# **Electronic Supplementary Information for**

# Cyclohexene Oxide/Carbon Dioxide Copolymerization by Chromium(III) Amino-bis(phenolato) Complexes and MALDI-TOF MS Analysis of the Polycarbonates

Katalin Devaine-Pressing,<sup>†</sup> Louise N. Dawe,<sup>†,‡</sup> and Christopher M. Kozak<sup>\*†</sup>

<sup>†</sup> Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7, Canada.

<sup>‡</sup> C-CART X-ray Diffraction Laboratory, Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7, Canada. Current address: Department of Chemistry and Biochemistry, Wilfrid Laurier University, 75 University Ave. W. Waterloo, Ontario, N2L 3C5, Canada

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## Experimental

# **General Experimental**

Unless otherwise stated, all manipulations were performed under an atmosphere of dry oxygenfree nitrogen by using standard Schlenk techniques or using an MBraun Labmaster glove box. Cyclohexene oxide was purchased from Aldrich and freshly distilled from CaH<sub>2</sub> under N<sub>2</sub> atmosphere into an ampule. THF was purified by distillation from sodium/benzophenone ketyl under nitrogen. All other solvents were dried and degassed using an MBraun Manual Solvent Purification System. CrCl<sub>3</sub>(THF)<sub>3</sub> and PPNN<sub>3</sub> were prepared via previously reported methods.<sup>1-</sup> <sup>2</sup> The synthesis of the proligand H<sub>2</sub>[L1] was previously reported.<sup>3-5</sup> Although the synthesis of H<sub>2</sub>[L2]<sup>6</sup> was also reported, here we report a modified synthesis in water and full characterization of H<sub>2</sub>[L2]. 99.998% (4.8 Supercritical fluid chromatography grade) CO<sub>2</sub> was supplied from Praxair in a high-pressure cylinder equipped with a liquid dip tube. All <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained in CDCl<sub>3</sub> purchased from Cambridge Isotope Laboratories, Inc.

# Instrumentation

<sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded on a Bruker AVANCE III 300 MHz spectrometer. All copolymerization reactions were carried out in a 100 mL stainless steel Parr<sup>®</sup> 5500 autoclave reactor with a Parr 4836 controller. N.B. Caution should be taken when operating such high-pressure equipment. UV-Vis spectroscopy was conducted on a dual-beam Evolution 300 UV-Vis spectrophotometer equipped with a xenon lamp. The samples were diluted to a concentration of 10<sup>-4</sup> mol/L in dichloromethane. Infrared spectroscopy was conducted on a Bruker Alpha FT-IR spectrometer equipped with a single bounce diamond ATR module. Melting points were measured on a Stanford Research Systems MPA100 OptiMelt Automated Melting Point System. Magnetic measurements were carried out using a Johnson-Matthey magnetic susceptibility balance. Elemental analysis was performed at Guelph Chemical Laboratories, Guelph, ON, Canada. Gel permeation chromatography (GPC) analysis was performed at 35 °C on a Viscotek VE 2001 GPCMax equipped with a Viscotek VE 3580 RI Detector, Phenogel narrow-bore 5 µm 100 Å and 5 µm Linear(2) columns (300 x 4.60 mm), and a 5 µm guard column. Samples were prepared at a concentration of 2 mg/mL and left to equilibrate for  $\sim 16$  h. The samples were filtered through 0.2 µm syringe filters before analysis. The GPC columns were eluted with HPLC grade chloroform at a flow rate of 0.30 mL/min

with a 100 µL injection volume. Eight polystyrene standards were used in making the calibration curve, bracketing molecular weights ranging from 1050 to 400,000 Da. No further corrections were performed on the molecular weights obtained. MALDI-TOF mass spectrometry was performed by using an Applied Biosystems 4800 MALDI-TOF/TOF Analyzer equipped with a reflectron, delayed extraction and high performance nitrogen laser (200 Hz operating at 355 nm). Anthracene was used as the matrix for analysis of 1 THF, 2 THF and 1 DMAP. The matrix and complex were dissolved separately in toluene at concentrations of 10 mg/mL. The matrix and chromium complex solutions were combined in a 1:1 ratio and the mixture was spotted on the MALDI plate and left to dry. Samples were prepared in the glove box and sealed under nitrogen in a plastic bag for transport to the spectrometer. For polymer analysis, either 2,5-dihydroxybenzoic acid (DHBA) or 1,8,9trihydroxyanthracene was used as the matrix with sodium trifluoroacetate (NaTFA) as cationizing agent. The matrix was dissolved in THF at a concentration of 10 mg/mL and  $\sim 2$ mg of NaTFA was added to the solution in the case of 1,8,9-trihydroxyanthracene. The polymer was dissolved at a concentration of 1 mg/mL. The matrix and polymer solutions were mixed together in a 3:1 ratio and this mixture was spotted on the MALDI plate and left to dry.



Synthesis of the amine-bis(phenol)  $H_2[L2]$ :  $H_2[L2]$ : N,N-dimethylethylenediamine (5.42 g, 0.0615 mol) was slowly added to a vigorously stirred mixture of 3-*tert*-butyl-4-hydroxyanisole (22.17 g, 0.123 mol) and formaldehyde (9.16 mL of a 37% aqueous solution, 0.123 mol) in deionized water (100 mL). This mixture was heated to reflux and stirred overnight. Upon cooling, a large quantity of dark

orange product formed. The solvent was decanted and the solid was washed with cold methanol, then recrystallized from a chloroform/methanol mixture to give a white powder (14.06 g, 48% yield). Anal. Calcd. For C<sub>28</sub>H<sub>44</sub>N<sub>2</sub>O<sub>4</sub>: C: 71.15, H: 9.38, N: 5.93. Found: C: 71.11, H: 9.14, N: 5.67. <sup>1</sup>H NMR (300 MHz, 298 K, CDCl<sub>3</sub>):  $\delta$  9.40 (br s, #14, 2H), 6.80 (d,  ${}^{4}J_{\text{HH}} = 3.08$  Hz, #7, 2H), 6.48 (d,  ${}^{4}J_{\text{HH}} = 3.06$  Hz, #4, 2H), 3.74 (s, #6, 6H), 3.57 (s, #10, 4H), 2.56, (d,  ${}^{3}J_{\text{HH}} = 2.34$  Hz, #11 and #12, 4H), 2.27 (s, #13, 6H), 1.38 (s, #1, 18H). <sup>13</sup>C NMR:  $\delta$  151.66 (#9), 149.86 (#8), 138.66 (#5), 123.18 (#3), 113.39 (#7), 112.76 (#4), 56.39 (#10),

55.86 (#6), 55.84 (#11), 49.21 (#12), 44.89 (#13), 35.22 (#2), 29.58 (#1). M.p.: 148.9 °C – 151.1 °C.

#### Synthesis of chromium complexes

1: Method A:  $H_2[L1]$  (3.00 g, 6.10 mmol) was dissolved in THF (~50 mL) and cooled to -78 °C. "BuLi (1.6 M in hexanes, 11.16 mL, 17.86 mmol) was added dropwise to give a red solution, which was warmed to room temperature and further stirred for 2 h. This solution was transferred via cannula to a suspension of CrCl<sub>3</sub>(THF)<sub>3</sub> (2.26 g, 6.03 mmol) in THF (~40 mL) cooled to -78 °C to give a dark brown mixture. Upon warming to room temperature and stirring for 24 h the solids dissolved and the color darkened to deep dark brown. The solvent was removed in vacuo and the solid residue was extracted into toluene. As the complex was sparingly soluble in toluene, the extraction was carried out by repeated addition of toluene to the solids. The extraction was stopped when the color of the toluene solution became very light brown. The remaining solids were filtered through Celite and the extracts combined. The solvent was removed in vacuo and the product was washed with pentane and dried to yield 2.81 g of green powder. Yield: 80%. Anal. Calcd for C<sub>30</sub>H<sub>38</sub>ClCrN<sub>2</sub>O<sub>4</sub> (1): C, 62.33; H, 6.63; N, 4.85. Anal. Calcd for C<sub>34</sub>H<sub>45</sub>ClCrN<sub>2</sub>O<sub>5</sub> (1·THF): C, 62.91; H, 6.99; N, 4.32. Found: C, 62.04; H, 6.48; N, 4.79. MS (MALDI-TOF) m/z (%, ion): 577.15 (100, [CrCl[L1]<sup>+</sup>], 542.19 (87,  $Cr[L1]^+$ ). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  in nm ( $\epsilon$  in L·mol<sup>-1</sup>cm<sup>-1</sup>): 228 (18 320), 311 (6280), 395 (1080), 562 (580), 752 (220). IR (cm<sup>-1</sup>): 2920.87 (alkane C – H stretch), 1610.70 (C = C phenyl stretch), 1462.96 and 1422.18 (sp<sup>3</sup> C – H bending), 1258.60 (C – N stretch), 1206.55 and 1052.22 (C – O stretches), 789.60 (sp<sup>2</sup> C – H bending).  $\mu_{eff}$  (solid, 27 °C) = 3.27  $\mu_B$ .

*Method B*: H<sub>2</sub>[L1] (3.00 g, 6.09 mmol) was dissolved in THF (~50 mL). THF was also transferred to a Schlenk flask containing NaH (0.58 g, 24.36 mmol). The ligand solution was transferred dropwise by cannula to the Schlenk flask containing the NaH suspension, which was cooled to -78 °C. The mixture was warmed to room temperature and further stirred for 2 h. This mixture was then cannula filtered to a suspension of CrCl<sub>3</sub>(THF)<sub>3</sub> (2.26 g, 6.09 mmol) in THF (~40 mL) cooled to -78 °C giving a dark brown mixture. Upon warming up to room temperature and stirring for 24 h the solids dissolved and the colour darkened to deep dark brown. The solvent was removed in vacuo and the solid residue was extracted into toluene. As the complex was sparingly soluble in toluene, the extraction was carried out by repeated

addition of toluene to the remaining solids as well as filtration through Celite. The extraction was stopped when the colour of the toluene solution became very light brown. The solvent was then removed in vacuo and the product was washed with pentane and dried to yield 2.75 g of green powder. Yield: 78%. Anal. Calcd for  $C_{30}H_{38}ClCrN_2O_4$  (1): C, 62.33; H, 6.63; N, 4.85; Anal. Calcd for  $C_{34}H_{45}ClCrN_2O_5$  (1·THF): C, 62.91; H, 6.99; N, 4.32. Found: C, 62.49; H, 6.37; N, 4.59; MS (MALDI-TOF) m/z (%, ion): 577.15 (100, [CrCl[L1]<sup>+-</sup>], 542.19 (87, Cr[L1]<sup>+</sup>). Crystals were grown from a toluene/THF mixture via slow evaporation at –35 °C.

**2**: Method A:  $H_2[L2]$  (3.00g, 6.35 mmol) was dissolved in THF (~50 mL) and cooled to -78 °C. "BuLi (1.6 M in hexanes, 7.90 mL, 12.64 mmol) was added dropwise to give a yellow solution, which was warmed to room temperature and further stirred for 2 h. This solution was transferred via cannula to a suspension of CrCl<sub>3</sub>(THF)<sub>3</sub> (2.23 g, 6.00 mmol) in THF (~ 40 mL) cooled to -78 °C to give a dark purple mixture. Upon warming to room temperature and stirring for 16 h the solids dissolved and the colour darkened to deep dark purple. The solvent was removed in vacuo and the solid residue was extracted into toluene. The mixture was filtered through Celite and the solvent was removed in vacuo. The product was washed with pentane and dried to yield 2.77 g of purple powder. Yield: 83%. Anal. Calcd for  $C_{28}H_{42}ClCrN_2O_4$  (2): C, 60.26; H, 7.59; N, 5.02. Anal. Calcd for C<sub>32</sub>H<sub>49</sub>ClCrN<sub>2</sub>O<sub>5</sub> (2 ·THF): C, 61.09; H, 7.85; N, 4.45. Found: C, 60.30; H, 7.38; N, 4.74. MS (MALDI-TOF) m/z (%, ion): 557.23 (67, [CrCl[L2]<sup>+-</sup>], 522.26 (81, Cr[L2]<sup>+</sup>). Crystals were grown a toluene/ THF mixture via slow evaporation at -35 °C. UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>)  $\lambda_{max}$  in nm ( $\epsilon$  in L·mol<sup>-1</sup>cm<sup>-1</sup>): 228 (13 280), 302 (6250), 397 (680 sh), 478 (420), 687 (140), IR (cm<sup>-1</sup>):  $\sim$  3300 (broad O – H stretch), 2951.28 (alkane C – H stretch), 1602.80 (C = C phenyl stretch), 1462.93 (sp<sup>3</sup> C – H bending), 1270.50 (C – N stretch), 1201.63 and 1061.53 (C – O stretches), 819.70 (sp<sup>2</sup> C – H bending).  $\mu_{eff}$  (solid, 27 °C) = 3.48  $\mu_B$ .

*Method B*: The synthesis was carried out the same way as described in Method B for complex 1 but using  $H_2[L2]$  to give 3.47 g of purple powder. Yield: 98%.

**1**•**DMAP**: 0.3000 g CrCl[**L1**] with 0.0634 g DMAP (1:1 mol ratio) was dissolved in ~ 8 mL dichloromethane (DCM). The solution was stirred for ~ 15 min. then it was filtered through glass fiber. Crystals were grown via slow evaporation at -35 °C. After crystallization, the solvent was removed in vacuo and the crystalline solid was used for copolymerization

reactions. Anal. Calcd. for C<sub>37</sub>H<sub>48</sub>ClCrN<sub>4</sub>O<sub>4</sub>: C, 63.46; H, 6.91; N, 8.00. Found: C, 63.32; H, 6.72; N, 7.75. MS (MALDI-TOF) *m/z* (%, ion): 699.23 (66.11, [CrCl[L1]DMAP]<sup>+</sup>), 664.27 (33, [Cr[L1]DMAP]<sup>+</sup>). UV-Vis (DCM)  $\lambda_{max}$  in nm ( $\epsilon$  in L·mol<sup>-1</sup>cm<sup>-1</sup>): 227 (35 600), 232 (29530), 257 (30 270), 280 (30 550), 286 (30 210), 315 (8820 sh), 409 (980 sh), 547 (200), 693 (140). IR (cm<sup>-1</sup>): ~ 3300 (broad O – H stretch), 2947.61 (alkane C – H stretch), 1615.35 (C = C phenyl stretch), 1419.56 (sp<sup>3</sup> C – H bending), 1261.41 (C –N stretch), 1061.03 and 1014.46 (C – O stretches), 808.04 (sp<sup>2</sup> C – H bending).  $\mu_{eff}$ (solid, 27 °C) = 3.31  $\mu_B$ .

## **Copolymerization procedure**

The appropriate amount of catalyst and co-catalyst were added to the monomer in a glove box. The reactant solution was stirred for ~ 5 min, then transferred via a long-needled syringe to a Parr autoclave, which was pre-dried under vacuum overnight at 80 °C. The autoclave then was charged with the appropriate pressure of  $CO_2$  and left to stir at the desired temperature and time period. After the appropriate time the autoclave was cooled in an ice bath and vented in the fume hood. An aliquot was taken immediately after opening the reactor for the determination of conversion by NMR. The copolymer was extracted with dichloromethane and re-precipitated in cold acidic methanol. For reactions done in the presence of PPNCl and PPNN<sub>3</sub>, the catalyst and co-catalyst were first combined in ~ 4 mL of  $CH_2Cl_2$  in the glove box, stirred for ~ 15 min and then dried in vacuo. This way the otherwise insoluble onium salts could be dissolved in cyclohexene oxide. The remaining procedure was followed in the same manner as described above.

## In situ monitoring of the copolymerizations by IR spectroscopy

In situ monitoring was carried out using a 100 mL stainless steel reactor vessel (Mettler-Toledo) equipped with a silicon sensor (SiComp), motorized mechanic stirrer and a heating mantle. The silicon sensor was connected to a ReactIR 15 base unit through a DS silver-halide Fiber-to-Sentinel conduit. The reactor vessel was cleaned and heated under vacuum at 80 °C overnight before experiments. In a glove box the appropriate amount of complex and DMAP (where needed) were weighed and then dissolved in 5 g CHO. The mixture was stirred for about 15 min after which the vial cap was replaced with a septum. The reaction solution was transferred into a 5 mL syringe with a cannula needle attached. The syringe was transferred out of the glove box and the solution was injected into the vessel through a port. Then the vessel

was then pressurized with 40 bar CO<sub>2</sub>. Heating and stirring were started and the reaction was monitored for the allotted time.

## X-Ray Crystallographic Experimental

Diffraction data for complex 1. THF, 2. THF and 1. DMAP were collected on a Rigaku Saturn70 CCD area detector with a SHINE optic Mo-Ka radiation and solved on an AFC8-Saturn 70 single crystal X-Ray diffractometer from Rigaku, equipped with an X-stream 2000 low temperature system. Crystallographic and structure refinement data are given in supporting information. The data were processed using CrystalClear<sup>7</sup> software and corrected for Lorentz and polarization effects and absorption.<sup>8</sup> Neutral atom scattering factors for all non-hydrogen atoms were taken from the International Tables for X-Ray Crystallography.<sup>9</sup> The structure was solved by direct methods using SIR92<sup>10</sup> and expanded using Fourier techniques.<sup>11</sup> All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Anomalous dispersion effects were included in Fcalc;<sup>12</sup> the values for  $\Delta f$  and  $\Delta f$ ' were those of Creagh and McAuley.<sup>13</sup> The values for the mass attenuation coefficients are those of Creagh and Hubbell.<sup>14</sup> All calculations were performed using the CrystalStructure<sup>15</sup> crystallographic software package except for refinement, which was performed using SHELXL-97.<sup>16</sup> Disordered lattice solvent for **2** · THF was removed through applying Platon's Sqeeze<sup>17</sup> procedure. Structural illustrations were created using ORTEP-III (v.2.02) for Windows.<sup>18</sup>

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Compound	1 · THF	2 · THF	1 · DMAP
Chemical formula	$C_{34}H_{46}CrN_2O_5Cl\bullet(C_4H_8O)$	$C_{32}H_{50}CrN_2O_5Cl\bullet(C_7H_8)$	$C_{37}H_{48}CrN_4O_4Cl \bullet$ 1.5(CH <sub>2</sub> Cl <sub>2</sub> )
Colour	Green	Green	Green
Habit	Prism	Prism	Prism
Formula weight	722.30	722.35	827.66
Crystal system	Orthorhombic	Monoclinic	Triclinic
<i>a</i> [Å]	17.119(3)	14.615(10)	8.751(4)
<i>b</i> [Å]	11.4910(18)	16.834(12)	11.960(5)
<i>c</i> [Å]	37.818(6)	16.342(13)	20.098(9)
a [°]	90	90	95.039(7)
β [°]	90	112.456(8)	97.965(9)
γ [°]	90	90	92.325(3)
Unit cell $V$ [Å <sup>3</sup> ]	7439(2)	3716(5)	2072.2(16)
Temperature [K]	163	123	163
Space group	Pca2 <sub>1</sub> (#29)	$P2_1/c$ (#14)	P-1 (#2)
Ζ	8	4	2
$D_c/\mathrm{g~cm}^{-3}$	1.290	1.291	1.326
Radiation type	ΜοΚα	ΜοΚα	ΜοΚα
$\mu$ (MoK $\alpha$ ) [cm <sup>-1</sup> ]	4.26	4.25	5.76
<i>F</i> (000)	3080	1548	868
Reflections measured	63954	42817	17169
Unique refl's	14421	7619	8454
R <sub>int</sub>	0.0455	0.0939	0.0296
$R_{l}$ (all)	0.0477	0.1168	0.0659
$wR(F_2)$ (all)	0.1177	0.2625	0.1535
$R_{I} (I \geq 2 \sigma (I))^{[a]}$	0.0446	0.0965	0.0616
$wR(F^2) (I \ge 2 \sigma(I))^{[b]}$	0.1133	0.2448	0.1496
Goodness of fit on $F^2$	1.068	1.082	1.059
CCDC Ref.	1408674	1408672	1408673

 Table S1: Crystallographic and Structure Refinement Data for 1. THF, 2. THF and 1. DMAP

 $\frac{(\text{CDC Ref.})^{14000/4}}{[a] R_1 = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|. [b] wR_2 = [\Sigma(w(F_0^2 - F_c^2)^2) / \Sigma w(F_0^2)^2]^{1/2}.}$ 



Figure S1. MALDI-TOF mass spectrum of complex 1. THF.



**Figure S2**. MALDI-TOF mass spectrum of complex 1. THF corresponding to  $[Cr_2Cl_2[L1]_2]^+$ 



Figure S3. MALDI-TOF mass spectrum of complex 2. THF



Figure S4. MALDI-TOF mass spectrum of complex 1.DMAP



**Figure S5**. UV-Vis absorption spectrum of **1**·THF. Expansion of the visible region shows peak wavelengths and molar extinction coefficients



**Figure S6**. UV-Vis absorption spectrum of **2**·THF. Expansion of the visible region shows peak wavelengths and molar extinction coefficients



**Figure S7**. UV-Vis absorption spectrum of **1**·DMAP. Expansion of the visible region shows peak wavelengths and molar extinction coefficients



Figure S8. IR spectrum of 1. THF



Figure S9. IR spectrum of 2. THF



Figure S10. IR spectrum of 1.DMAP



**Figure S11.** The first 20 min of the reaction profile of the growth of the polycarbonate v(C=O) catalyzed by 1·THF, 1·DMAP and CrCl[O<sub>2</sub>NN']<sup>BuBuPy</sup>. Reaction conditions: 40 bar CO<sub>2</sub>, 60 °C, 24 h, [Cr]:[CHO]:[DMAP] = 1:500:1.



**Figure S12.** The second stage of the propagation of the reaction catalyzed by  $CrCl[O_2NN']^{BuBuPy}$ .  $r_{obs} = 0.75 \pm 0.024 \times 10^{-2} \text{ min}^{-1}$  (or  $1.2 \pm 0.04 \times 10^{-4} \text{ s}^{-1}$ ).



**Figure S13**. <sup>1</sup>H-NMR of the aliquot taken right after polymerization corresponding to Table 2, entry 3. % Conversion calculation = polymer peak integration (4.60 at 4.65 ppm) divided by the sum of the polymer (4.60 at 4.65 ppm) and monomer (1.00 at 3.12 ppm) peak integrations.



Figure S14. <sup>1</sup>H-NMR of the cleaned and dried polymer (Table 2, entry 3)



**Figure S15**. Carbonyl region of the  ${}^{13}C{}^{1}H$  NMR spectrum of a typical poly(cyclohexene) carbonate (Table 2, entry 3) showing the presence of both isotactic and syndiotactic isomers



**Figure S16.** (A) Lower mass region (m/z 1900 – 2700, n = 11 – 16) of the MALDI-TOF MS spectrum produced by 1. THF according to Table 2, entry 3. with calculated masses of fragments shown beneath the observed spectrum. (B) Proposed structures of the lower mass range polymers (a), (b), (c) and (d).







[35 (Cl) + 142*n* (repeating unit) + 82 (C<sub>6</sub>H<sub>10</sub>) + 35 (Cl)]

**Figure S17.** (A) Lower mass region of the MALDI-TOF mass spectrum produced by 1.THF according to Table 2, entry 5. (m/z 2100 – 2600, n = 14 - 17) of the spectrum with modeled polymer peaks. (B) Plausible structures of the polymers based on the calculations shown (a), (b) and (c).



**Figure S18.** Lower mass region ( $m/z \ 2000 - 2400$ , n = 13 - 16) of the MALDI-TOF MS spectrum produced by 1·DMAP according to Table 2, entry 10, with calculated masses of fragments shown beneath the observed spectrum and the proposed structures of polymers (a), (b) and (c).



**Figure S19.** Lower mass region (m/z 1800 – 2300, n = 13 - 16) of the MALDI-TOF MS spectrum produced by 1. THF according to Table 2, entry 6., with modeled polymer peaks and the plausible structures of the different polymer chains (a) and (b).



**Figure S20.** A) MALDI-TOF MS spectrum produced by 1·DMAP according to Table 2, entry 11. (B) Higher mass region (m/z 7400 – 8000, n = 51 - 55) of the spectrum with calculated masses of fragments shown beneath the observed spectrum. (C) Proposed structure of the high mass range polymer.