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Methacrylate Polymerization using a Dinuclear Zirconocene Initiator: A New Approach for the Controlled Synthesis of Methacrylate Polymers

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EXPERIMENTAL

General Experimental

All manipulations of air-sensitive compounds were performed using standard Schlenk techniques, under a dry N_2 atmosphere.[1] All air-sensitive compounds were weighed and stored in an Innovative Technology Glovebox filled with N_2. All glassware was either flamed dried in vacuo or dried in an oven overnight at 130 °C prior to use. All solvents and chemicals were purchased from commercial sources and purified as outlined below.

Tetrahydrofuran (THF), diethyl ether, dichloromethane, hexane and toluene were purified and dried by passing through activated La Roche A-2 Alumina (12 x 32 mesh) and Engelhard CU-0226s (Q-5) catalyst under N_2 prior to use.[2] For all polymerization reactions, dichloromethane and THF were further dried by distillation from P_2O_5 and Na/benzophenone, respectively. Iso-octane was dried by distillation from sodium. Di-isopropylamine was dried by distillation from CaH_2.

Prior to use, *n*-butyllithium was titrated using 1,3-diphenylacetone *p*-tosylhydrazone as an indicator.[3] *N*,*N*-Dimethylanilinium tetrakis(pentafluorophenyl) borate, was donated by BFGoodrich Co. Ltd. and purified further by washing with toluene and drying *in vacuo*. Tris(pentafluorophenyl)borane was donated by Nova Chemicals Ltd. and was purified by recrystallization from hexane solution. The compounds $(Cp_2ZrCl)_2O$ (**5**),[4] $(Cp_2ZrMe)_2O$,[5]

$LiOC(O^tBu)=CMe_2$,[6] and $Cp_2Zr[OC(O^tBu)=CMe_2]_2$ (**10**)[7] and were prepared by literature methods.

Methyl methacrylate was purified by methods outlined by Allen *et al.*[8] Methyl methacrylate was dried over CaH_2 under N_2 for 24 h prior to distillation under vacuum. The monomer was then diluted with dry toluene and further purified by titration with $AlEt_3$/toluene mixture (1 g/10 mL) until a pale yellow endpoint was reached and then more $AlEt_3$/toluene was added to ensure complete elimination of impurities (such as alcohols). This yellow solution was vacuum distilled at 3 mmHg to give a stock solution of MMA in toluene (3.33 M) which was used for all polymerization experiments in toluene (see Table). Titration of this stock solution to a pale yellow end-point with the same solution of $AlEt_3$/toluene indicated a residual impurity level of 8.7_5 mM expressed as OH. For polymerization experiments in CH_2Cl_2, the same procedure was used but the monomer was not diluted with toluene prior to distillation from $AlEt_3$; the toluene content of the purified monomer was determined by ^1H NMR spectroscopy.

All deuterated solvents for NMR studies were dried prior to use. Dichloromethane-d_2 was distilled from P_2O_5 and pyridine-d_5 from CaH_2 under N_2. Tetrahydrofuran-d_8, benzene-d_6, and toluene-d_8 were distilled from Na/benzophenone while bromobenzene-d_5 was distilled from Na under N_2.

All ^1H, ^{13}C and ^{19}F NMR spectra were acquired using a Varian Mercury or Gemini 300 MHz NMR spectrometers. All variable temperature NMR studies were conducted using a Varian Inova 400 MHz spectrometer.

^{1}H NMR spectra were referenced to the residual proton impurities in the deuterated solvents and for ^{13}C NMR spectra relative to the deuterated solvent. The ^{19}F NMR spectra were referenced to an internal standard, 2,3,5,6-tetrafluoro-p-xylene (-145.67 ppm, CD_2Cl_2). For variable temperature NMR studies, the temperature was calibrated using neat MeOH.

Elemental analyses were performed by Galbraith Laboratories Inc., Tennessee. Mass spectra were recorded on a Micromass GCT Time of Flight mass spectrometer with an electron impact (EI) ionization energy of either 30 or 70 eV. Infrared spectra were recorded on an ATI Mattson Genesis Series FT-IR spectrometer with sample conditions as indicated with each spectra. The mineral oil used for IR was stirred over Na and distilled under reduced pressure prior to sample preparation.

Gas chromatography (GC) was used to monitor the kinetics of the polymerization. The gas chromatograph was a HP 5890 Series II. The GC conditions are as follows: 30 m x 0.32 mm Restek Rtx-5amine column, 30 °C/2.5 min to 200 °C/10min @ 20 °C/min.

Matrix-Assisted Laser Desorption Time of Flight (MALDI-TOF) mass spectra were recorded on a desorption/ionization mass spectrometer with a time-of-flight mass analyzer (Bruker Daltonics, Billerica, MA, USA). The instrument was equipped with a LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion source and a two-stage grid-less reflector. Solutions of dithranol (20 mg/ml) (Fluka, 1,8,9-anthracenetriol, 99%), sample (10 mg/ml),

and sodium trifluoroacetate (10 mg/ml) (Aldrich, 98%) were prepared in tetrahydrofuran (Aldrich, 99.9%). These solutions were mixed in the ratio matrix:cationizing salt:polymer (5:1:2), and 0.5 μL of the solution was deposited on the sample holder and allowed to dry.

Synthesis of Bisenolate Zirconocene Complex **6a** (R=Me)

Diisopropylamine (1.3 mL, 9.3 mmol) was dissolved in 10 mL of dry THF and cooled to -78 °C in a 250 mL round bottom flask. A 1.85 M n-butyllithium solution in hexane (4.9 mL, 9.1 mmol) was added to this solution which was then allowed to warm to room temperature. After stirring for 1 hr at 25 °C, this solution was cooled to −78 °C and methyl isobutyrate (1.05 mL, 9.2 mmol, distilled from CaH_2) was slowly added by syringe. The resulting solution was warmed to 0 °C and stirred for 1 h. Next, at 0 °C, a solution of complex **5** (2.2 g, 4.2 mmol) in 50 mL THF was added by syringe drop wise to the solution and the solution was allowed to warm up to 25 °C over a 1 h and then stirred additionally for 1 h at 25 °C. Next, iso-octane (20 mL) was added to the solution and a precipitate formed. The solvent was reduced to 20 mL *in vacuo* and then 20 mL hexane was added and the solution was filtered under N_2. After washing the lithium chloride with hexanes, approximately 40 mL of toluene was added to the filtrate so that the ratio was 1:1:2 iso-octane:hexane:toluene and this mixture was placed in the freezer at −30 °C in the glovebox. The product was isolated as a yellow-orange precipitate and this was filtered cold and washed with cold hexane. Yield (83%, 2.5 g) ^{1}H NMR

(300 MHz, C_6D_6) δ 6.12 (s, 20*H*, Cp), 3.51 (s, 6*H*, O*Me*), 1.98 (s, 6*H*, =C*Me*$_2$), 1.81 (s, 6*H*, =C*Me*$_2$) ^{13}C NMR (75 MHz, C_6D_6) δ 159.94 (-O*C*(OMe)=CMe$_2$), 113.52 (*Cp*), 82.76 (=*C*Me$_2$), 56.71 (=O*Me*), 18.37 (=C*Me*$_2$), 17.48 (=C*Me*$_2$) IR (Nujol) 1678 (w), 1258 (w), 1212 (w), 1184 (v.w), 1140 (v.w), 1017(v.w), 793 (w), 720 (w) cm $^{-1}$ Elemental Analysis for $C_{30}H_{38}O_5Zr_2$; Calculated: C: 54.48 H: 5.80 Found: C: 54.01 H: 5.76.

Synthesis of Bisenolate Zirconocene Complex **6b** (R = *t*-butyl)

Zirconocene complex **5** (4.00 g, 7.6 mmol) was added to a dry 250 mL flask and 150 mL of dry THF was then added. In a separate 250 mL flask, the lithium enolate of *t*-butyl isobutyrate (2.61 g, 17 mmol) was dissolved in 50 mL of dry THF and stirred until completely dissolved. At room temperature, the solution of **5** was added to the lithium enolate over 1 h by syringe. The resulting mixture was allowed to stir for 3 hours at room temperature. Work up involved pumping off the THF *in vacuo* to dryness leaving a yellowish residue and then taking up the residue in 30 mL of toluene and filtering off the lithium chloride. Next, hexanes (30 mL) were added the filtrate and the mixture was put into the freezer at −30 °C for 2 days. The yellowish-white product precipitated out and was washed with hexanes and dried *in vacuo*. Yield (4.37 g, 78%) ^{1}H NMR (300 MHz, C_6D_6) δ 6.20 (s, 20*H*, *Cp*), 1.94 (s, 6*H*, =C*Me*$_2$), 1.82 (s, 6*H*, =C*Me*$_2$), 1.41 (s, 9*H*, -C*Me*$_3$) ^{13}C NMR (75 MHz, C_6D_6) δ 157.24 (-O*C*OCMe$_3$), 113.37 (*Cp*), 88.11

(-OCMe_3), 78.00 (=CMe_2), 30.14 (-OCMe_3), 19.85 (=CMe_2), 19.26 (=CMe_2) IR (Nujol) 1667 (w), 1364 (v.w), 1260 (w), 1210 (w), 1169 (w), 1144 (w), 1128 (w), 1015 (v.w), 864 (v.w), 797 (m), 715 (m), 686 (w), 612 (v.w), 580 (v.w) Mass Spectrum (Electron Impact): *m/z* 742 (M+, $C_{36}H_{50}O_5Zr_2$) Elemental Analysis for $C_{36}H_{50}O_5Zr_2$; Calculated: C: 58.01 H: 6.76 Found: C: 58.23 H: 6.71.

Crystals for X-ray analysis were obtained by dissolving 50 mg of complex **6b** in minimal toluene and then adding hexanes to obtain a 1:1 mixture and placing this resulting mixture in a −30 °C freezer in the dry box. The resulting crystals were yellowish prisms. A crystal of dimensions 0.22 x 0.21 x 0.18 mm was mounted on the goniometer head of a Bruker/AXS Apex 3000 CCD diffractometer equipped with an Oxford Cryostream LT at 180 K, and data was collected using □ frames. From 44,003 total reflections collected [2θ(max) = 60.0 °], 10,228 were unique (R_{int} = 0.038). The structure was solved using direct methods and refined by full-matrix, least-squares methods based on F^2 (SHELXTL-IRIX). Final $R(F)$ and $\omega R(F^2)$ were 0.0264 and 0.0525 with maximum residuals of 0.373 and −0.344 e $Å^{-3}$. Complete crystallographic and refinement data are shown in Tables S2-S6.

In situ Generation of Cationic Enolate Complex **8** (R = *t*-butyl)

A. In THF-d_8 solution at 25 °C

In a 5 mm NMR tube, complex **6b** (25 mg, 33.5 μmol) was dissolved in 0.25 mL of THF-d_8. In a separate vial, [PhNHMe_2][B(C_6F_5)$_4$] (27 mg, 33.6 μmol) was weighed and dissolved into 0.25 mL THF-d_8. Next, at

room temperature, the salt solution was added dropwise to complex **6b** in the NMR tube and the color changed from pale yellow to bright yellow. The NMR tube was shaken several times and the spectrum was recorded at 25 °C. ^{1}H NMR (300 MHz, THF-d_8) δ 6.65 (s, 10*H*, *Cp*), 6.41 (s, 10*H*, *Cp*), 1.70 (s, 3*H*, ZrOC(O^{t}Bu)=C*Me*$_2$), 1.66 (s, 3*H*, ZrOC(O^{t}Bu)=C*Me*$_2$), 1.36 (s, 9*H*, ZrOC(O^{t}*Bu*)=CMe$_2$) ^{13}C (75 MHz, THF-d_8, -40 °C) δ 156.92 (ZrO*C*O^{t}Bu=CMe$_2$), 148.99 (dm, J = 240 Hz, *m*-*C*, B(*C*$_6$F$_5$)$_4^-$), 139.08 (dm, J = 245 Hz, *p*-*C*, B(*C*$_6$F$_5$)$_4^-$), 137.05 (dt, J = 248 Hz, *o*-*C*, B(*C*$_6$F$_5$)$_4^-$), 125.06 (br m, ipso *C*, B(*C*$_6$F$_5$)$_4^-$), 116.54 (s, *Cp*), 114.85 (s, *Cp*), 88.97 (s, ZrOCO(C(CH$_3$)$_3$)=*C*Me$_2$), 78.79 (s, ZrOCO(*C*(Me$_3$)=CMe$_2$), 29.85 (s, ZrOC(O(C(*C*H$_3$)$_3$))=CMe$_2$), 19.48 (s, ZrOCO(C(CH$_3$)$_3$)=C*Me*$_2$), 18.95 (s, ZrOCO(C(CH$_3$)$_3$)=C*Me*$_2$) ^{19}F NMR (288 MHz, THF-d_8) δ -167.30 (m, *m*-*F* (B(C$_6$*F*$_5$)$_4^-$)), -163.81 ((t, J = 19.6 Hz, *p*-*F* (B(C$_6$*F*$_5$)$_4^-$)), -131.63 (m, *o*-*F* (B(C$_6$*F*$_5$)$_4^-$)). These spectra are depicted in Figures S-1 to S-3, respectively.

B. In CD_2Cl_2 solution at -40 °C

In a glovebox, a 5 mm septum-capped NMR tube was charged with bisenolate complex **6b** (22.3 mg, 0.030 mmol) in 0.5 mL CD_2Cl_2. To this solution was added 12.1 μL of THF (5 equiv.) and the mixture was stirred. In a separate 1.0 mL vial was added [PhNHMe$_2$][B(C$_6$F$_5$)$_4$] (24.0 mg, 0.030 mmol) in 0.5 mL CD_2Cl_2. Next, both the tube and vial were taken outside the glove box and the solution of complex **6b** was cooled in a bath of dry ice/acetonitrile to -40 °C. Next, the solution of [Me$_2$PhNH][B(C$_6$F$_5$)$_4$] was added drop wise over 10 min, by syringe. The

solution changed from pale yellow to bright yellow and the NMR tube was transferred to the NMR spectrometer at −40 °C with vigorous shaking to mix. ^{1}H NMR spectra revealed complete consumption of **6b** in ≤ 30 min at −40 °C. Above −20 °C, complex **8** began to decompose with liberation of i-butene. ^{1}H NMR (400 MHz, CD_2Cl_2, -40 °C) δ 6.48 (s, 10*H*, *Cp*), 6.29 (s, 10*H*, *Cp*), 1.62 (s, 6*H*, ZrOC(O^{t}Bu)=C*Me*$_2$), 1.39 (s, 9*H*, ZrOC(O^{t}*Bu*)=CMe$_2$).

Synthesis of $[(Cp_2Zr)_2(\mu\text{-}^{i}PrCO_2)(\mu\text{-}O)][B(C_6F_5)_4]$ (**9**)

To a dry 50 mL flask, complex **6b** (120 mg, 0.161 mmol) was dissolved into 3 mL of CH_2Cl_2 and in another dry flask (25 mL), $[PhNHMe_2][B(C_6F_5)_4]$ (129 mg, 0.161 mmol) was dissolved into 3 mL of CH_2Cl_2. Next, at room temperature, the $[Me_2PhNH][B(C_6F_5)_4]$ solution was added to complex **6b** dropwise, via syringe. An initial bright yellow solution was observed followed by a rapid change to a colorless solution with gas evolution. This solution was stirred for 1 hour at room temperature. The resulting solution was pumped down to dryness *in vacuo* and taken up in dry CH_2Cl_2 (3 mL). To this concentrated solution was added hexane (3 mL) and the resulting mixture was allowed to crystallize, at room temperature, overnight. The product was isolated as colorless crystals. Yield (166 mg, 81%) ^{1}H NMR (300 MHz, CH_2Cl_2) δ 6.50 (s, 20*H*, *Cp*), 2.71 (septet, J = 7 Hz, 1*H*, -C*H*Me$_2$), 1.24 (d, J = 7 Hz, 6*H*, -CH*Me*$_2$) ^{13}C (75 MHz, CD_2Cl,) δ 194.26 (O*C*OCHMe$_2$), 148.71 (dm, J = 250 Hz, *o-C* (B(*C*$_6$F$_5$)$_4$)), 138.83 (dm, J = 252 Hz, *p-C* (B(*C*$_6$F$_5$)$_4$)), 136.81 (dm, J = 246 Hz, *m-C* (B(*C*$_6$F$_5$)$_4$)),

124.29 (br m, ipso *C* ($B(C_6F_5)_4$)), 116.04 (*Cp*), 37.16 (-*C*HMe_2), 19.13 (-$CH(CH_3)_2$) ^{19}F NMR (288 MHz, CD_2Cl_2, standard (tetrafluoro-*p*-xylene, -145.68 ppm) δ -166.92 (m, *m-F* ($B(C_6F_5)_4^-$)), -163.09 (t, J = 19.6 Hz, *p-F* ($B(C_6F_5)_4^-$)), -132.53 (m, *o-F* ($B(C_6F_5)_4^-$)) IR (Nujol) 1643 (m), 1513 (s), 1299 (m), 1273 (m), 1083 (s), 1015 (m), 975 (s), 814 (s), 694 (s), 661 (m) cm^{-1}. Analysis calc'd for $C_{48}H_{27}BF_{20}O_3Zr \cdot CH_2Cl_2$: C 48.29; H 2.40. Found: C 48.06; H 2.22.

Single crystals were obtained by crystallization from dichloromethane and hexane. Although data collection, structure solution and refinement was attempted [Monoclinic, Space group $C_{2/c}$, a = 21.062(1), b = 12.565(1) c = 18.649(1) Å, β = 90.55(1)°, R_1 = 0.0622 for 5270 reflections with I > 2σ(I)] the dinuclear cation is disordered positionally with respect to both metals, Cp rings and bridging groups across a center and the ^{i}Pr group of the carboxylate moiety was disordered with a CH_2Cl_2 molecule in a manner that could not be satisfactorily modeled. The perfluorophenylborate anion is perfectly ordered.

Polymerization of MMA with initiators **6b** or **10** and **7**

Stock solutions of $[Me_2PhNH][B(C_6F_5)_4]$ (**7**, 240 mg, 0.30 mmol) in 10.0 mL of 3.33 M MMA in toluene and enolate **6b** (101 mg, 0.20 mmol) in 10.0 mL toluene were prepared in the glove-box in 20.0 mL vials capped with septa. Both vials were removed from the glove-box and were cooled to the reaction temperature under N_2. To a separate 20.0 mL vial containing a spin bar and septum was added 1.60 mL of the salt solution via syringe. To this solution was added 2.25 mL of the

pre-cooled enolate solution with vigorous stirring. After the time indicated, the solution was quenched by addition of MeOH. The polymer was precipitated into hexanes, dried *in vacuo* at 100 °C for 24 hours, weighed and characterized by ^{1}H NMR spectroscopy and GPC. The results are summarized in the Table while a MALDI-TOF spectrum of PMMA prepared using a 10:1 ratio of MMA to **6b** at –20 °C is shown in Figure S-4.

Essentially similar procedures were followed using complex **10** and **7**.

Kinetic Experiments involving pre-formed enolate complex **8**

The kinetic experiments were set up in the following manner: A stock solution of initiator **8** in CH_2Cl_2 (30 mM) was prepared at – 40 °C as follows:

In a glovebox, a 50 mL flask was charged with bisenolate complex **6b** (223 mg, 0.299 mmol) in 5 mL CH_2Cl_2. To this solution was added 121 μL of THF (5 equiv.) and the mixture was stirred. In a separate 10 mL flask was added $[PhNHMe_2][B(C_6F_5)_4]$ (240 mg, 0.299 mmol) in 5 mL CH_2Cl_2. Next, both flasks were taken outside the glovebox and the solution of complex **6b** was cooled in a bath of dry ice/acetonitrile to obtain an internal temperature of –40 °C. Next, the solution of $[Me_2PhNH][B(C_6F_5)_4]$ was added drop wise over 10 min, by syringe. The solution changed from pale yellow to bright yellow. This solution was allowed to stir for an additional 30 min at –40 °C.

A solution of MMA in CH_2Cl_2 (15 mL of 3.11 M) containing 0.5 mL of *n*-decane as an internal standard was prepared and titrated to a pale yellow endpoint with a solution of $AlEt_3$ in toluene (40-50 μL of a 1.0 M solution). This procedure[7] was found to not affect the kinetics, polymer microstructure or MWD etc. but did allow the use of lower (< 10 mM) initiator concentrations in CH_2Cl_2.

To three separate vials labeled 1, 2 and 3 were added 4.5, 4.0 and 3.5 mL, respectively, of the monomer stock solution. All these vials were then cooled to – 20 °C under N_2. Then 0.5, 1.0 and 1.5 mL of the initiator solution were added to vials 1, 2 and 3, respectively rapidly via syringe with effective stirring.

Aliquots (0.1 mL) were extracted at various times with 1 mL disposable syringes and quenched into 2.5 mL of wet hexanes. The samples were stored in the freezer at – 20 °C prior to GC or GPC analysis. The time/conversion data for various [**8**] are summarized in Table S-1 and a plot of M_n and M_w/M_n vs. conversion for [**8**] = 6 mM appears in Figure S-5.

Polymer Characterization

The polymers were characterized by ^1H NMR spectroscopy. ^1H NMR samples were prepared in 5 mm NMR tubes with approximately 5 mg of polymer in 0.5 mL of $CDCl_3$.The spectra were recorded on a 300 MHz Varian NMR spectrometer. The tacticity was determined by the integration of the triads (% mm, % mr, % rr) methyl signals in the NMR spectra at δ 1.22, 1.03 and 0.87.

The polymer molecular weights were analyzed using a Waters 510 GPC equipped with a multi-angle light scattering (MALLS) detector (Wyatt Tech. LS Dawn EOS), differential viscometer (Viscotek Model 110) and refractive index detectors (Waters 410). The software used for data collection and analysis was Viscotek Tri-Sec and column calibration was performed using polystyrene standards. Three 7.8 x 300 mm Styragel (mixed bed) columns were used. The software used for the collection and analysis of multi-angle light scattering data was Astra (Wyatt Tech.). PMMA standard samples from Polymer Laboratories LTD (U.K), one with low molecular weight of 1.97×10^4 and PDI = 1.09 and one with high molecular of 1.85×10^5 g/mol and PDI = 1.11 were analyzed and found to be fairly accurate and within 10 % error (Low $M_w = 1.95 \times 10^4$ with PDI = 1.07, High $M_w = 1.89 \times 10^5$ with PDI = 1.02). These analyses were preformed at 25 °C and THF was used as the eluent at a flow rate of 1.0 mL/min.

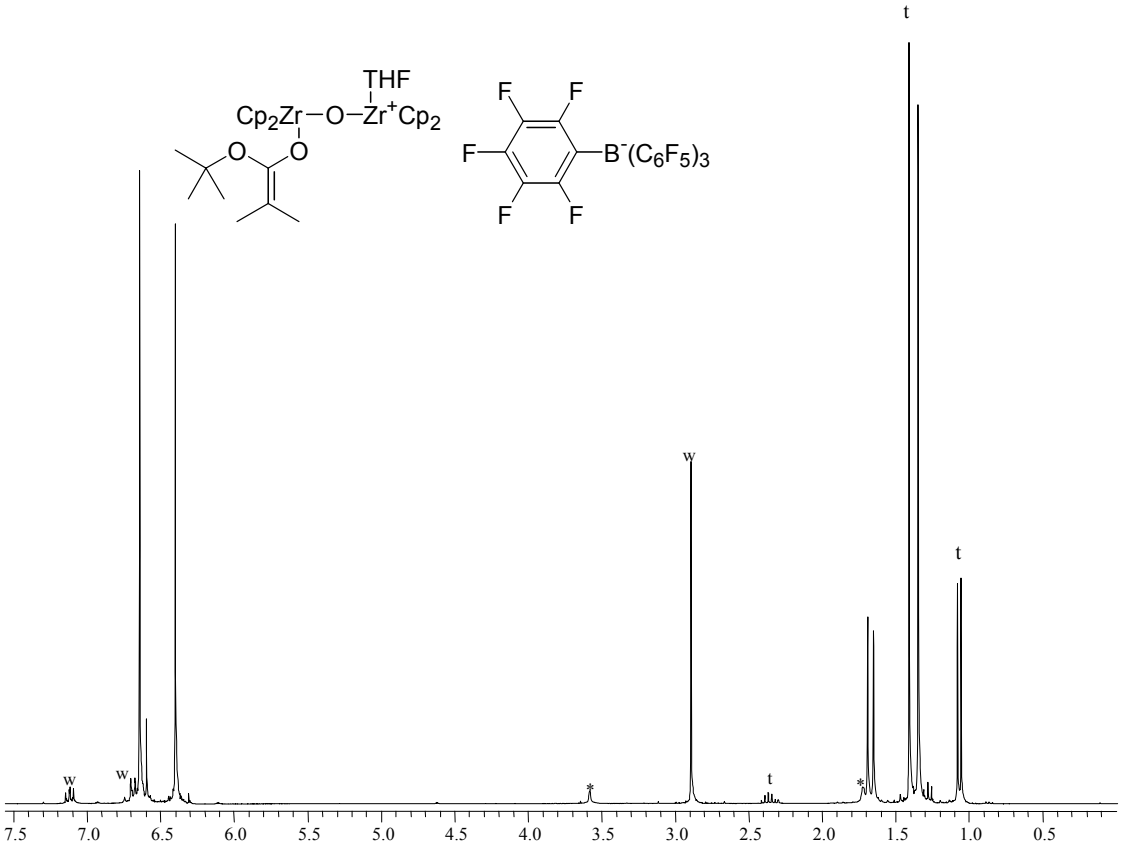

Figure 1 ^{1}H NMR spectrum (300 MHz, THF-d_8) for complex **8** at 25 °C. Signals marked with t correspond to free *t*-butyl isobutyrate, and w for free *N,N* dimethylaniline.

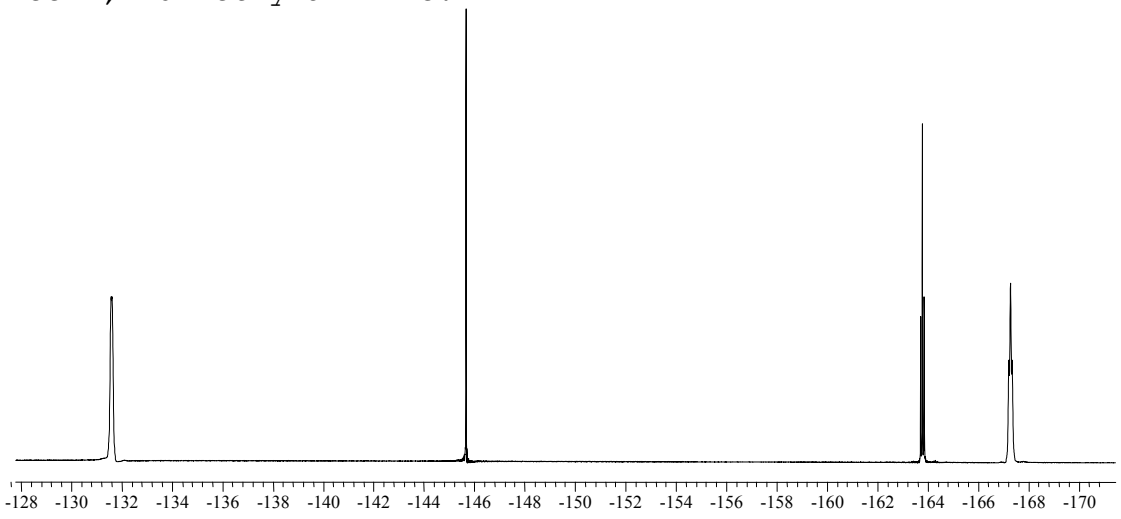

Figure 2 ^{19}F NMR spectrum (282 MHz, THF-d_8) for complex **8** at 25 °C referenced to 2,3,5,6-tetrafluoro-p-xylene at −145.69 ppm.

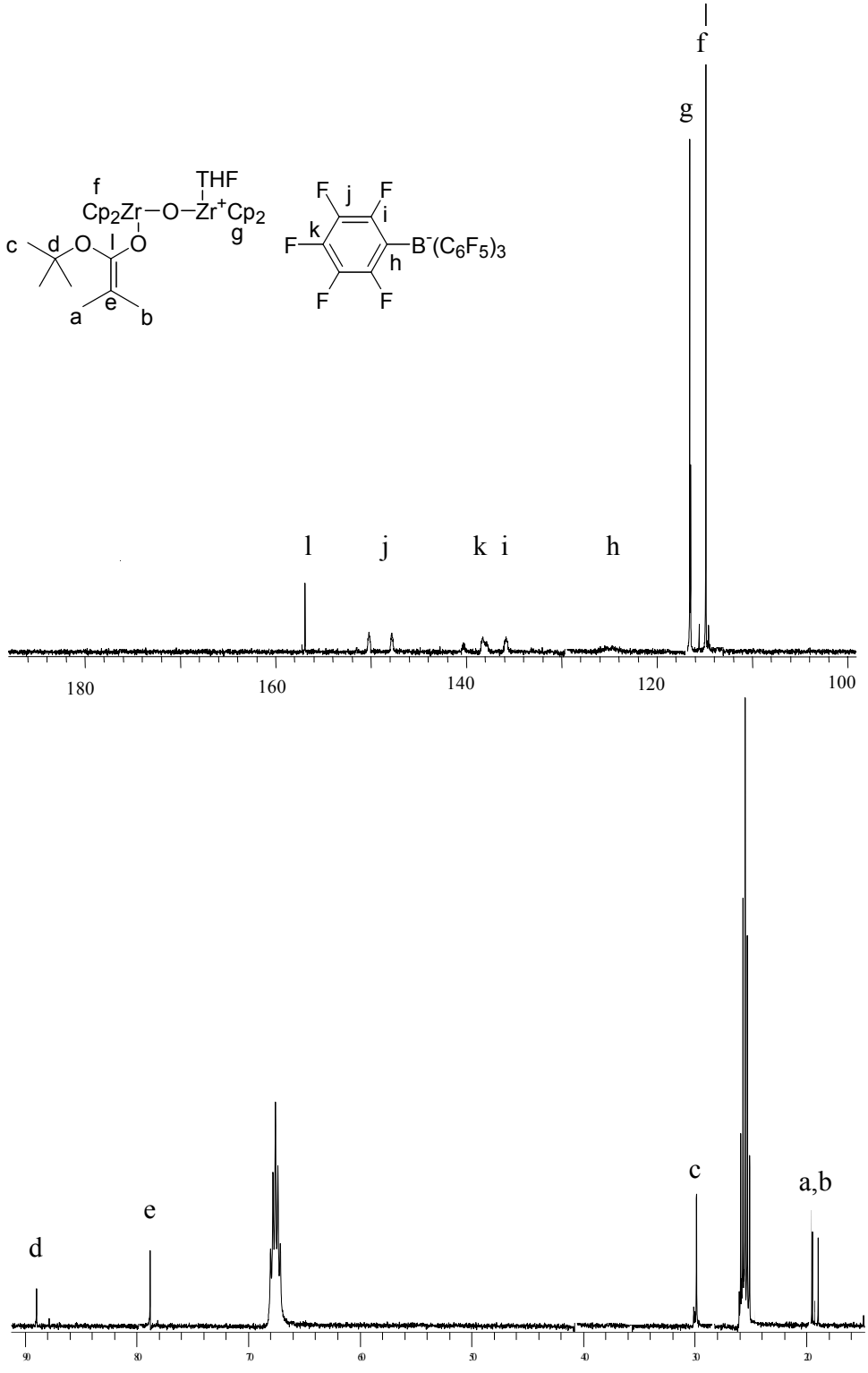

Figure 3.^{13}C NMR spectrum (75 MHz, THF-d_8) for complex **8** at –40 °C. Expanded regions a) 160 –110 ppm b) 90 – 15 ppm (signals for *t*-butyl isobutyrate, and *N,N* dimethylaniline have been *edited out* for clarity).

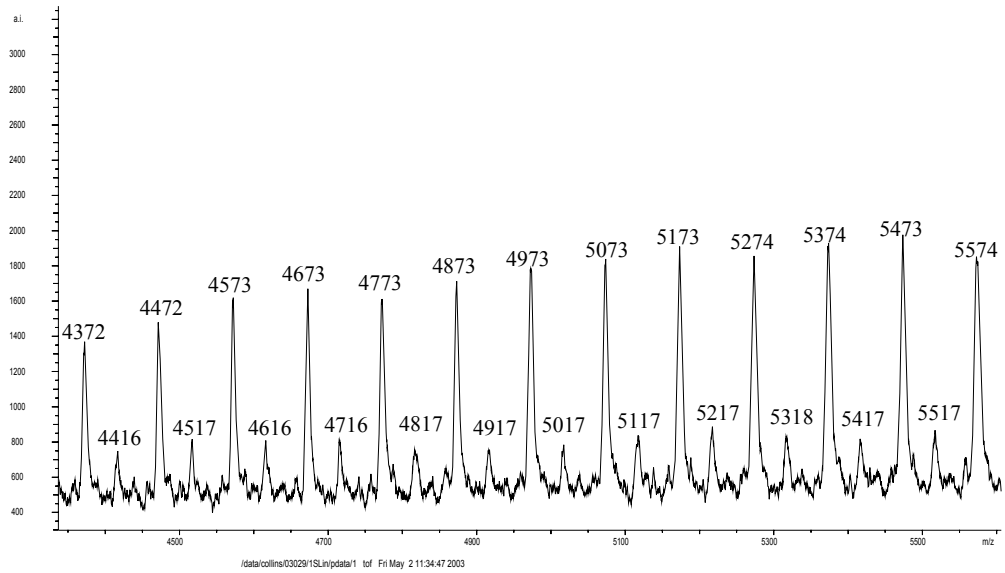

Figure 4 MALDI-TOF mass spectrum (linear mode) of pMMA prepared using initiator **6b** with [MMA]:[**6b**] = 10:1 using CF_3CO_2Na and dithranol matrix. The major set of peaks corresponds to the formula $^tBuO_2CCMe_2$-$(MMA)_n$-H.

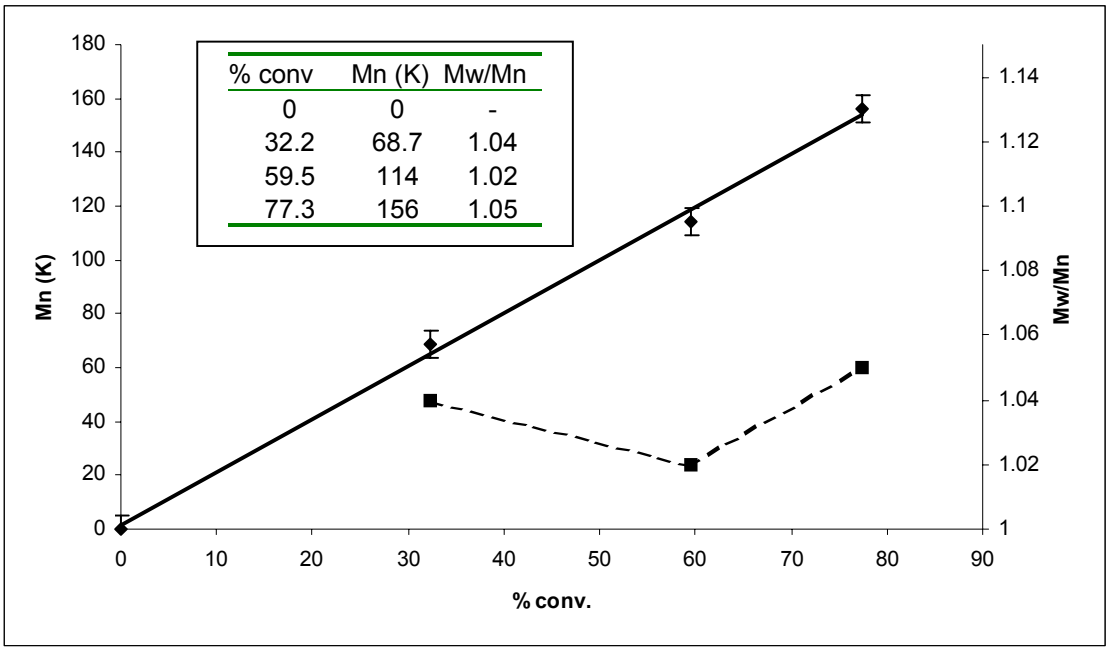

Figure 5 Plot of M_n and M_w/M_n vs. conversion for a polymerization of MMA initiated by 6.0 mM **6b** at –20 °C in CH_2Cl_2.

Table 1 Conversion vs. time data for polymerizations initiated by complex **8** (see Figure 1).

	Time (s)	[MMA] (M)
a)	0	2.223
	300	2.007
	900	1.220
	1500	0.704
	1800	0.526
b)	0	1.937
	150	1.653
	300	1.263
	600	0.642
	750	0.376
c)	0	1.650
	30	1.568
	60	1.461
	120	1.336
	300	0.799
d)	0	1.694
	30	1.651
	60	1.515
	90	1.399
	120	1.173
	240	0.765

[1]. Shriver, D. F.; Drezdon, M. A. *The Manipulation of Air-Sensitive Compounds*; Eds. Wiley: New York, **1986**.

[2]. Pangborn, A. B.; Giardello, M.A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F.J. *Organometallics* **1996**, *15*, 1518-1520.

[3]. Lipton, M.F.; Sorensen, C.M.; Sadler, A.C.; Shapiro, R.H. *J. Organometal. Chem.* **1980**, *186*, 155.

[4]. Reid, A. F.; Shannon, J. S.; Swan, J. M.; Wailes, P. C. *Aust. J. Chem* **1965**, *18*, 173.

[5]. Hunter, W. E.; Hrncir, D. C.; Bynum, V.; Penttila, R. A.; Atwood, J. L. *Organometallics* **1983**, *2*, 750-755.

[6]. Kim, Y. J.; Berstein, M. P.; Galiano, Roth, A. S.; Rosmesberg, F. E.; Willard, P.G.; Fuller, D. J.; Harrison, A. T.; Collum, D. B. *J. Org. Chem.* **1991**, *56*, 4435.

[7]. a) S. Collins, D. G. Ward, *J. Am. Chem. Soc.* **1992**, *114*, 5460-62; b) Y. Li, D. G. Ward, S. S. Reddy, S. Collins, *Macromolecules* **1997**, *30*, 1875-83; c) S. Collins, D. G. Ward, K. H. Suddaby, *Macromolecules* **1994**, *27*, 7222-24.

[8]. Allen, R. D.; Long, T. E.; McGrath, J. E.; *Polym. Bull* **1986**, *15*, 127.