Synthesis and X-ray Crystal Structure of Dichloro[*N*-{6-methyl-2-pyridyl)methyl}-(S)-1-phenylethylamine]zinc(II) and Its Catalytic Application to *rac*-Lactide Polymerization

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Received September 29, 2008, Accepted November 25, 2008

Key Words: *N*-{6-Methyl-2-pyridyl)methyl}-(S)-1-phenylethylamine, Chiral Zn(II) complex, PLA, X-ray structure

Poly(lactic acid) or polylactide (PLA) is a biodegradable synthetic polymer.[1] A typical degradation time is months to years for L-PLA and weeks to months for *rac*-PLA.[2] This time scale is several orders of magnitude shorter than that of petroleum-based polymers, which makes it possible to compost PLA waste just into soil amendments. In addition to this green benefit, PLA's raw material is from annually renewable resources such as corn and sugar beats or even from the food wastes. Moreover, basic physical properties of PLA that include narrow MWD, low haze, high mechanical strength, high gas permeability and easy processibility are acceptable enough to utilize this material in many applications such as fiber, film, and blow molding.[3] Due to these merits not to mention sky-scraping natural oil price, PLA have emerged as an environmentally friendly plastic materials that can replace many petroleum-based ones.

It has been known that the catalyst-initiated ring-opening polymerization reaction of purified lactide is advantageous over the condensation reaction of lactic acid in terms of a higher polymerization rate, a higher MW, and a better conversion. Among many different kinds of metal species for the polymerization catalysts, relatively non hazardous magnesium and zinc,[4-13] or aluminum[4,10,14-31] have attracted more attention than highly toxic tin,[6,32-41] lead and bismuth,[42] or lanthanides[43-48] because the major application fields of PLA are biomedical[49] and food packaging[3] and even ppm level catalyst residues are potentially harmful for these application. Along this line, we attempted to prepare PLA with the newly synthesized zinc complex ligated by the chiral *N*-{6-methyl-2-pyridinyl)methyl}-(*S*)-1-phenylethylamine (MPMA) ligand. Instead of a direct complexation reaction between MPMA and dialkylzinc to prepare an active catalyst species as in our previous work,[50] we first synthesized air and moisture stable (MPMA)$ZnCl_2$ complex and generated the active catalyst species by treating it with benzylmagnesium chloride (BnMgCl) *in situ*. Herein, we report the synthesis of MPMA ligand as well as its $ZnCl_2$ complex, the X-ray crystal structural characterization of the complex, and the polymerization results of *rac*-lactide with in situ generated (MPMA)$ZnBn_2$.

Experimental Section

Materials. All manipulations were carried out under nitrogen prepurified by passage through an O_2 scrubbing tower (Schweizerhall R3-11 catalyst) and a drying tower (Linde 3-Å molecular sieves) unless otherwise noted. Standard Schlenk and drybox techniques were employed to manipulate air sensitive materials. All solvents were purchased from Duksan Chemical Co. (reagent grade). Tetrahydrofuran (THF) was dried over Na/benzophenone ketyl, while CH_2Cl_2 was dried over CaH_2; these solvents were subsequently distilled from these reagents under nitrogen prior to use. Methyl alcohol was used as received. The *rac*-lactide was purchased from Aldrich and was sublimed prior to use. 6-Methyl-2-piridine carboxaldehyde, (*S*)-(-)-α-methylbenzylamine, sodium borohydride, zinc chloride and benzylmagnesium chloride (2 M in THF) were purchased from Aldrich and used as received.

Instuumentation. ^{1}H-NMR spectra were recorded on a Bruker advance digital 400-NMR Spectrometer at ambient temperature and chemical shifts were referenced to tetramethylsilane as internal standard and are reported in ppm. All coupling constants are reported in Hertz. Elemental analyses were determined using EA 1108-Elemental Analyzer at the Chemical Analysis Laboratory of the Center for Scientific Instruments of Kyungpook National University. Gel permeation chromatography (GPC) analyses were carried out on a Waters Alliance GPCV2000, equipped with differential refractive index detectors. The GPC columns were eluted with tetrahydrofuran with 1 mL/min rate at 25 °C and were calibrated with monodisperse polystyrene standards.

***N*-{6-Methyl-2-pyridinyl)methyl}-(*S*)-1-phenylethylamine (MPMA)**. Reported method for MPMA was modified as followings.[51] In the first step, 6-methyl-2-piridine carboxaldehyde (1.05 g, 8.5mmol) and (*S*)-(-)-α-methylbenzylamine (1.1mL, 8.5mmol) were mixed in 15mL methanol and were stirred overnight at ambient temperature. $NaBH_4$ (0.33g, 8.8mmol) was added slowly in the second step and the reaction mixture was stirred for 3 hours. After removing methanol by rotary evaporation, the residue was partitioned in CH_2Cl_2 (50 mL) and H_2O (25 mL). The organic layer was washed with H_2O (2 × 25 mL), dried over $CaCl_2$, filtered, and evaporated. MPMA was obtained as yellowish oil; isolated yield = 1.86g (8.2 mmol, 96%). ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.39 (t, 1H, *J* = 7.52 Hz, Ar*H*), 7.30-7.22 (m, 4H, Ar*H*), 7.19-7.14 (m,1H, Ar*H*), 6.90 (t, 2H, *J* = 6.52Ar*H*), 3.74 (q, *J* = 6.56 Hz, 1H, C*H*), 3.59 (s, 2H, CH_2), 2.45 (s, 3H, PyCH_3), 2.19 (br, s, 1H, N*H*), 1.30 (d, *J* = 6.56 Hz, 3H, CH_3).

(MPMA)$ZnCl_2$. A 100 mL, one-necked round-bottomed flask was charged with MPMA (1.02g, 4.5 mmol), $ZnCl_2$ (0.62g, 4.5 mmol) and THF (15 mL). The mixture was stirred at am-

bient temperature for 3 days and then the solvent was removed under reduced pressure. The residual solids were dissolved in CH_2Cl_2 and filtered through filter paper. The filtrate was evaporated *in vacuo* to afford white solids. Recrystallization of the crude product from a solvent pair of CH_2Cl_2/Hexane gave white crystals: isolated yield =1.42g (3.9 mmol, 87% based on 4.5 mmol of MPMA). ^{1}H-NMR (400 MHz, CD_3CN): δ 7.89 (t, 1H, J = 7.89 Hz, ArH), 7.48-7.40 (m, 6H, ArH), 7.16 (d, J = 7.79 Hz, 1H, ArH), 4.15 (m, 2H, NH & CH), 3.77 (m, 2H, CH_2), 2.78 (s, 3H, PyCH_3), 1.70 (d, J = 3.24 Hz, CH_3). Elemental Analysis $C_{15}H_{18}Cl_2N_2Zn$: Calc: C 49.68; H 5.00; N, 7.73. Found: C 49.79; H 5.01; N 7.74%.

Polymerization with *in situ* generated (MPMA)ZnBn$_2$. A 100 mL Schlenk tube previously dried at 150 °C and cooled under nitrogen, was charged with (MPMA)$ZnCl_2$ (361 mg, 1.0 mmol) and dried THF (9 mL). After cooling the solution to −78 °C, 1.0 mL of BnMgCl (2.0 M in THF) was added drop wise into the stirred solution. The white suspension became clear immediately. The mixture was allowed to warm to room temperature. After being stirred overnight at ambient temperature, the resulting catalyst solution was used for the polymerization reaction. The general procedure for the polymerization reaction was as follows. A 100 mL of Schlenk tube previously dried at 150 °C and cooled under nitrogen was charged with *rac*-Lactide (1.44 g, 10.0 mmol) in the glove box. Dried THF (10 mL) was transferred to the reaction vessel via cannula. The reaction was initiated by adding the catalyst solution (2 mL, 1 mL and 0.5 mL for the [M]/[cat] = 50, 100 and 200, respectively.) with syringe. The reaction mixture was stirred at ambient temperature for 2 hours. The reaction was quenched by adding 1 mL of water and partitioned with CH_2Cl_2 (100 mL) and 0.05 N HCl; the organic layer was washed with 0.05 N HCl (2×25 mL) and H_2O (1×50 mL), following which it was dried over $CaCl_2$, filtered, and evaporated, giving a white gum. Unreacted monomeric lactide was removed by sublimation. The resulting gummy product was dissolved in small amount of CH_2Cl_2 (~5 mL), filtered, and quickly dried *in vacuo*. White crumble solids was obtained. Isolated yield: 1.4 g, 97% based on *rac*-Lactide. ^{1}H NMR(300 MHz, $CDCl_3$): δ 5.19-5.04 (m, 1H), 1.52-1.47 (m, 3H)

X-ray crystallographic analysis for (MPMA)ZnCl$_2$. An X-ray quality single crystal was mounted in a thin-walled glass capillary on an Enraf-Noius CAD-4 diffractometer with Mo-Kα radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections ($10^\circ < \theta < 13^\circ$). Intensity data were collected with θ range of 1.88-24.97° in $\omega/2\theta$ scan mode. Three standard reflections were monitored every 1 hr during data collection. The data were corrected for Lorentz-polarization effects and decay. Empirical absorption corrections with Ψ-scans were applied to the data. The structure was solved by using Patterson method and refined by full-matrix least-squares techniques on F^2 using SHELX-97 and SHELX-97 program packages.[52,53] All non-hydrogen atoms were refined anisotrpically and all hydrogen atoms were constrained by using riding model. The final cycle of the refinement converged with R_1 = 0.025 and wR_2 = 0.067. Crystal data, details of the data collection, and refinement parameters are listed in Table 1. Selected bond distances and angles are presented in Table 2.

Table 1. Selected bond lengths (Å) and angles (°) for (MAPA)$ZnCl_2$.

Zn-N(1)	2.049(3)	Zn-N(2)	2.082(3)
Zn-Cl(1)	2.191(1)	Zn-Cl(2)	2.227(1)
N(1)-C(2)	1.343(4)	N(1)-C(6)	1.338(4)
N(2)-C(7)	1.474(4)	C(6)-C(7)	1.511(4)
N(1)-Zn-N(2)	83.17(11)	N(1)-Zn-Cl(2)	116.99(8)
N(2)-Zn-Cl(2)	116.51(8)	N(1)-Zn-Cl(1)	111.00(8)
N(2)-Zn-Cl(1)	110.13(8)	Cl(1)-Zn-Cl(2)	114.99(4)
C(2)-N(1)-C(6)	120.0(3)	C(2)-N(1)-Zn	127.2(2)
C(6)-N(1)-Zn	112.5(2)	C(7)-N(2)-C(8)	112.6(3)
C(7)-N(2)-Zn	106.4(2)	C(8)-N(2)-Zn	115.0(2)

Results and Discussion

The MPMA ligand was readily synthesized from the 2-steps one-pot reaction comprising the condensation reaction between 6-methylpyridine-2-carboxyaldehyde and chiral (S)-1-phenylethylamine and the following reduction of the corresponding Schiff base imine intermediate. For the reduction reaction of the intermediate imine compound for the conversion of the imine intermediate to the amine analogue, we used $NaBH_4$ as a reducing agent. This approach was quite efficient giving rise to 96% of overall yield, which is much higher than that conducted separately (Scheme 1).[51]

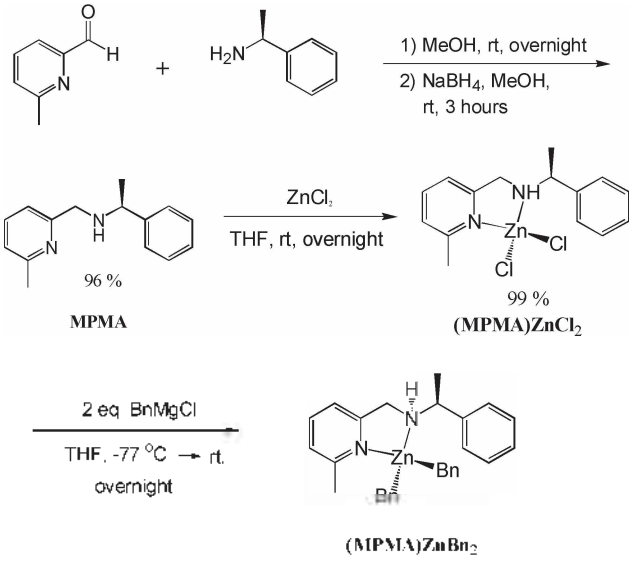
The complexation reaction between MPMA ligand and $ZnCl_2$ was followed by the method reported previously.[50] Since both MPMA and $ZnCl_2$ are freely soluble in THF while (MPMA)$ZnCl_2$ is not, the desired product was easily isolated by filtration. It should be noted that the early studies regarding (2-aminomethylpyridine)$_n$$ZnCl_2$ complexes (n = 1, 2, and 3) revealed that the ligand-to-metal ratio of the product is critically dependent on the ligand-to-metal ratio of reactants used in the preparation stage. Given the fact that MPMA ligand has a similar skeleton with 2-aminomethylpyridine, we were careful about the controlling the stoichiometry between MPMA and $ZnCl_2$ to avoid possible contamination of bis- or tris-ligated side products. Although we have not carried out a kinetic control, the obtained product was solely (MPMA)$ZnCl_2$, which was confirmed by ^{1}H NMR, elemental analysis, and X-ray crystal structural determination.

A single crystal suitable for the X-ray crystallography was obtained by a diffusional crystallization of (MPMA)$ZnCl_2$ in

Table 2. Polymerization of *rac*-Lactide with *in situ* prepared (MPMA)$ZnBn_2$.

Entry	[*Monomer*]/[*Cat*]	Conversion (%)	$M_n \times 10^3$	$M_w \times 10^3$	MWD	Tg °C
1	50	97	9800	10500	1.07	43.8
2	100	67	13100	13700	1.05	43.4
3	200	61	23400	27800	1.18	50.0

CH_2Cl_2 and hexane. An ORTEP drawing of the complex is shown in Figure 1 with the atomic labeling. Selected bond distances and angles are listed in Table 1. The geometry of the complex is a distorted tetrahedron comprising zinc metal as a center linked with two N atoms of MPMA ligand in a bidentate manner along with two chloride ions. The angle between Cl(1)-Zn-Cl(2) and N(1)-Zn-N(2) planes are 89.76(7)°. Two binding sites of the tetrahedron are occupied by large chloride ions while the other two are chelated by a bidentate ligand, which give rise to much smaller N-Zn-N bite angle (83.17°) than Cl-Zn-Cl angle (114.99°). This is a common structural feature in L_2ZnX_2 type complex where L_2 is a nitrogen donor bidentate ligand and X is a halogen ion. For example, a similar complex (propylideneaminomethylpyridine) $ZnCl_2$ reported by Westerhuasen *et al.*[54] exhibit 82.2° and 115.52° of N-Zn-N and Cl-Zn-Cl angles. On the other hand, bond distances for Zn-N(1) and Zn-N(2) of (MPMA)$ZnCl_2$ are 2.049(3) and 2.082(3) Å, respectively. Slightly longer distance of Zn-N(2) bond relative to that of Zn-N(1) might be due to the sp^3 character of N(2) atom in contrast to sp^2 one of N(1). It is interesting to note that the bond distance of Zn-Cl(2) is significantly longer (+0.036 Å) than that of Zn-Cl(1). In case of



Scheme 1. Synthesis of (MPMA)$ZnCl_2$ and (MPMA)$ZnBn_2$.

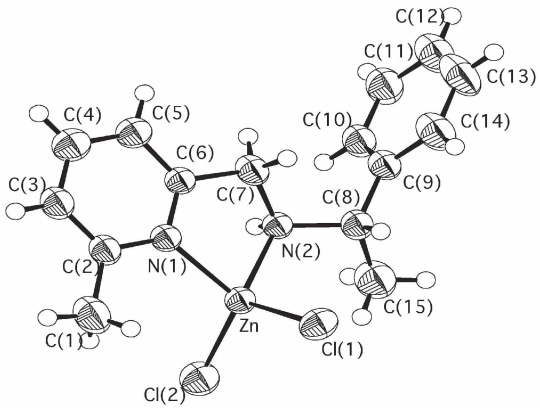


Figure 1. ORTEP drawing of (MPMA)$ZnCl_2$ with the numbering scheme and 40% probability ellipsoids.

(propylideneaminomethylpyridine)$ZnCl_2$, for example, two Zn-Cl bond distances were 2.050 and 2.054 Å.[55] (*N,N,N'*-trimethylethylenediamine)$ZnCl_2$ complex exhibited 2.207 and 2.212 Å of Zn-Cl bond distances.[56] Considering the fact that the difference of two Zn-Cl bond distances of both (propylideneaminomethylpyridine)$ZnCl_2$ and (*N,N,N'*-trimethylethylenediamine)$ZnCl_2$ were only 0.004 and 0.005 Å, 0.036 Å difference between two Zn-Cl bond distances in our result is exceptional. It is not likely that this phenomenon is derived from the effect of two nitrogen atoms of different hybridization character because two Zn-Br bond distances in (aminomethylpyridine)$ZnBr_2$ complex, for example, in which one nitrogen has sp^3 character and another has sp^2 one similar to (MPMA)$ZnCl_2$, are very similar each other (2.360 and 2.357 Å).

Between two nitrogen atoms in MPMA ligand, only N(2) atom is able to become a chiral center when it is coordinated to the zinc metal. The inherent chirality located on C(8) atom should remain unchanged after coordination. The resulting structure determined by X-ray crystallography revealed that only one stereogenic species was generated by the complexation reaction, giving rise to enantiomerically pure *R* configurations for N(2) atoms.

Polymerization reaction of *rac*-lactide was carried out with *in situ* prepared Zn catalyst, (MPMA)$ZnBn_2$, which was prepared by treating two equivalent of BnMgCl to (MPMA) $ZnCl_2$ in THF solvent. We have run the polymerization reaction in three different [monomer]/[catalyst] ratios. The polymerization results were summarized in Table 2. When the [monomer]/[catalyst] ratio ($R_{monomer\ cat}$) is 50, the polymerization reaction was completed in 2 hours with near quantitative yield. However, the conversions of polymerization reaction with increased $R_{monomer\ cat}$ values decreased to 67 and 61% for $R_{monomer\ cat}$ = 100 and 200, respectively. Increasing the reaction period did not improve the conversion.

If the polymerization reaction undergoes *via* living polymerization mechanism, the number averaged molecular weight (M_n) of the polymer is expected to be ~$C \times M \times R$ approxi-

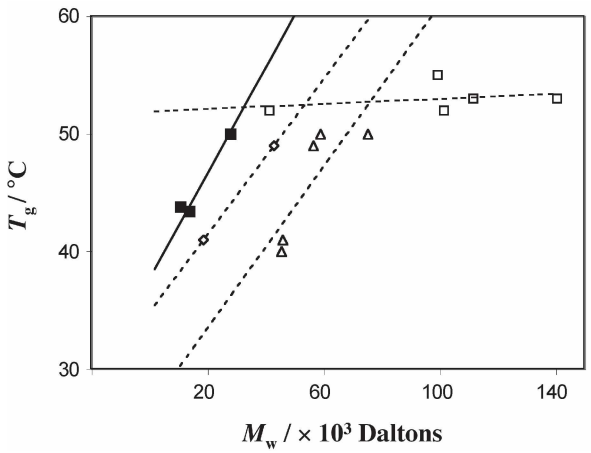


Figure 2. The relation between T_g vs M_w of PLAs prepared by (MPMA)$ZnBn_2$ (closed squares). The open marks and the dashed trend lines are from the previous work that describes a sharp (circles and triangles) and a shallow (open squares) dependence of T_g on the M_w of PLAs in the narrow and the broad MWD regime for the former and the latter, respectively.[20]

mately, where C is the conversion, M is the molecular weight of a monomer, and R is the [M]/[cat] ratio. Observed M_ns of PLAs ranged from 9800 to 23000 D for three different [M]/[cat] ratios (Table 2). Given the fact that M_ns of produced PLAs have linear relationship with those predicted theoretically and observed molecular weight distributions (MWDs) of these polymers are very narrow (1.05-1.18) indicate that the major mechanism of polymerization is likely having a living polymerization character.

We have reported the trend of glass transition temperature (T_g) in relation with MW and MWD in the previous work.[50] Shortly, T_g was critically dependent on M_w within the narrow MWD regime but the dependence became significantly shallow when the MWD was broadened (Figure 2). PLAs produced in this work have very narrow MWD and T_g values of PLAs again exhibit sharp dependence on the M_w similar to our previous results.

In sum, a new approach towards the synthesis of a ring-opening polymerization catalyst for the preparation of PLA has been achieved. The air and moisture stable (MPMA) $ZnCl_2$ complex was first prepared and its structure was determined by X-ray crystallography. Replacing two Cl ions with benzyl groups under mild condition afforded (MPMA) $ZnBn_2$, which are active for the PLA synthesis.

Supplementary data. CCDC 698373 contains the supplementary crystallographic data for (MPMA)$ZnCl_2$. These data can be obtained free of charge *via http://www.ccdc.cam.ac.uk/conts/retrieving.html*, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: *deposit@ccdc.cam.ac.uk*

References

1. Tsuruta, T.; Matsuura, K.; Inoue, S. *Macromol. Chem.* **1964**, *75*, 211.
2. Park, T. G. *J. Controlled Release* **1994**, *30*, 161.
3. Auras, R.; Harte, B.; Selke, S. *Macromol. Biosci.* **2004**, *4*, 835.
4. Kricheldorf, H. R.; Berl, M.; Scharnagl, N. *Macromolecules* **1988**, *21*, 286.
5. Bero, M.; Kasperczyk, J.; Jedlinski, Z. J. *Macromol. Chem. Phys.* **1990**, *191*, 2287.
6. Nijenhuis, A. J.; Grijpma, D. W.; Pennings, A. J. *Macromolecules* **1992**, *25*, 6419.
7. Chisholm, M. H.; Eilerts, N. W. *Chem. Commun.* **1996**, 853.
8. Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *Polym. Int.* **1998**, *46*, 177.
9. Cheng, M.; Attygalle, A. B.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 11583.
10. Chisholm, M. H.; Eilerts, N. W.; Huffman, J. C.; Iyer, S. S.; Pacold, M.; Phomphrai, K. *J. Am. Chem. Soc.* **2000**, *122*, 11845.
11. Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229.
12. Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350.
13. Chen, H. Y.; Tang, H. Y.; Lin, C. C. *Macromolecules* **2006**, *39*, 3745.
14. Dubois, P.; Jacobs, C.; Jerome, R.; Teyssie, P. *Macromolecules* **1991**, *24*, 2266.
15. Spassky, N.; Wisniewski, M.; Pluta, C.; LeBorgne, A. *Macromol. Chem. Phys.* **1996**, *197*, 2627.
16. Emig, N.; Nguyen, H.; Krautscheid, H.; Reau, R.; Cazaux, J. B.; Bertrand, G. *Organometallics* **1998**, *17*, 3599.
17. Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114.
18. Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **1999**, *121*, 4072.
19. Eguiburu, J. L.; Fernandez-Berridi, M. J.; Cossio, F. P.; San Roman, J. *Macromolecules* **1999**, *32*, 8252.
20. Ko, B. T.; Lin, C. C. *Macromolecules* **1999**, *32*, 8296.
21. Cameron, P. A.; Jhurry, D.; Gibson, V. C.; White, A. J. P.; Williams, D. J.; Williams, S. *Macromol. Rapid Commun.* **1999**, *20*, 616.
22. Radano, C. P.; Baker, G. L.; Smith, M. R. *J. Am. Chem. Soc.* **2000**, *122*, 1552.
23. Kitayama, T.; Yamaguchi, H.; Kanzawa, T.; Hirano, T. *Polym. Bull.* **2000**, *45*, 97.
24. Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316.
25. Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938.
26. Chakraborty, D.; Chen, E. Y. X. *Organometallics* **2002**, *21*, 1438.
27. Zhong, Z. Y.; Dijkstra, P. J.; Feijen, J. *Angew. Chem. Int. Ed.* **2002**, *41*, 4510.
28. Li, H.; Wang, C. H.; Bai, F.; Yue, J.; Woo, H. G. *Organometallics* **2004**, *23*, 1411.
29. Hormnirun, P.; Marshall, E. L.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **2004**, *126*, 2688.
30. Doherty, S.; Errington, R. J.; Housley, N.; Clegg, W. *Organometallics* **2004**, *23*, 2382.
31. Lewinski, J.; Horeglad, P.; Dranka, M.; Justyniak, I. *Inorg. Chem.* **2004**, *43*, 5789.
32. Dittrich, W.; Schulz, R. C. *Angew. Makromol. Chem.* **1971**, *15*, 109.
33. Kricheldorf, H. R.; Sumbel, M. V.; Kreisersaunders, I. *Macromolecules* **1991**, *24*, 1944.
34. Schwach, G.; Coudane, J.; Engel, R.; Vert, M. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3431.
35. Stridsberg, K.; Ryner, M.; Albertsson, A. C. *Macromolecules* **2000**, *33*, 2862.
36. Duda, A.; Penczek, S.; Kowalski, A.; Libiszowski, J. *Macromol. Symp.* **2000**, *153*, 41.
37. Moller, M.; Nederberg, F.; Lim, L. S.; Kange, R.; Hawker, C. J.; Hedrick, J. L.; Gu, Y. D.; Shah, R.; Abbott, N. L. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 3529.
38. Dove, A. P.; Gibson, V. C.; Marshall, E. L.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **2001**, 283.
39. Finne, A.; Albertsson, A. C. *Biomacromolecules* **2002**, *3*, 684.
40. Amsden, B.; Wang, S.; Wyss, U. *Biomacromolecules* **2004**, *5*, 1399.
41. Nimitsiriwat, N.; Marshall, E. L.; Gibson, V. C.; Elsegood, M. R. J.; Dale, S. H. *J. Am. Chem. Soc.* **2004**, *126*, 13598.
42. Kricheldorf, H. R.; Serra, A. *Polym. Bull.* **1985**, *14*, 497.
43. Stevels, W. M.; Ankone, M. J. K.; Dijkstra, P. J.; Feijen, J. *Macromolecules* **1996**, *29*, 3332.
44. Simic, V.; Spassky, N.; HubertPfalzgraf, L. G. *Macromolecules* **1997**, *30*, 7338.
45. Yuan, M. L.; Xiong, C. D.; Li, X. H.; Deng, X. M. *J. Appl. Polym. Sci.* **1999**, *73*, 2857.
46. Chamberlain, B. M.; Sun, Y. P.; Hagadorn, J. R.; Hemmesch, E. W.; Young, V. G.; Pink, R.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **1999**, *32*, 2400.
47. Giesbrecht, G. R.; Whitener, G. D.; Arnold, J. *J. Chem. Soc., Dalton Trans.* **2001**, 923.
48. Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.
49. Jeong, B.; Bae, Y. H.; Lee, D. S.; Kim, S. W. *Nature* **1997**, *388*, 860.
50. Jeong, J. H.; An, Y. H.; Kang, Y. K.; Nguyen, Q. T.; Lee, H.; Novak, B. M. *Polyhedron* **2008**, *27*, 319.
51. Mizushima, E.; Ohi, H.; Yamaguchi, M.; Yamagishi, T. *J. Mol. Catal. A: Chem.* **1999**, *149*, 43.
52. Sheldrick, G. M. *Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.
53. Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.
54. Westerhausen, M.; Bollwein, T.; Polborn, K. *Z. Naturforsch., B: Chem. Sci.* **2000**, *55*, 51.
55. Zhang, D. H.; Xu, J. Y.; Alcazar-Roman, L.; Greenman, L.; Cramer, C. J.; Hillmyer, M. A.; Tolman, W. B. *Macromolecules* **2004**, *37*, 5274.
56. Johansson, A.; Hakansson, M. *Acta Crystallogr. Sect. E: Struct. Rep. Online* **2004**, *60*, M955.