Catal Lett (2013) 143:717–722
DOI 10.1007/s10562-013-1021-7

# Effect of Ion-Pair Strength on Ethylene Oligomerization by Divalent Nickel Complexes

**Deepak Chandran · Seong Jin Byeon ·**
**Hongsuk Suh · Il Kim**

Received: 21 March 2013 / Accepted: 2 May 2013 / Published online: 15 May 2013

**Abstract** Detailed ethylene oligomerizations were performed over highly active nickel complexes ligated by *N*-((4-butyl-6-phenylpyridin-2-yl)methylene)-2,6-diisopropylaniline derivatives. The activity trend according to the structure of the complex was attempted to understand using the concept of ion-pair formation during activation process. The active species were characterized by comparing the oligomerization results with the UV–Vis spectroscopic and the cyclic voltammetry experiments.

**Keywords** Catalyst · Ethylene · Oligomerization · Nickel · Transition metal chemistry

## 1 Introduction

Alkyl or hydride anion abstraction reactions using strong Brønsted or Lewis acids from transition metal complexes are the pivotal activation step in homogeneous 'single site' Ziegler–Natta catalysis [1–7]. This abstraction process mediated by Lewis acidic reagents and reaction conditions yields highly electrophilic and mononuclear ion pairs, exhibiting unprecedented olefin polymerization activity and selectivity [8]. A detailed investigation on the formation and strength at various reaction conditions for these ion-pairs are important in understanding and optimizing the performances of various types of complexes in catalysis. Most of such studies reported so far are based on early transition metal complexes [1–5]. Even though a large number of complexes of N^N and N^N^N ligands bearing various late transition metals such as Ni, Pd, Co, Fe and Cr are widely employed catalysts in ethylene polymerization/oligomerization [6, 9–13] attempts to study their performance based on the ion-pair strength are hardly made.

We have recently reported the synthesis of a series of Ni-diimine catalysts based on *N*-((4-butyl-6-phenylpyridine-2-yl)methylene)-2,6-diisopropylaniline derivatives [14]. Apart from the interesting observation and information obtained during their synthesis, these complexes were observed with high catalytic potential in ethylene oligomerization (EO) which serves them suitable candidates to study the ion-pair formation and strength at various reaction conditions. Three different complexes having the same core structure has been adopted in order to investigate this effect in this study. We found that, as in the case of early transition metal complexes, the ion-pair formation and its stability are equally influential in the cationic late transitions metal complexes. Here, attempts have been made to study EO by using the three Ni(II) complexes based on the ion-pair concept.

## 2 Experimental

### 2.1 General Methods and Materials

All reactions and operations were performed under a purified nitrogen atmosphere using the standard glove box and Schlenk techniques. Polymerization grade ethylene (SK Co., Korea) was purified by passing it through columns of Fisher RIDOXTM catalyst and molecular sieve

D. Chandran · S. J. Byeon · I. Kim (✉)
The WCU Center for Synthetic Polymer Bioconjugate Hybrid
Materials, Department of Polymer Science and Engineering,
Pusan National University, Busan 609-735, Korea
e-mail: ilkim@pusan.ac.kr

H. Suh
Department of Chemistry and Chemistry Institute
for Functional Materials, Pusan National University,
Busan 609-735, Korea

5 Å/13X. All solvents were purified according to the standard procedures and stored over molecular sieves (4 Å) under nitrogen condition. Methylalumoxane (MAO) (8.4 wt% total Al in toluene) was donated by LG Chemicals, Korea was used without purification. All other reagents including diethylaluminum chloride (DEAC), methylaluminum dichloride (MADC), and ethylaluminum sesquichloride (EASC) were purchased from Sigma–Aldrich and used without further purifications.

### 2.2 Characterization

UV–Vis spectra were recorded on a Shimadzu UV-1650 PC spectrometer in toluene at room temperature under nitrogen atmosphere. $^{1}H$ (300 MHz) and $^{13}C$ (75 MHz) NMR spectra were recorded on a Varian Gemini 2000 spectrometer and chemical shifts were reported in parts per million relative to internal $(CH_3)_4Si$. Oligomerization products were analyzed by a 7,890 A gas chromatograph (GC) (Agilent Tech.) with a J&W Scientific 30 m column with 0.250 mm inner diameter. Cyclic voltammetry (CV) measurements were conducted on a BAS CV-50 W voltammetric analyzer with scan rates of 100 mV/s. The electrolytic cell used was a conventional three-compartment cell, in which a glass carbon working electrode, a platinum counter electrode, and Ag/AgCl reference electrode were employed. The CV measurements of the complexes were performed under a nitrogen atmosphere at room temperature in *N*,*N*-dimethylformamide (DMF) using 0.10 M tetrabutylammonium perchlorate (TBAP) purchased from TCI as the supporting electrolyte.

### 2.3 Oligomerization

EOs were performed at 1.3 bar by using a 250 mL round bottom flask equipped with a magnetic stir bar as a reactor [14]. After the given reaction time the reactor was cooled to 0 °C and the samples for analysis were collected from the reactor by passing a 10 mL of this cold mixture through a silica column to remove Al species.

### 2.4 Synthesis of Complexes

Synthesis of the complexes for EO study is summarized in Scheme 1 and a detailed description of their structure has been previously reported [14].

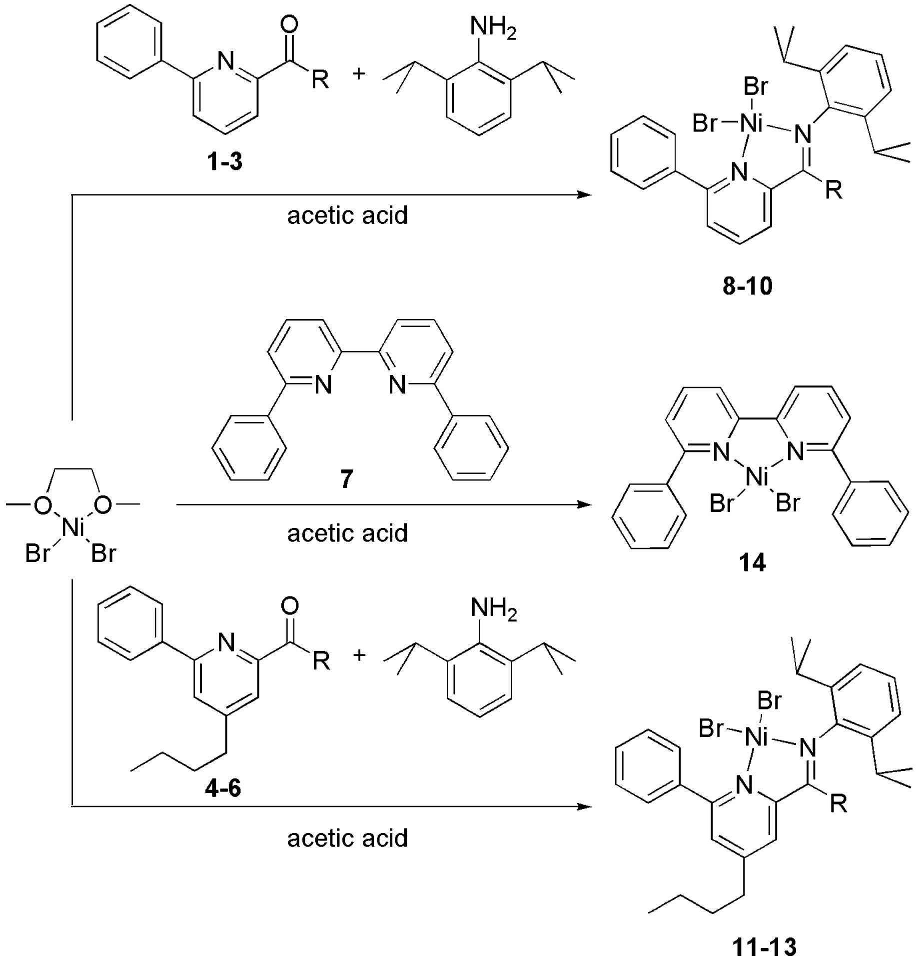
## 3 Results and Discussion

As previously reported, complexes **8–14** were synthesized according to the Scheme 1 by using different ligands [14]. Complexes **8–13** retain the same core structure with varying steric and electronic demands. These complexes can be divided into two groups based on the type of substituent position. Complexes **8–10** have different methylenic substituents, –H, –Me and –Ph. The different substituents on the core structure vary the steric and electronic effects on the metal center. Complexes **11–13** possess an n-butyl tail in common. This n-butyl tail does not change the steric pattern of the metal center, but may influence electronically. Complexes **11–13** were obtained in high yields and showed better activity than complexes **8–10**. Accordingly, complexes **11–13** were employed for the detailed EOs. These complexes can shed light into the effect of structural factors on the ion-pair strength.

EOs have been performed at different conditions of solvent, temperature, co-catalysts and ethylene pressure and the results are summarized in Table 1. The complex **12** has been chosen for general study due to its intermediate steric demands. EO at high ethylene pressure (5.5 bar) gave a higher activity ($42.3 \times 10^{6}$ g-oligomer/mol-Ni h bar), keeping the oligomer distribution similar (run no. 19). Even at 1.3 bar of ethylene pressure the activity was considerably high in chlorobenzene ($26.5 \times 10^{6}$ g-oligomer/mol-Ni h bar). The complex **13** gave the highest activity among the catalysts ($35.7 \times 10^{6}$ g-oligomer/mol-Ni h bar), while **11** with the lowest activity ($16.3 \times 10^{6}$ g-oligomer/mol-Ni h bar) at the same conditions. The gradual change in activity pattern can be explained based on the electronic and steric parameters of the substituents.

Among the substituents employed in this study –Ph and –Me groups are electron donating with the former group slightly higher, and —H is the least electron donating group. Higher electron donating –Ph group makes the metal center more electron rich, while less electron donating –Me group makes the metal center only moderately electron rich. As the least electron donation group, the influence of –H group on electron availability on the metal center will be the lowest. This type of electronic influences has been successfully monitored previously by using CV studies [13–15]. The CV curves of the complexes showed reduction waves between 0.0 and –1.0 V (Fig. 1). The reduction potentials obtained from CVs are −0.99, −0.74 and −0.46 V for complexes **11**, **12** and **13**, respectively, showing the electron density on the metal center is highest for **13**, lowest for **11** and intermediate for **12**. It is a direct consequence of electron donating effects exerted by the substituents on the organic backbone of the complexes. In general as the electron density on the metal center becomes higher, the oxidative addition of the neutral ligand, ethylene to the metal center becomes easier and hence the activity in EO/ethylene polymerization is enhanced. Thus, the CV results can be a reasonable evidence to explain the activity trend: **13** > **12** > **11**.

Irrespective of these electronic and structural factors all the complexes give oligomer distribution in more or less



**Scheme 1** Synthesis of complexes **8**–**14**

| | 1 | 2 | 3 | 4 | 5 | 6 | 8 | 9 | 10 | 11 | 12 | 13 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| R | H | Me | Ph | H | Me | Ph | H | Me | Ph | H | Me | Ph |

similar pattern. All the complexes gave exclusively butenes and minor amount of hexenes (Table 1). A maximum amount of butenes (93 %) was obtained when **12** is combined with EASC ([Al]/[Ni] = 250) at 30 °C. In all conditions α-olefins dominate both in hexenes and butenes. At −10 °C **12** gave 98 % total α-olefins. There is no conspicuous trend according to experimental parameters with slight change in the amounts of the individual oligomers. As the temperature increases, the amount of internal olefins increases; and with the increasing alkylaluminum (AA) content overall hexene content decreases.

The activity of the catalysts has also been investigated combined with different types of co-catalyst such as MAO, EASC, MADC and DEAC. It is generally recognized that AAs have different abilities to reduce organometallic complex in a higher valence state. The replacement of one or two alkyl groups by halogens bearing heteroatoms usually dramatically alters the activity of the catalyst [16, 17]. Two possible structures have been identified as active species. Firstly, a bimetallic Al–metal bridged species can be the active species. Secondly, an ion-pair model containing cationic metal species formed through the abstraction of halide anions by the Al containing co-catalyst can act as the active species. Here the Al co-catalyst with halogen can further transform to a halogen-Al counterion. Possibility of bridged structure alone being the active species was ruled out by the spectroscopic investigation [18] and also by the kinetic studies [19]. There are growing experimental evidences that, in catalyst co-catalyst architecture, the co-catalyst counterion's structural matching and fitting with cation play significant role in the structure and energetics of the ion pairing and hence catalytic activities and selectivity of the system [19].

In the present study, DEAC gave no activity while MAO a negligible activity (Table 1) due to the drastic deactivation.

**Table 1** Ethylene oligomerization results over Ni(II) complexes in combination with various organoaluminum co-catalysts at different reaction environments

| Run no. | Cat. | Cocat.[a] | [Cocat.]/[Ni] | $P_{C2H4}$ (bar) | T (°C) | Solvent | $R^{b}_{avg}$ x $10^{-6}$ | Selectivity[c] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $C_4^=$ | | $C_6^=$ | |
| | | | | | | | | $\alpha^{=d}$ | $\Sigma C_{4i}^{=e}$ | $\alpha^{=d}$ | $\Sigma C_{6i}^{=e}$ |
| 1 | **11** | EASC | 150 | 1.3 | 30 | PhCl | 16.3 | 86 | 5 | 5 | 4 |
| 2 | **12** | EASC | 150 | 1.3 | 30 | PhCl | 26.5 | 84 | 2 | 9 | 5 |
| 3 | **13** | EASC | 150 | 1.3 | 30 | PhCl | 35.7 | 81 | 7 | 8 | 4 |
| 4 | **12** | MAO | 150 | 1.3 | 30 | PhCl | 0.3 | 78 | 6 | 10 | 6 |
| 5 | **12** | MADC | 150 | 1.3 | 30 | PhCl | 23.4 | 83 | 3 | 10 | 4 |
| 6 | **12** | DEAC | 150 | 1.3 | 30 | PhCl | – | – | – | – | – |
| 7 | **12** | EASC | 50 | 1.3 | 30 | PhCl | 17.3 | 83 | 4 | 10 | 3 |
| 8 | **12** | EASC | 100 | 1.3 | 30 | PhCl | 19.7 | 84 | 3 | 8 | 5 |
| 9 | **12** | EASC | 200 | 1.3 | 30 | PhCl | 8.6 | 85 | 4 | 7 | 4 |
| 10 | **12** | EASC | 250 | 1.3 | 30 | PhCl | 2.1 | 86 | 7 | 4 | 3 |
| 11 | **12** | EASC | 150 | 1.3 | 50 | PhCl | 0.5 | 80 | 7 | 8 | 5 |
| 12 | **12** | EASC | 150 | 1.3 | 70 | PhCl | 0.1 | 76 | 7 | 9 | 8 |
| 13 | **12** | EASC | 150 | 1.3 | 0 | PhCl | 1.8 | 85 | 2 | 11 | 2 |
| 14 | **12** | EASC | 150 | 1.3 | −10 | PhCl | 1.4 | 86 | 1 | 12 | 1 |
| 15 | **12** | EASC | 150 | 1.3 | −20 | PhCl | – | – | – | – | – |
| 16 | **12** | EASC | 150 | 1.3 | 30 | Toluene | 2.0 | 80 | 4 | 13 | 3 |
| 17 | **12** | EASC | 150 | 1.3 | 30 | Hexane | – | – | – | – | – |
| 18 | **12** | EASC | 150 | 1.3 | 30 | $CH_2Cl_2$ | 3.6 | 82 | 6 | 10 | 3 |
| 19 | **12** | EASC | 150 | 5.5 | 30 | PhCl | 42.3 | 80 | 3 | 14 | 3 |

Oligomerization conditions: catalyst = 2.5 μmol, solvent = 80 mL, and time = 30 min

[a] Organoaluminum co-catalysts: *EASC* ethylaluminum sesquichloride, *MAO* methylaluminoxane, *MADC* methylaluminum dichloride, and *DEAC* diethylaluminum chloride

[b] Average rate of oligomerization over a period of reaction in g-oligomer/mol-Ni h bar

[c] Determined by GC

[d] α-Olefin

[e] Sum of internal olefins other than α-olefin

Side reactions such as alkyl exchange and H-exchange reactions or the reduction of metal ion to its lower oxidation state can cause deactivation. In the case of MAO the major deactivation process is α-hydrogen transfer which will lead to the production of methane [16]. Combining with EASC, complex **12** showed the highest activity (26.5 × $10^6$ g-oligomer/mol-Ni h bar). MADC also gave a considerably high activity with relatively slow deactivation (23.4 × $10^6$ g-oligomer/mol-Ni h bar). As described above the difference in activity is mainly caused by the nature of ion-pair formed from the catalyst co-catalyst assembly, resulting from the difference in structure, electronic demands and the strength of counterion formed from these Al co-catalysts.

The effect of co-catalyst concentration has also been studied. As [EASC]/[Ni] ratio increases from 50 to 150, the activity gradually increases but a further increase in EASC amount results in the decrease of activity. During the activation process the metal complexes, $LNiBr_2$ (L = ligand), react with AA co-catalysts producing an alkylated cationic complex, $LNi–R^+$, which may again condense with the AA to form inactive LNi–R–NiL and/or LNi–R–Al species. Such inactive species can be reactivated with excess amount of AAs [16]. Thus, the lower activity at lower co-catalyst concentration may be due to the formation of these inactive species that are not further reactivated. In the presence of suitably excess amount of co-catalyst, the inactive species might be dissembled to form active $LM–R^+$ again. The increase of the co-catalyst concentration to a large excess results in a situation where the population of highly coordinating Lewis acidic species is increased. This can nullify the effective ion-pair separation resulting in a decrease in activity.

Interestingly all the complexes gave higher activity in chlorinated solvents than in nonpolar solvents. While the

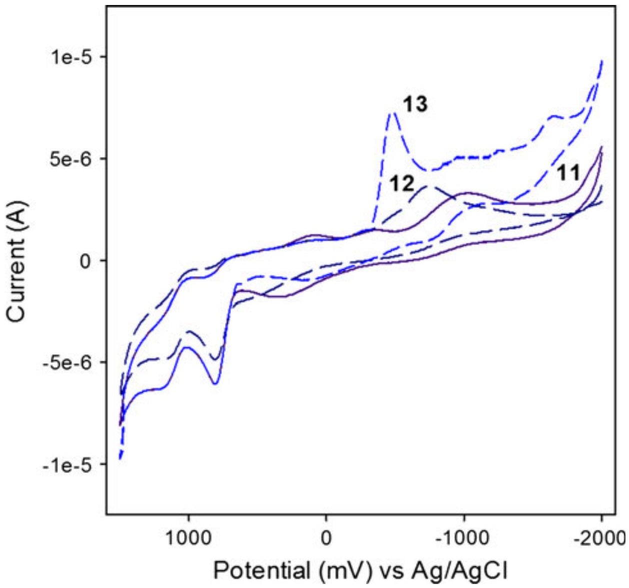


**Fig. 1** Cyclic voltammograms of various nickel complexes, **11**–**13** in DMF at 25 °C with scan rate of 100 mV/s

complexes give a very high activity in methylene chloride and chlorobenzene, they show very low activity in toluene and no activity in n-hexane. Increasing the polarity of the solvent can increase the ion pair separation. Activation energy for ethylene insertion is lower in cationic systems than that in ion-pair system [20]. Thus, the reason for giving a lower or no activity in nonpolar solvents might be due to an inefficient ion-pair separation, while high activities in chlorinated solvents are related with the facilitated separation of ion-pair in polar medium.

An expedition on the influence of temperature on EO activities revealed that the maximum activity of 26.5 × $10^6$ g-oligomer/mol-Ni h bar for complex **12** is observed at 30 °C. At higher temperature a drastic decrease in activity was noticed (run no. 11 and 12 in Table 1). For α-diimine nickel complexes, Brookhart has found that the catalyst life time is significantly short at elevated temperatures [21]. Along with the low solubility of ethylene at high temperatures, catalyst decay plays an important role in this decreased activity. However, the catalyst showed a considerable activity at a very low temperature (1.4 × $10^6$ g-oligomer/mol-Ni h bar at −10 °C). The inactive LNi–R–NiL or LNi–R–Al species are predominantly reversible at lower temperatures, which increase the population density of active species in the system giving a remarkable activity even at a low temperature.

Separation of ion-pair is directly related to the formation of active species and thus to the activity. In order to investigate the active species formation, UV–Vis spectroscopic technique has recently been used [17, 22]. The UV–Vis spectra were recorded for a chlorobenzene solution containing 2.5 μmol of complex **12** by varying the co-catalyst concentration from [EASC]/[Ni] = 50 to 250 for simulating the EO conditions. Note that EOs were carried out in this range of co-catalyst concentration (Table 1). By adding EASC to the solution, a new absorption peak is observed at around 850 nm (Fig. 2). Absorbance of this peak reaches the maximum at [EASC]/[Ni] = 150 and then starts to decrease by further increase of the EASC concentration.

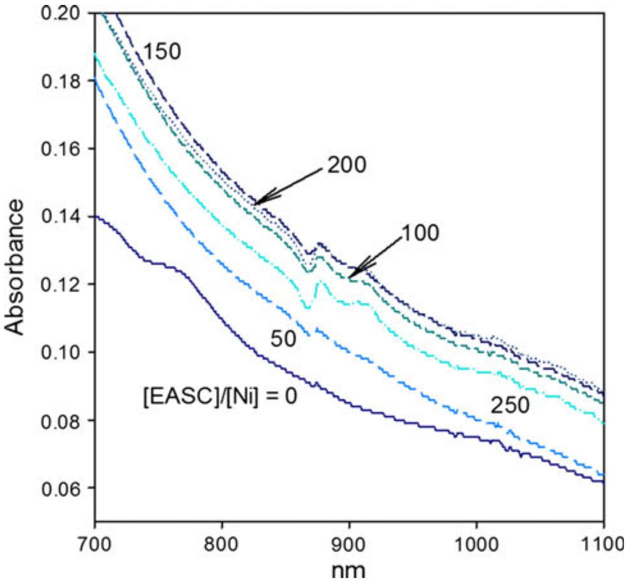


**Fig. 2** UV–Vis spectra of nickel complex **12** (2.5 μmol) combined with different amounts of EASC ([EASC]/[Ni] = 0–250) in chlorobenzene

This trend of absorbance of the peak at around 850 nm is in line with the trend of activity observed in EO. A plot of activity and molar extinction coefficient against the EASC concentration gives a better idea about the correlation between the population density of active species and activity (Fig. 3). Since the activity is directly related to the ion-pair separation, a correlation between population density of active species and ion-pair separation can be understood. According to this observation, the population density of active species will be less at lower co-catalyst concentration. It is interesting to note that this trend matches with the trend of activity according to EASC concentration, demonstrating the absorption peak observed at around 850 nm is generated due to the formation of the active species.

## 4 Conclusions

A series of N^N type bidentate nickel complexes bearing *N*-((4-butyl-6-phenylpyridin-2-yl)methylene)-2,6-diisopropylaniline derivatives as ligands have been prepared by one-pot reactions

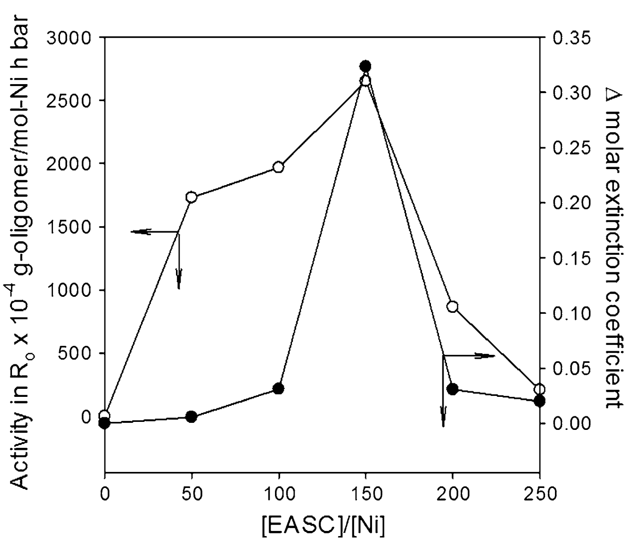


**Fig. 3** Ethylene oligomerization activity and difference in molar extinction coefficients from UV–Vis spectra estimated by complex **12** combined with different amounts of EASC ([EASC]/[Ni] = 0–250)

with 2,6-diisopropyl aniline and nickel bromide derivatives. All these complexes exhibited considerably high activity toward ethylene when activated with EASC and MADC to give butenes and hexanes with the butenes and µ-olefins as dominating products. Detailed EO reactions have been carried out at different experimental parameters such as the type and the amount of co-catalyst, temperature and solvents. The activity difference according to the structure of the complex was attempted to analyze using the concept of a possible ion-pair formation during activation process. The ion-pair formation and its stability were equally influential in cationic late transition metal complexes as in their early metal counterparts. An attempt to assign the active species was made by comparing the EO results with UV–Vis spectroscopic study, successfully identifying an absorption peak assignable to active species. The CV experiments were also made to get an idea about the electronic influence of the structure of ligands on metal center.

**Acknowledgments** This work was supported by Basic Science Research Program (2012R1A1A2041315) and the Fusion Research Program for Green Technology (2012M3C1A1054502) through the National Research Foundation of Korea funded by the Ministry of Education, Science and Technology.

## References

1. Kaminsky W, Arndt M (1997) Adv Polym Sci 127:143
2. Bochmann M (1996) J Chem Soc Dalton Trans 255
3. Grubbs RH, Coates GW (1996) Acc Chem Res 29:85
4. Brintzinger HH, Fischer D, Mülhaupt R, Rieger B, Waymouth RM (1995) Angew Chem Int Ed 34:1143
5. Baumann R, Davis WM, Schrock RR (1997) J Am Chem Soc 119:3830
6. Ittel SD, Johnson LK, Brookhart M (2000) Chem Rev 100:1169
7. Zurek E, Ziegler T (2001) Organometallics 21:83
8. Deck PA, Beswick CL, Marks TJ (1998) J Am Chem Soc 120:1772
9. Köhn RD, Haufe M, Kociok-Köhn G, Grimm S, Wasserscheid P, Keim W (2000) Angew Chem Int Ed 39:4337
10. Johnson LK, Killian CM, Brookhart M (1995) J Am Chem Soc 117:6414
11. Small BL, Carney MJ, Holman DM, O'Rourke CE, Halfen JA (2004) Macromolecules 37:4375
12. Chandran D, Kwak CH, Oh JM, Ahn IY, Ha CS, Kim I (2008) Catal Lett 125:27
13. Chandran D, Bae C, Ahn IY, Ha CS, Kim I (2009) J Organomet Chem 694:1254
14. Chandran D, Lee KM, Chang HC, Song GY, Lee J-E, Suh H, Kim I (2012) J Organomet Chem 718:8
15. Gibson VC, Long NJ, Oxford PJ, White AJP, Williams DJ (2006) Organometallics 25:1932
16. Bahuleyan BK, Son GW, Park D-W, Ha C-S, Kim I (2008) J Polym Sci Part A: Polym Chem 46:1066
17. Appukuttan V, Zhang L, Ha C-S, Kim I (2009) Polymer 50:1150
18. Long WP (1959) J Am Chem Soc 81:5312
19. Fink G, Zoller W (1981) Makromol Chem 182:3265
20. Yang SH, Huh J, Jo WH (2005) Macromolecules 38:1402
21. Gates DP, Svejda SA, Oñate E, Killian CM, Johnson LK, White PS, Brookhart M (2000) Macromolecules 33:2320
22. Chandran D, Kwak CH, Ha C-S, Kim I (2008) Catal Today 131:505