Macromolecular Research, Vol. 16, No. 8, pp 745-748 (2008)

Polymerization of Methyl Methacrylate by Sterically Modulated Bis(salicylaldiminate)-Cobalt(II) Complexes Combined with Methylaluminoxane

Bijal Kottukkal Bahuleyan, Deepak Chandran, Chang Hun Kwak, Chang-Sik Ha, and Il Kim*

Department of Polymer Science and Engineering, Pusan National University, Busan 609-735, Korea

Received February 21, 2008; Revised June 27, 2008; Accepted July 10, 2008

Introduction

Kim and coworkers demonstrated that nickel(II) catalysts incorporating α-diimine ligands and iron(II) and cobalt(II) catalysts incorporating tridentate bis-imine ligands produced syndiotactic poly(methyl methacrylate) (PMMA).[1,2] Groups VI-VIII transition metal derivatives and organoaluminium compounds have been reported to be effective catalysts for the polymerization of various polar vinyl monomers because of their remarkably functional group tolerant and high electrophilicities.[3] However, coordinative homo- and copolymerization of polar monomers with these transition metals are still one of the challenging topics, because simple coordination of the functional group to the metal may block monomer access to vacant coordination sites.

Production of functionalized olefinic polymers with polar groups by direct synthesis is one of the most challenging research goals never successfully achieved by conventional industrial chemical process. Aiming at the synthesis of polyolefins functionalized with polar groups by ethylene/MMA copolymerization, the polymerization of MMA with a series of sterically modulated bis(salicylaldiminate) cobalt (II) complexes in combination with methylaluminoxane (MAO) has been preliminarily examined.

Experimental

General Methods and Materials. All reactions were performed under inert atmosphere.[4] Methyl methacrylate (Aldrich) washed twice with aqueous sodium hydrioxide (10 wt%) and twice with water, followed by drying over $MgSO_4$ and finally distilled over calcium hydride under N_2 atmosphere at reduced pressure. Solvents were dried under nitrogen using standard reagents. MAO (8.4 wt% total Al solution in toluene) was obtained from Akzo Chemical. 2,6-Dimethylaniline, 2,6-diethylaniline, 2,6-diisopropylaniline and salicylaldehyde purchased from Aldrich were used as-received. Cobalt(II) acetate tetrahydrate (Aldrich) was used without further purification. (2,6-Dimethylphenyl)salicylaldimine, (2,6-diethylphenyl)salicylaldimine and (2,6-diisopropyl-phenyl)salicylaldimine ligands were prepared according to the literature.[5]

Characterization. The molecular weight and its distribution of PMMA were determined by gel permeation chromatography (GPC) using a Hewlett Packard Model 1100 series system in tetrahydrofuran (THF) at 25 °C as calibrated with polystyrene standards. The triad tacticity of PMMA was determined by using ^{1}H-NMR spectra recorded on a Varian Unity Plus 300 (300 MHz) spectrometer in $CDCl_3$ at 25 °C, using tetramethylsilane as the internal reference. Both ^{1}H NMR spectra (300 MHz) of compounds and ^{13}C-NMR spectra (75 MHz) of the triad tacticity of PMMA were recorded on a Varian Unity Plus 300 spectrometer in $CDCl_3$, using tetramethylsilane as an internal reference. FT-IR spectra of the samples were recorded on KBr pellets by a Bruker IFS55 FT-IR spectrometer. Element analysis was carried out using Vario EL.

Synthesis of Complexes. Bis(salicylaldiminate)-cobalt(II) complexes were prepared according to a general method employed for the preparation of bis(salicylaldiminate)nickel(II) complexes (Scheme I).[6]

Bis(2,6-dimethylphenylsalicylaldiminate)Cobalt(II) [Co(dmps)$_2$]. (2,6-Dimethylphenyl)-salicylaldimine (1.20 g, 5.33 mmol) in THF was added slowly at 50 °C to a solution of cobalt(II) acetate tetrahydrate (0.65 g, 2.62 mmol) in THF and stirred vigorously for 8 h. Bright violet solid was slowly precipitated from the solution. After treating with 20 mL of *n*-hexane, the resulting slurry was filtered, washed with *n*-hexane, and finally dired in vacuo. Co(dmps)$_2$ was obtained as a violet powder (yield = 67.8%). FT-IR (KBr): 1574 cm^{-1} ($\nu_{C=N}$) and no peaks representing ν_{O-H} (cf. 1634 cm^{-1} ($\nu_{C=N}$) and 3462 cm^{-1} (ν_{O-H}) for ligand). Anal. Calcd. for $C_{30}H_{28}CoN_2O_2$: C, 71.00; H, 5.56; N, 5.52. Found: C, 70.93; H, 5.51; N, 5.56.

Bis(2,6-diethylphenylsalicylaldiminate)Cobalt(II) [Co(deps)$_2$]. Co(deps)$_2$ complex was prepared by reacting (2,6-diethylphenyl)salicylaldimine ligand with cobalt(II) acetate tetrahydrate according to similar procedures above (yield = 64.2%). FT-IR (KBr): 1574 cm^{-1} ($\nu_{C=N}$) and no peaks representing ν_{O-H} (cf. 1634 cm^{-1} ($\nu_{C=N}$) and 3460 cm^{-1} (ν_{O-H}) for ligand). Anal. Calcd. for $C_{34}H_{36}CoN_2O_2$: C, 72.46; H, 6.44; N, 4.97. Found: C, 72.43; H, 6.50; N, 4.93.

Bis(2,6-isopropylphenylsalicylaldiminate)Cobalt(II) [Co(dipps)$_2$]. Co(dipps)$_2$ complex was prepared by reacting (2,6-diisopropylphenyl)salicylaldimine ligand with cobalt(II) acetate tetrahydrate according to similar procedures above

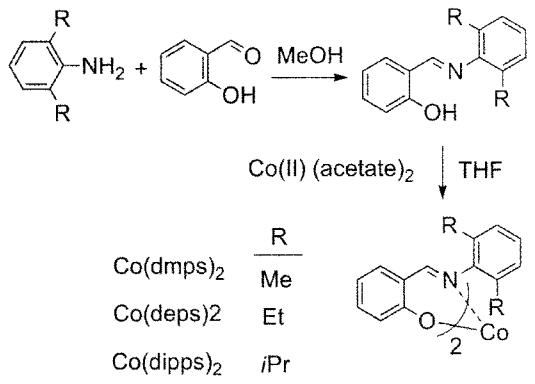
*Corresponding Author. E-mail: ilkim@pusan.ac.kr

(yield = 68.3%). FT-IR (KBr): 1576 cm^{-1} ($\nu_{C=N}$) and no peaks representing ν_{O-H} (cf. 1632 cm^{-1} ($\nu_{C=N}$) and 3460 cm^{-1} (ν_{O-H}) for ligand). Anal. Calcd for $C_{38}H_{44}CoN_2O_2$: C, 73.65; H, 7.16; N, 4.52. Found: C, 73.50; H, 7.20; N, 4.49.

Polymerization of MMA. All the polymerizations were carried out in a Schlenk tube (50 mL) with a connection to a vacuum system.[1,2]

Results and Discussion

The syntheses of salicylaldiminate ligands bis-ligated complexes of nickel were previously reported.[7-9] (2,6-Dialkylphenyl)salicylaldimine ligands were conveniently prepared in high yield (> 90%) by Schiff base condensation of the appropriate aniline and salicylaldehyde. Bis(salicylaldiminate)cobalt(II) complexes were also prepared in good yields (64.2-68.3%) by treating the salicylaldiminate ligands with $Co(OAc)_2 \cdot 4H_2O$ (Scheme I). Similar bis-ligated analogue compound of nickel have been noted and the bis-ligated complex was not an active catalyst for ethylene polymerization. In this sense, it was assumed that bis-ligation has an important implication in catalyst stability and lifetime.[7] However, bis(salicylaldiminate)-cobalt(II) complexes were highly active catalysts for ethylene oligomerizations, producing up to 8.13×10^5 g-oligomer mol-Co^{-1} h^{-1} atm^{-1} with $Co(dmps)_2$, 8.11×10^5 g-oligomer mol-Co^{-1} h^{-1} atm^{-1} with $Co(deps)_2$, and 9.12×10^5 g-oligomer mol-Co^{-1} h^{-1} atm^{-1} with $Co(dipps)_2$ in the presence of MAO at 30 °C. This activity is attributed to the lability of the salicylaldiminate ligand, resulting in its ready displacement by the reaction with MAO to generate active sites.



Scheme I. Preparation of Bis(salicylaldiminate)-cobalt(II) complexes.

In order to check the oxophilicity of the active sites generated by bis-ligated cobalt complexes combined with MAO, MMA polymerizations were performed by an array of bis(salicylaldiminate)cobalt(II) complexes prepared by modulating the steric bulk of the *ortho* substituents of the N-aryl ring. Table I shows the results of the solution polymerizations of MMA. The $Co(dmps)_2$ catalyst containing methyl substituents in the aryl rings showed the highest activity and the $Co(dipps)_2$ complex containing relatively bulkier isopropyl groups the least activity in an hour of polymerization. MAO alone showed no activity.

The earlier reports for the stereoselective polymerizations of MMA utilized a variety of main group organometallic catalysts, specifically those based on lithium and magnesium, and to a lesser extent, aluminum. These catalysts were considered to operate via anionic mechanisms, and the development of well-defined organometallic complexes developed later might be a logical extension of the earlier catalysts.[1] Both anionic and coordinative pathways are proposed to propagate through metal enolate species, and the difference between the two mechanisms may be simply recognized by means of the degree of dissociation of the enolate/anion. Many transition metal complexes were examined experimentally and theoretically to elucidate their active species formed during olefin polymerizations via UV/VIS spectroscopy.[10-14]

These attempts on several zirconocene/MAO systems[10-13] and α-diimine-[*N,N*]$NiBr_2$/MAO system[14] for olefin polymerization have contributed to understand the successive elementary steps involved in the formation of cationic

Table I. Polymerization of Methyl Methacrylate by Bis(salicyladiminate) Cobalt(II) Complexes Combined with Methylaluminoxane. T = 25 °C, [Co] = 15 μmol, and $[MMA]_0/[MAO]_0/[Co]_0$ = 3100:200:1

Run no.	Catalyst	Time (h)	Yield[a] (%)	R_p[b]	M_n[c] $\times 10^{-4}$	M_w/M_n[c]	Triad Fractions[d] (%)		
							mm	mr	rr
1	$Co(dmps)_2$	1	19.8	10239	4.5	14.9	0.8	25.7	73.5
2	$Co(deps)_2$	1	18.6	9611	4.2	15.7	0.5	22.7	76.8
3	$Co(dipps)_2$	0.5	3.64	11266	4.6	6.96	1.1	21.7	77.2
4	$Co(dipps)_2$	1	12.6	6511	4.2	15.9	0.9	21.1	78.0
5	$Co(dipps)_2$	2	17.9	4271	5.4	11.7	1.1	21.7	77.2
6	$Co(dipps)_2$	5	21.4	5107	5.9	8.5	1.3	21.4	77.3

[a]Yield defined a mass of dry polymer recovered/mass of monomer used. [b]Rate of polymerization expressed as g of polymer/(mol-Co x h). [c]Determined by GPC eluted with THF with polystyrene calibration. [d]Observed in ^{13}C-NMR spectra of α-Me resonance; from low to high field in the spectra (δ = 16.94-21.3 ppm).

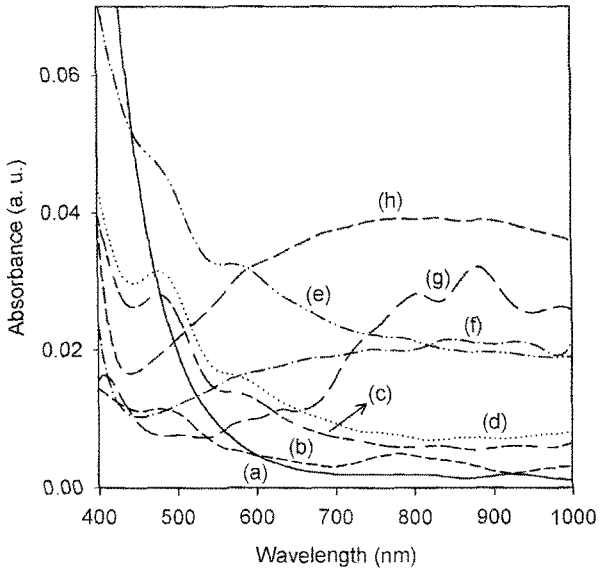
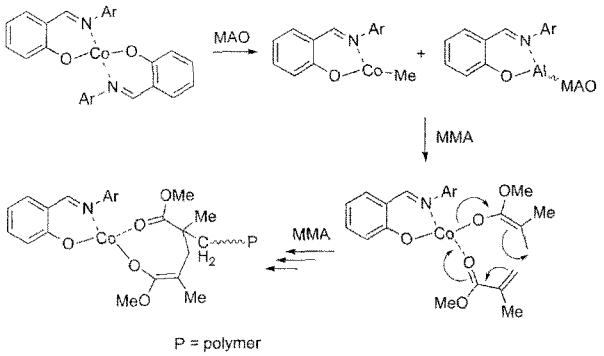


Figure 1. UV/VIS spectra of $Co(deps)_2$/methyl methacrylate (MMA)/methylaluminoxane (MAO) system: (a) MAO alone, (b) $Co(deps)_2$/MAO, (c) $Co(deps)_2$ alone, (d) $Co(deps)_2$/MMA, (e) $Co(deps)_2$/MMA/MAO (1/100/30, molar ratio), (f) $Co(deps)_2$/MMA/MAO (1/100/60), (g) $Co(deps)_2$/MMA/MAO (1/100/150), and (h) $Co(deps)_2$/MMA/MAO (1/100/250).

active species.

On this background, an investigation of cobalt salicylaldimine complex $Co(deps)_2$/MAO in the presence of MMA was made to get an idea about the active species involved in these polymerization reactions. The formation of various types of cobalt species upon incremental addition of MAO has been identified in this process. As can be seen in Figure 1, MAO alone has no characteristic absorption between 400 to 1,000 nm (curve a) while $Co(deps)_2$/MAO gave two absorption peaks around 500 and 800 nm (curve b). From the Figure 1(curve c) it is clear that $Co(deps)_2$ complex alone has an absorption maximum around 500 nm. Note that addition of a small quantity of MMA to $Co(deps)_2$ alone makes no difference in the pattern of the spectrum. Hence the new peaks around 800-900 nm may be related to the formation of active species. Increasing the amount of MAO ([Al]/[Co] = 60), there is a considerable change in the spectral pattern. The absorption at 500 nm almost disappears and the absorption around 900 nm dominates. Further addition of MAO makes this absorption considerably broadened, most probably due to the increase of population density of active species in the system.

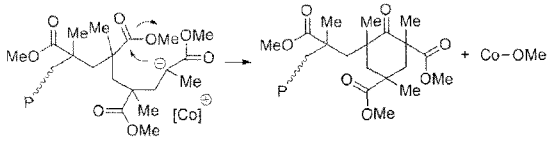
Considering both the results obtained in this study and the reported results, addition of the propagating PMMA can be proposed (Scheme II). Oxygen-metalated enolate species (as opposed to carbon-bound keto tautomers) undergo 1,4-addition of a coordinated monomer, in a similar manner to the Michael addition, leading to the formation of the backbone carbon-carbon bond and the generation of a new eno-



Scheme II. Polymerization of methyl methacrylate using bis(salicylaldiminate)cobalt(II)/methylaluminoxane catalysts.

late ligand capable of repeating the insertion.

As indicated in Table I, the molecular weights of all polymers are moderately high (say, M_n = 45,000 for $Co(dmps)_2$/MAO); however, no clear trends can be found according to the steric bulk of substituents. Considering the fact the same catalyst yields only low molecular weight products like butenes and hexanes in the ethylene polymerizations, the increase of steric bulk of the *ortho* substituents of the *N*-aryl ring is not a necessary condition to achieve high molecular weight PMMA and, unlike ethylene polymerizations using the same catalysts, chain transfer reactions in MMA polymerization is quite slow relative to chain propagation, and thus, high molecular weight polymer is produced. In MMA polymerization, the functional groups themselves may provide alternative mechanisms that facilitate propagation through intermediates unique to their structures (Scheme II). The most plausible termination process is an intramolecular cyclization with concomitant formation of metal methoxide species which is permanently inactive as shown in eq. (1).[15]



(1)

Steric bulk of MMA monomer results in sterically hindered chains, preventing them from susceptible cyclo-termination.[16]

The data in Table I show that all catalysts produce PMMA's with large MWD values, indicating multiple active species. It is premature to conclude the reason for this only with the data collected here; however, it is said that MMA polymerizations with the present bis-ligated Co(II)/MAO catalyst are proceeded through complicated propagation and termination procedures.

The microstructure of PMMA was investigated by using ^{13}C-NMR.[17] As summarized in Table I, all catalysts produce predominantly syndiotactic PMMA. The sterical modulation of the catalyst made no dramatic effect on the syndio-

tacticity (as *rr* triad) of PMMA, even though the value decreases in the order of $Co(dipps)_2 > Co(deps)_2 > Co(dmps)_2$. In addition the variations of experimental parameter like temperature and [Al]/[Co] ratio made no mentionable differences in the sindiotacticity (not shown). Triad tests may be a good clue to differentiate between enantiomorphic site control and chain-end control.[17] In the former case, $2(mm)/mr$ should equal one, and in the latter, $4(rr)(mm)/(mr)^2$ is theoretically unity. All catalysts of the present study yield polymers that cannot be described exactly as having been formed under a specific control mechanism, enantiomorphic site control or chain-end control.[18]

Recently, the possibility of free radical polymerization mechanism or coordination-insertion mechanism has been proposed for transition metal catalyzed polymerization of acrylates.[19-24] Novak and coworkers have reported for neutral Pd catalysts in acrylate polymerization that an efficient radical inhibitor, galvinoxyl, can completely inhibit the process of polymerization, suggesting that the polymerization occurs via a radical mechanism.[19] Li and coworkers reported that the syndiospecific polymerization of MMA catalyzed by the neutral nickel complexes bearing ketoamino ligands did not occur via a radical mechanism, as the adding galvinoxyl as a free radical inhibitor cannot inhibit the polymerization.[20] Since MAO can react with galvinoxyl, this test is not reliable which may lead to wrong conclusion.[21] It was reported that the polymerization of MMA by $Ni(acac)_2$[22] and salicylaldiminate nickel complexes[23,24] with MAO proceeds by a coordination-insertion mechanism. However, we evaluated the effect of radical inhibitor on the polymerization of MMA for Co(deps) system. Under standard conditions and adding 5 equivalent (per metal) of TEMPO as a free radical inhibitor, polymer yield and catalyst productivity remained substantially the same, thus strongly suggesting that the polymerization of MMA catalyzed by the cobalt(II) complexes did not occur via a radical mechanism.

Conclusions

A series of sterically modulated bis(salicylaldiminate) cobalt(II) complexes were synthesized and applied to the polymerization of MMA in the presence of MAO as a cocatalyst. All catalysts showed moderate activities and yielded syndiotactic-rich PMMA with syndiotacticity more than 73.5%.

Acknowledgments. This work was supported by Ministry of Commerce, Industry and Energy. The authors are also grateful to the BK 21 Project and the Center for Ultramicrochemical Process Systems (ERC), the NCRC Program from MOST and KOSEF (R15-2006-022-01001-0) and the NRL Program.

References

(1) I. Kim, J. M. Hwang, J. K. Lee, C. S. Ha, and S. I. Woo, *Macromol. Rapid Commun.*, **24**, 508 (2003).
(2) I. Kim, J. S. Kim, B. H. Han, and C. S. Ha, *Macromol. Res.*, **11**, 514 (2003).
(3) (a) S. H. Byun, H. S. Seo, S. H. Lee, C. S. Ha, and I. Kim, *Macromol. Res.*, **15**, 393 (2007). (b) B. Liu, H. Li, C. S. Ha, I. Kim, and W. Yan, *Macromol. Res.*, **16**, 441 (2008). (c) S. H. Byun, H. S. Seo, S. H. Lee, C. S. Ha, and I. Kim, *Macromol. Res.*, **15**, 393 (2007). (d) S. H. Lee, C. S. Ha, and I. Kim, *Macromol. Res.*, **15**, 202 (2007).
(4) I. Kim, C. H. Kwak, G. W. Son, J. S. Kim, S. Abraham, K. B. Bijal, C. S. Ha, B. U. Kim, N. J. Jo, J. W. Lee, and J. K. Lee, *Macromol. Res.*, **12**, 316 (2004).
(5) C. Wang, S. Friedrich, T. R. Younkin, R. T. Li, R. H. Grubbs, D.A. Bansleben, and M. W. Day, *Organometallics,* **17**, 3149 (1998).
(6) K. Yamanouchi, *Bull. Chem. Soc. Jpn.,* **55**, 1083 (1982).
(7) C. Carlini, A. Macinai, F. Masi, A. M. R. Galletti, R. Santi, G. Sbrana, and A. Sommazzi, *J. Polym. Sci. Part A: Polym. Chem.*, **42**, 2534 (2004).
(8) D. Meinhard, M. Wegner, G. Kipiani, A. Hearley, P. Reuter, S. Fischer, O. Marti, and B. Rieger, *J. Am. Chem. Soc.*, **129**, 9182 (2007).
(9) I. Kim, C. H. Kwak, J. S. Kim, and C.-S. Ha, *Appl. Catal., A: General,* **287**, 98 (2007).
(10) L. Porri, A. Giarrusso, and G. Ricci, *Prog. Polym. Sci.*, **16**, 405 (1991).
(11) T. M. Kooistra, Q. Knijnenburg, J. M. M. Smith, A. D. Horton, P. H. M. Budzelaar, and A. W. Gal, *Angew. Chem. Int. Ed.*, **40**, 4719 (2001).
(12) D. Coevet, H. Cramail, and A. Deffieux, *Macromol. Chem. Phys.*, **199**, 1451 (1998).
(13) J.-N. Pedeutour, D. Coevet, H. Cramail, and A. Deffieux, *Macromol. Chem. Phys.*, **200**, 1215 (1999).
(14) D. Coevet, H. Cramail, A. Deffieux, C. Maldenov, J.-N. Pedeutour, and F. Peruch, *Polym. Int.*, **48**, 257 (1999).
(15) T. P. Davis, D. M. Haddleton, and S. N. Richard, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C34**, 243 (1994).
(16) T. Kitano, T. Fujimoto, and M. Nagasawa, *Polym. J.*, **9**, 153 (1977).
(17) P. A. Cameron, V. C. Gibson, and A. J. Graham, *Macromolecules,* **33**, 4329 (2000).
(18) Y. Li, D. G. Ward, S. S. Reddy, and S. Collins, *Macromolecules,* **30**, 1875 (1997).
(19) G. Tian, H. W. Boone, and B. M. Novak, *Macromolecules*, **34**, 7656 (2001).
(20) X. F. Li, Y. G. Li, Y. S. Li, Y. X. Chen, and N. H. Hu, *Organometallics*, **24**, 2502 (2005).
(21) M. Nagel, W. F. Paxton, A. Sen, L. Zakharov, and A. L. Rheingold, *Macromolecules*, **37**, 9305 (2004).
(22) K. Endo and A. Inukai, *Polym. Int.*, **49**, 110 (2000).
(23) C. Carlini, M. Martinelli, A. M. R. Galletti, and G. Sbrana, *J. Polym. Sci. Part A: Polym. Chem.,* **41**, 2117 (2003).
(24) C. Carlini, V. D. Luise, M. Martinelli, A. M. R. Galletti, and G. Sbrana, *J. Polym. Sci. Part A: Polym. Chem.,* **44**, 620 (2006).