymer (PDTC) was precipitated from ethanol and dried in vacuum at room temperature overnight (97.3%).

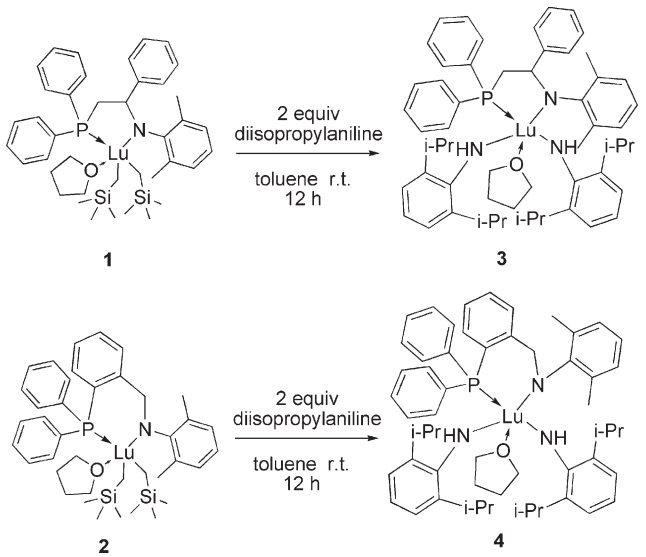
Polymerization in NMR tube

In a typical experiment, complex **2** (0.020 g, 0.025 mmol), 0.5 mL of benzene-d_6 was added to an NMR tube. After dissolution, DTC (0.032 g, 0.250 mmol) was added. The NMR tube was quickly shaken for 5 min and was mounted at 25°C on a Bruker AV300 (FT, 300 MHz for ^{1}H) spectrometer to record ^{1}H NMR spectrum.

RESULTS AND DISCUSSION

Synthesis and characterization of complexes 3–6

Amination reaction between lutetium alkyl complexes **1** and **2** with 2 equiv 2,6-diisopropylaniline afforded the corresponding lutetium bis(amino) complexes **3** and **4** (Scheme 1), respectively. The solid-state structures of **3** (Fig. 1) and **4** (Fig. 2) were characterized by X-ray analysis to be monomers, adopting trigonal-bipyramidal geometry around metal centers. Atoms N(1), N(2), N(3), and Lu are equatorial with Lu lying out 0.1666 Å (**3**) and 0.2149 Å (**4**) above the plane, respectively, whereas atoms P and O locate at the axial positions. The two amino species arrange in *cis*-



Scheme 1 Preparation of complexes **3** and **4**.

positions. The bond distance Lu—N(1) of 2.275(5) Å in **3** is longer than that of 2.179(7) Å in **4** when compared with the corresponding Lu—N single bond values in the literatures.[24,25,27] The N(2)—Lu—N(3) bond angle [**3**: 126.2(2)°, **4**: 119.7(3)°] is larger than that [101.8(3)°] in lutetium bis(amino) complex bearing cyclopentadienyl ligand.[27] In the ^{1}H NMR spectra of **3** and **4**, the resonances arising from the metal alkyl species LuCH_2SiMe_3 at the upfield region could not be observed, instead, a downfield singlet at 4.70 ppm

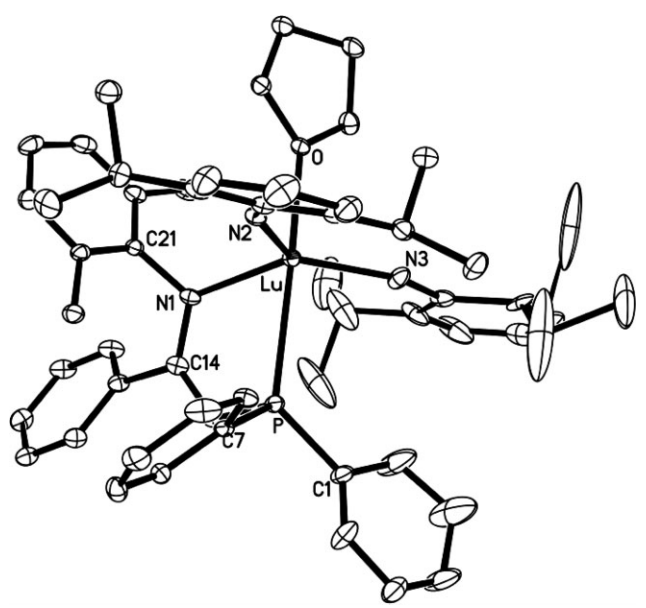


Figure 1 Molecular structure of **3** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (°): Lu—N(2), 2.140(4); Lu—N(3), 2.185(5); Lu—N(1), 2.275(5); N(2)—Lu—N(3), 126.2(2).

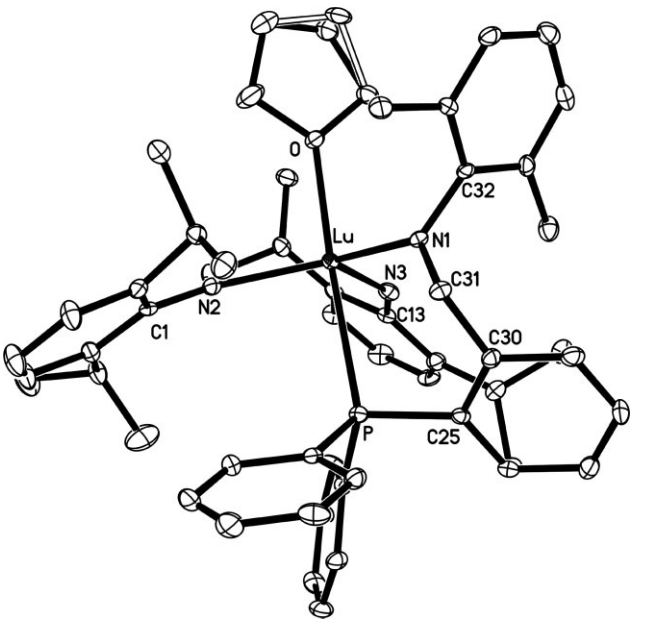
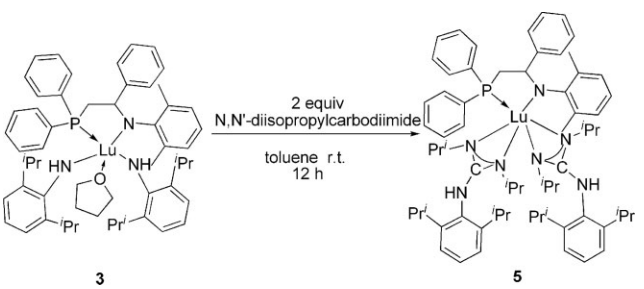


Figure 2 Molecular structure of **4** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (°): Lu—N(1), 2.179(7); Lu—N(3), 2.180(7); Lu—N(2), 2.212(7); N(3)—Lu—N(2), 119.7(3).

showed up, which could be assigned to the amino protons of N*H*C_6H_3(*i*-Pr)$_2$ moieties.

Addition of 2 equiv DIPCDI to a toluene solution of **3** started the reaction immediately. After 12 h, concentrating the reaction solution under reduced pressure followed by dissolving with 1 mL hexane and then cooling at −30°C for several days gave crystals of complex **5** (Scheme 2). In the ^{1}H NMR spectrum of **5**, the resonance of amino proton, N*H*C_6H_3(*i*-Pr)$_2$, shows at 5.60 ppm downfield shift when compared with 4.70 ppm of N*H*C_6H_3(*i*-Pr)$_2$ in complex **3**, owing to the insertion of DIPCDI into the lutetium anino bond. The molecular structure of **5** was figured out eventually by X-ray diffraction analysis to be a heteroleptic monomer (Fig. 3). The Lu ion coordinate to the amino-phosphine ligand via N and P atoms and to the bidentate *N,N*-guanidinato ligands, adopting a twisted octahedron



Scheme 2 Preparation of complex **5**.

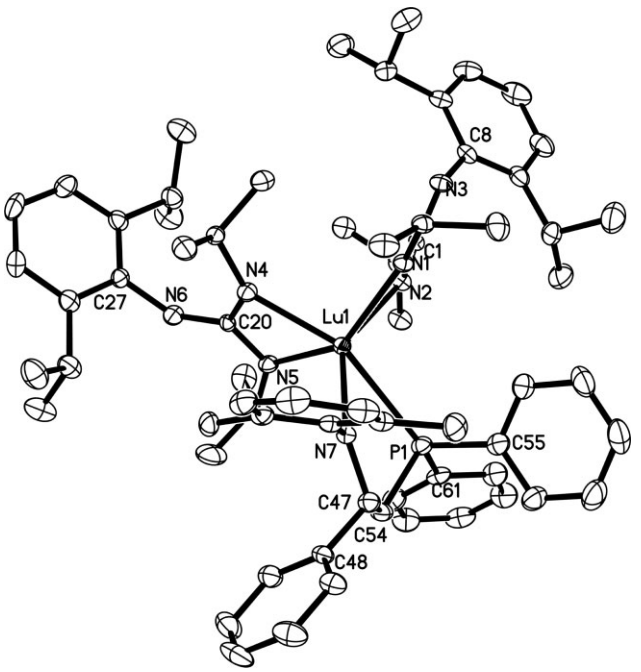
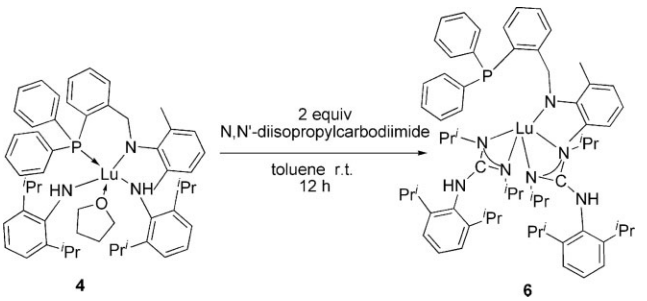


Figure 3 Molecular structure of **5** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (°): Lu(1)—N(7), 2.259(2); Lu(1)—N(5), 2.289(3); Lu(1)—N(4), 2.320(3); Lu(1)—N(2), 2.331(2); Lu(1)—N(1), 2.335(3); N(1)—C(1), 1.356(4); N(2)—C(1), 1.327(4); N(4)—C(20), 1.327(4); N(5)—C(20), 1.347(4); N(5)—Lu(1)—N(4), 57.77(9); N(2)—Lu(1)—N(1), 57.69(9).

geometric metal center. The Lu—N(7) bond length of 2.259(2) Å is longer than the corresponding values in the literatures.[24,25,27,28] The bond distances Lu—N(1) 2.335(3) Å, Lu—N(2) 2.3331(2) Å, Lu—N(4) 2.320(3) Å, and Lu—N(5) 2.289(3) Å are within the reasonable range for a lanthanide–amide interaction,[19,20,29,30] which are longer than those in its precursor. The bond lengths C(1)—N(1) (1.356(4) Å), C(1)—N(2) (1.327(4) Å), C(20)—N(4) (1.327(4) Å), and C(20)—N(5) (1.347(4) Å) are close to each other, shorter than that for C—N single bond but longer than that for C=N double bond. This indicates that π-electrons delocalizes within N—C—N of the guanidinato unit, consistent with the η^2 coordination mode.[31] Following the same procedure, the reaction between complex **4** with DIPCDI afforded complex **6** (Scheme 3). The solid-state structure shows that P atom does not coordinate to Lu ion because of the sterics and the rigidity of backbone between the P and N atoms (Fig. 4).

Polymerization of DTC

These lutetium complexes bearing various initiators and ligands have been attempted to initiate the ROP of DTC. The polymerization results are listed in



Scheme 3 Preparation of complex **6**.

Table I. All initiators induced the polymerization rapidly at 25°C to reach conversions over 95% within 30 min (Table I, entries 2, 4, 6, 8, 10, and 12), which were more active than rare earth calixarene complexes.[17] Among these initiators, the alkyl exhibited similar catalytic activity to the guanidinate, higher than the amide (Table I, entries 1, 5, 9 and 3, 7, 11). This could be attributed to the polarity of Lu—C bond and the weak interaction between metal atom and N atom in guanidinato complexes. In addition, complexes **1**, **3**, and **5** with flexible backbone between P and N atoms of the ligand initiated more rapid polymerization when compared with complexes **2**, **4**, and **6** with rigid backbone ligand (Table I, entries 1, 3, 5, 7, 9, and 11). It is noteworthy that the GPC curves of all polymers were bimodal with each having narrow distribution (Fig. 5). Although this result was different from the

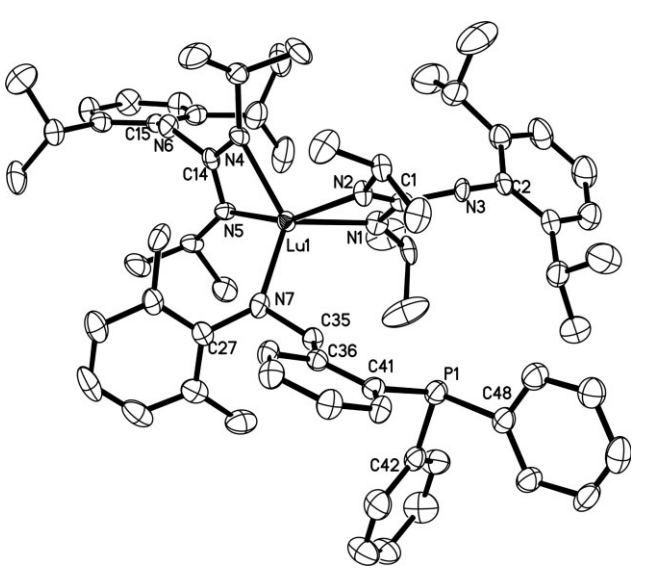


Figure 4 Molecular structure of **6** (hydrogen atoms omitted for clarity; thermal ellipsoids drawn to 50% probability level). Selected bond distances (Å) and angles (°): Lu(1)—N(7), 2.192(8); Lu(1)—N(1), 2.264(8); Lu(1)—N(2), 2.269(8); Lu(1)—N(4), 2.289(8); Lu(1)—N(5), 2.331(7); N(1)—Lu(1)—N(2), 59.8(3); N(4)—Lu(1)—N(5), 59.3(3).

TABLE I
Polymerization of DTC with Various Complexes[a]

Entry	Complex	Time (min)	Yield (%)[b]	M_n $\times 10^{-4}$[c]	PDI	T_m (°C)[d]
1	**1**	10	93.0	1.35; 0.66	1.10; 1.03	n.d.
2	**1**	30	97.3	1.39; 0.68	1.09; 1.04	107.29
3	**2**	10	75.5	1.36; 0.67	1.10; 1.03	n.d.
4	**2**	30	96.9	1.50; 0.71	1.12; 1.04	106.80
5	**3**	15	81.3	0.98; 0.51	1.06; 1.04	n.d.
6	**3**	30	96.4	1.15; 0.57	1.08; 1.04	104.82
7	**4**	15	57.9	0.81; 0.42	1.06; 1.04	n.d.
8	**4**	30	95.8	1.14; 0.54	1.08; 1.07	104.92
9	**5**	15	92.8	1.31; 0.62	1.10; 1.04	n.d.
10	**5**	30	97.8	1.32; 0.63	1.10; 1.05	107.07
11	**6**	15	83.8	1.23; 0.61	1.08; 1.04	n.d.
12	**6**	30	99.6	1.38; 0.66	1.09; 1.04	107.53

[a] Conditions: 25°C; toluene, $[DTC]_0$ = 0.5 mol/L; $[DTC]_0$: [Lu] = 250 : 1.
[b] The polymer yield was determined gravimetrically.
[c] Determined by GPC against polystyrene standard.
[d] n.d., not determined.

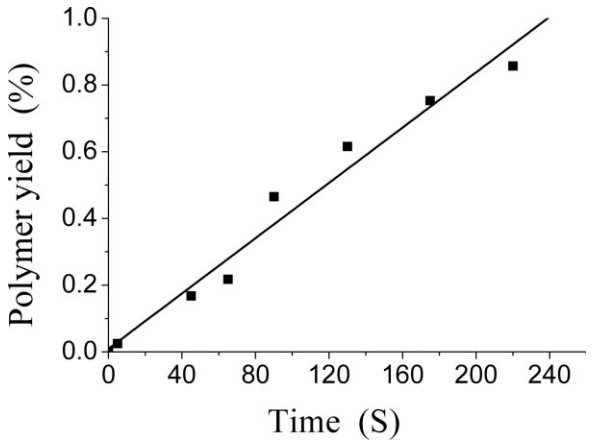


Figure 6 Plot of reaction time versus polymer yield. Conditions: 25°C, toluene, [DTC] = 0.5 mol/L, [DTC] : [Lu] = 250 : 1.

polymerization of DTC initiated by homoleptic rare earth aryloxide complexes,[16] it had once been observed by Hocker and coworkers.[10] The T_m values of these polymers were around 107°C ($\Delta H \approx 16.9$ J/g), which is lower than the literature value because of the low molecular weight.[22,32]

Some kinetic behaviors of the ROP of DTC initiated by complex **2** were investigated. Figure 6 showed a linear relationship (the linear coefficient: 0.969) between the reaction time and the polymer yield. Similarly as depicted in Figure 7, the linear correlation (the linear coefficient: 0.997) of the reaction time with $\ln([M]_0/[M])$ clearly demonstrated that the polymerization reaction was in the first order in monomer (DTC) concentration at ambient temperature while the concentration of catalytic active species kept constant throughout the process. The plots of molecular weights and molecular weight distributions of the polymers versus polymer yields are shown in Figure 8. For each fraction, the molecular weight of polymer increased linearly with the yield, whereas the polydispersity index was narrow and remained constant. These results demonstrated that the polymerization of DTC with this system was in pseudo-living fashion. The different slopes of the two lines suggested the presence of two kinds of active species, which had different rate constants. Thus, the bimodal mode of the molecular weight distribution of PDTC should be attributed to the presence of two initiation sites and not to the cyclic oligomer.[10] This was proved further by the

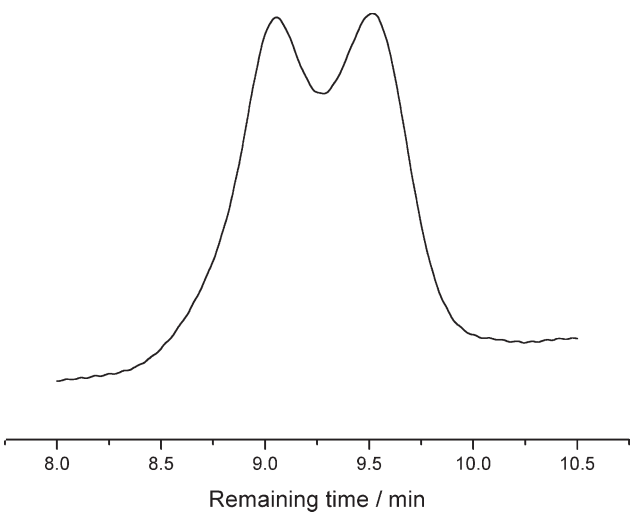


Figure 5 GPC curves of polyDTC initiated by complex **4** (Table I, entry 8).

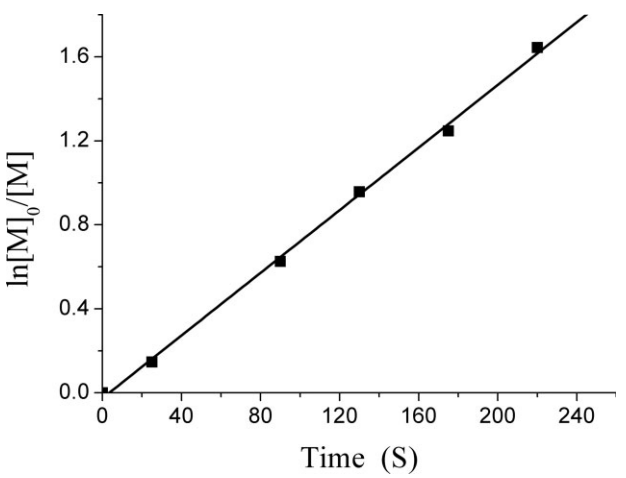


Figure 7 Plot of reaction time versus ln $[M]_0/[M]$. Conditions are the same as Figure 6.

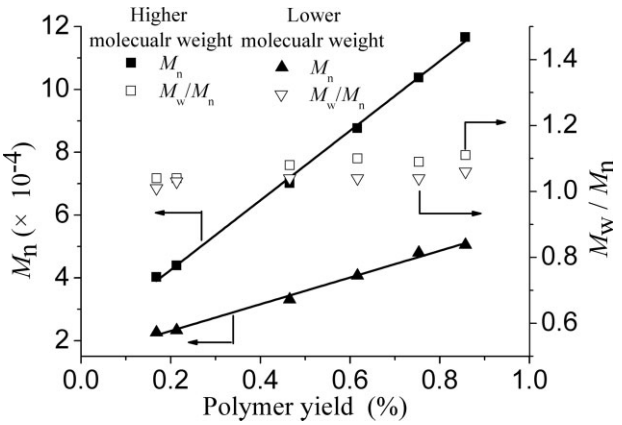


Figure 8 Plot of polymer yield versus M_n and M_w/M_n. Conditions are the same as Figure 6.

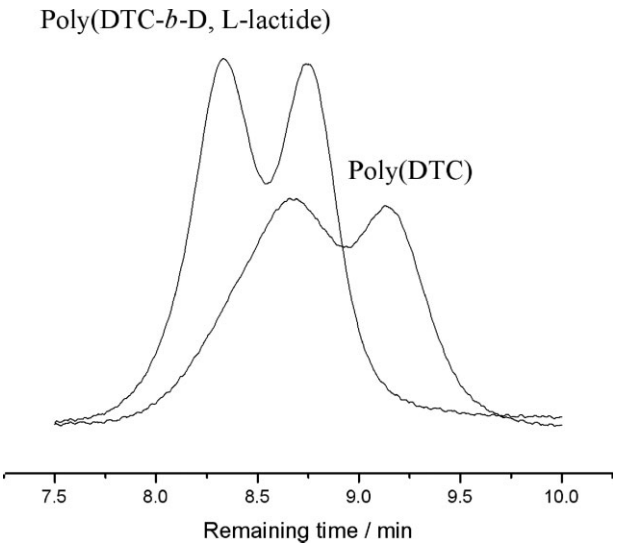


Figure 9 GPC curves of polyDTC and poly(DTC-*b*-D,L-LA) initiated by complex **2**.

result of block copolymerization of D,L-LA with DTC [block copolymerization of D,L-LA with DTC was performed by adding D,L-LA to the polymerization solution of DTC (complex **2** as the initiator)]. The GPC curve of the obtained copolymer remained in the bimodal fashion similar to that of homopolymer PDTC but shifted to the higher molecular weight region (Fig. 9).

Mechanism

To gain some insight into the initiation sites, the oligomeric DTC living species attached to complex **2** in C_6D_6 was monitored by NMR technique. According to the ^{1}H NMR spectrum analysis (Fig. 10), the resonances for the methylene protons of LuOCH_2 (H_h) from **A** were found at 4.28 ppm, whereas a singlet at 1.87 ppm was assigned to the methylene protons of C(O)CH_2Si(CH_3)$_3$ (H_b).[33] Meanwhile for species **B**, broad resonances at 1.33 ppm[24] and a triplet at 1.22 ppm belonged to the methylene protons (H_b' and H_c') of the alkyl group C(CH_3)$_2$CH_2CH_2Si(CH_3)$_3$. In addition, the silylmethyl protons, H_a and H_a', from

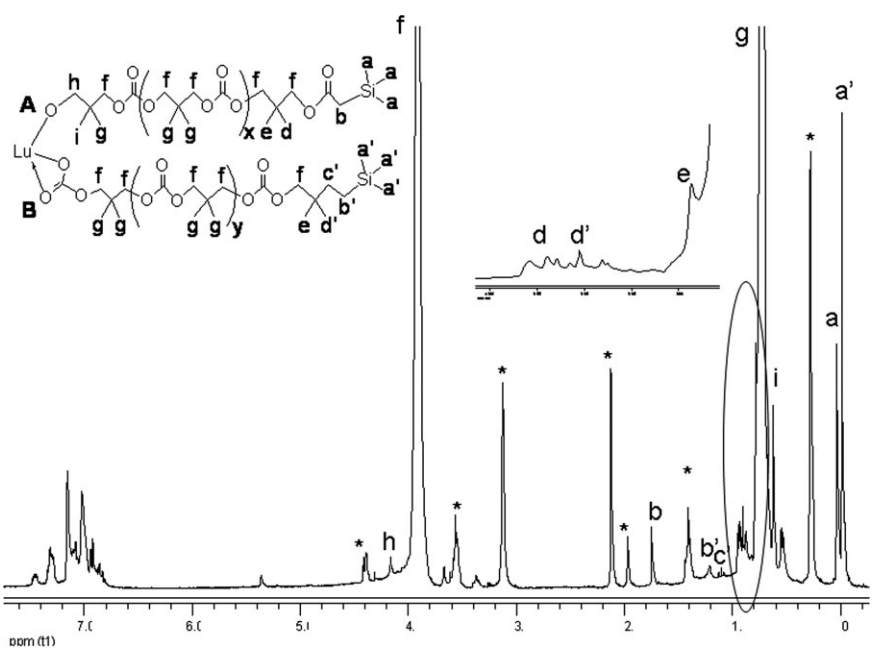


Figure 10 ^{1}H NMR spectrum of the oligomeric DTC living species attaching to complex **2**.

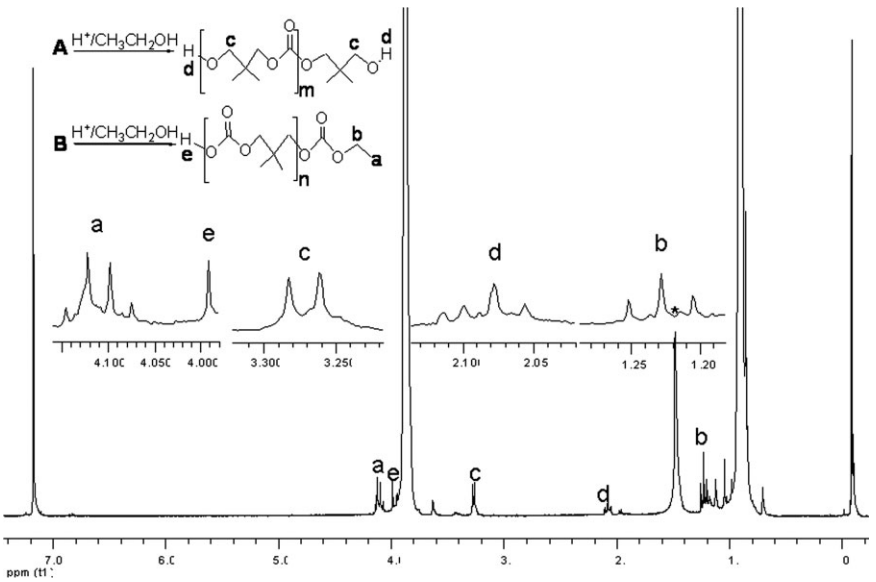
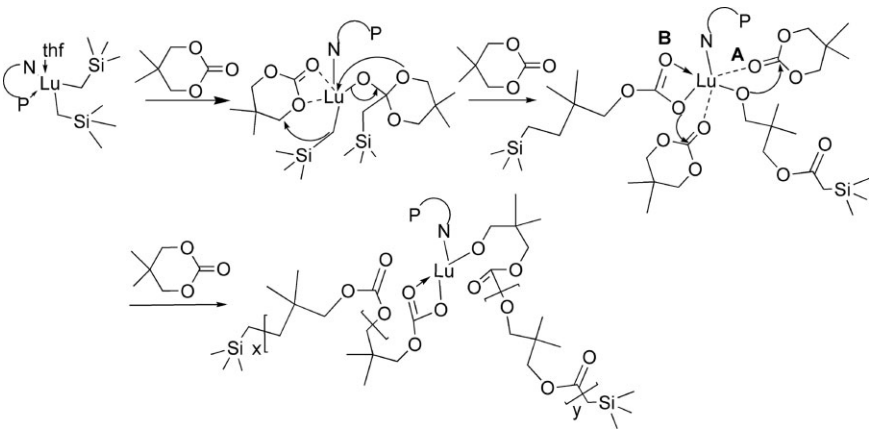


Figure 11 ^{1}H NMR spectrum of PDTC oligomers.

both **A** and **B** exhibited singlets at 0.11 ppm (a) and 0.16 ppm (a′), respectively.

Terminating this oligomeric living species with H^+/CH_3CH_2OH afforded oligomers capped with three types of end groups, which further confirmed the presence of two active sites **A** and **B** in the system (Fig. 11). A singlet at 4.00 ppm[23] was assigned to the end group —OC(O)O*H* (H_e), which was formed by the decomposition of metal oxygen bond of species **B**. The end group —$OC(O)OCH_2CH_3$ was generated by transesterification of the alkoxy end group from **B** with ethanol, which gave the typical triplet–quartet signals at 1.23 ppm (H_a) and 4.11 ppm (H_b). The hydroxyl end group —$C(CH_3)_2CH_2OH$ was generated by the decomposition of metal oxygen bond from species **A** with ethanol. This hydroxyl group could also be formed by the transesterification of acyloxy group from species **A** with ethanol. The doublet signals at 3.27 ppm was assigned to the methylene protons (H_c),[14] whereas the multiresonances at 2.07 ppm were attributed to the hydroxyl proton (H_d).[34]

Thus, the probable mechanism was depicted as follows: the acyl group of DTC inserted into the metal–carbon bond of $LuCH_2SiMe_3$ with the cleavage of acyl–oxygen bond to generate the metal-alkoxy species **A**. The end group was $OOCCH_2Si(CH_3)_3$ (Scheme 4). Another DTC molecule coordinated to the lutetium ion via the two carboxylate oxygen atoms, and then through alkyl–oxygen cleavage, to form the four-membered metallocyclic active species **B**. The end group was $C(CH_3)_2CH_2CH_2Si(CH_3)_3$.



Scheme 4 Probable mechanistic pathway for the ring-opening polymerization of DTC initiated by lutetium alkyl complex **2**.

CONCLUSION

A series of lutetium alkyl, amino, and guanidinato complexes based on amino-phosphine ligand were synthesized and well defined. The catalytic activity toward the ROP of DTC was assayed. The type of the initiator and the flexibility of backbone between P and N atoms of the ligand significantly influenced the catalytic activities of the complexes. There are two distinct initiation sites in each metal center, which initiate the polymerization of DTC in living fashion, respectively, leading to bimodal homo-PDTC.

References

1. Albertsson, A.-C.; Varma, I. K. Adv Polym Sci 2002, 157, 1.
2. Stridsberg, K. M.; Ryner, M.; Albertsson, A.-C. Adv Polym Sci 2002, 157, 42.
3. Vert, M. Biomacromolecules 2005, 6, 538.
4. Albertsson, A.-C.; Varma, I. K. Biomacromolecules 2003, 4, 1466.
5. Andronova, N.; Albertsson, A.-C. Biomacromolecules 2006, 7, 1489.
6. Rokicki, G. Prog Polym Sci 2000, 25, 259.
7. Kricheldorf, H. R.; Rost, S. Macromolecules 2005, 38, 8220.
8. Pego, A. P.; Zhong, Z.; Dijkstra, P. J.; Gripjma, D. W.; Feijen, J. Macromol Chem Phys 2003, 204, 747.
9. Darensbourg, D. J.; Ganguly, P.; Billodeaux, D. Macromolecules 2005, 38, 5406.
10. Wurm, B.; Keul, H.; Hocker, H.; Sylvester, G.; Leitz, E.; Ott, K.-H. Makromol Chem Rapid Commun 1992, 13, 9.
11. Akatsuka, M.; Aida, T.; Inoue, S. Macromolecules 1995, 28, 1320.
12. Schmidt, P.; Keul, H.; Hocker, H. Macromolecules 1996, 29, 3674.
13. Darensbourg, D. J.; Choi, W.; Ganguly, P.; Richers, C. P. Macromolecules 2006, 39, 4374.
14. Takeuchi, D.; Aida, T.; Endo, T. Macromol Rapid Commun 1999, 20, 182.
15. Takeuchi, D.; Aida, T.; Endo, T. Macromol Chem Phys 2000, 201, 2267.
16. Ling, J.; Shen, Z.; Huang, Q. Macromolecules 2001, 34, 7613.
17. Ling, J.; Shen, Z.; Zhu, W. J Polym Sci Part A: Polym Chem 2003, 41, 1390.
18. Ling, J.; Zhu, W.; Shen, Z. Macromolecules 2004, 37, 758.
19. Zhou, L.; Sun, H.; Chen, J.; Yao, Y.; Shen, Q. J Polym Sci Part A: Polym Chem 2005, 43, 1778.
20. Li, C.; Wang, Y.; Zhou, L.; Sun, H.; Shen, Q. J Appl Polym Sci 2006, 102, 22.
21. Yasuda, H.; Aludin, M.-S.; Kitamura, N.; Tanabe, M.; Sirahama, H. Macromolecules 1999, 32, 6047.
22. Tsutsumi, C.; Nakagawa, K.; Shirahama, H.; Yasuda, H. Polym Int 2003, 52, 439.
23. Palard, I.; Schappacher, M.; Belloncle, B.; Soum, A.; Guillaume, S. M. Chem Eur J 2007, 13, 1511.
24. Liu, B.; Yang, Y.; Cui, D.; Tang, T.; Chen, X.; Jing, X. Dalton Trans 2007, 4252.
25. Liu, B.; Cui, D.; Ma, J.; Chen, X.; Jing, X. Chem Eur J 2007, 13, 834.
26. Sarel, S.; Pohoryles, L. A. J Am Chem Soc 1958, 80, 4596.
27. Cameron, T. M.; Gordon, J. C.; Scott, B. L. Organometallics 2004, 23, 2995.
28. Cameron, T. M.; Gordon, J. C.; Michalczyk, R.; Scott, B. L. Chem Commun 2003, 2282.
29. Bambirra, S.; Bouwkamp, M. W.; Meetsma, A.; Hessen, B. J Am Chem Soc 2004, 126, 9182.
30. Bambirra, S.; Leusen, D.; Meetsma, A.; Hessen, B.; Teuben, J. H. Chem Commun 2003, 522.
31. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. J Chem Soc Perkin Trans 2 1987, S1.
32. Ling, J.; Shen, Z. Macromol Chem Phys 2002, 203, 735.
33. Cui, D.; Nishiura, M.; Hou, Z. Macromolecules 2005, 38, 4089.
34. Ma, H.; Okuda, J. Macromolecules 2005, 38, 2665.