In situ UV–VIS studies on late-transition metal catalysts for ethylene polymerization

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Abstract

In situ UV–VIS spectroscopic system for ethylene polymerization under atmospheric pressure was designed and built, and was used to mechanistic studies for late-transition metal catalysts. Four catalytic systems with four different iron, cobalt and nickel complexes as catalyst precursor were studied. The corresponding complexes are 2,6-bis(1-(2,6-dimethyl-phenylimino)ethyl)pyridine iron(II) dichloride (a), 2,6-bis[1-(2,4,6-trimethylphenylimino)ethyl]pyridine iron(II) dichloride (b), 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine cobalt dichloride (c) and 1,2-bis(2,6-diisopropylphenyl)ethane nickel(II) dibromide (d). The experimental results showed that the step of activation of MAO to procatalyst is very fast; active absorptions at 560, 640, 580 and 545 nm were observed, respectively, and were probably assigned to catalytically active species which were coordinatively cationic alkyl complexes. For active absorptions, the increasing regularity in polymerization initiation and the decreasing regularity during the catalyst being poisoned by anhydrous batches ethanol, were investigated. Catalytically active species and catalytic mechanism were discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron; Nickel; In situ UV–VIS; Ethylene; Polymerization

1. Introduction

Polyethylene is one of the largest amount of synthetic resins, and is playing a more and more important role in human beings life and industry. For satisfying the increasing demands of people for material civilization, it is important to develop new generation catalyst for producing polyethylene with improved properties, which is an important aim that scientific researchers studied for many years. For example, to study and develop new generation catalyst with low cost, high activity, high selectivity, stronger

regulating ability to control molecular weight distribution (MWD) and more tolerating ability to polar monomers, etc. and was used to develop polyethylene with both good physical properties and excellent processability. Non-metallocene single-site catalyst has been developed to be a very new and active research area in the past 5 years [1], providing a more broad research field for developing new catalyst. In these studies, late-transition metal catalysts including 2,6-diiminepyridine/iron or cobalt catalysts and α-diimine/nickel catalyst is a new kind of catalysts with great significance in industrial application in the near future.

Iron series catalyst was found independently by Brookhart and co-workers [2,3] of The University of

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North Carolina in USA financed by Du Pont Company, Gibson and coworkers [4,5] of Imperial College of UK financed by BP Company. α-Diimine/nickel catalyst was also developed by Brookhart and co-workers [6,7]. We have ever studied ethylene polymerization behavior for iron catalyst [8]. Compared with metallocene catalyst, iron catalyst has comparable or even higher catalytic activity under similar conditions, and iron catalyst is more easily to be synthesized, has low cost, the obtained polyethylene has linear molecular chain with high crystallinity and broad MWD. Therefore, polyethylene produced with iron catalyst has no processing problem that has ever hindered the development of metallocene catalyst. So iron catalyst shows excellent prospect in industrial application. α-Diimine/nickel catalyst could also be synthesized more easily than metallocene catalyst. The most significant advantage is that α-diimine/nickel catalyst could catalyze ethylene polymerization directly to highly branched polyethylene without adding α-olefins.

In order to modify late-transition metal catalysts, and to promote its industrialization space, it is necessary to study it's catalytic mechanism. At the same time these mechanistic studies could provide theoretical guidance for developing new generation catalyst for ethylene polymerization. Brookhart and coworkers [9], Gibson and coworkers [10] and Ziegler and coworkers [11] have studied the catalytic mechanism, especially the chain propagation and chain transfer mechanism were discussed. It is proposed that the size of phenyl group is the key factor affecting catalytic activity and chain transfer reaction.

Single-site polyethylene catalysts, such as metallocene catalyst, α-diimine/nickel catalyst, and 2,6-diiminepyridine/iron catalyst, all have very strong conjugated system in molecular structure, therefore, they all show strong absorptions in UV–VIS spectroscopy, and the change in catalyst structure or component would cause shift in UV–VIS absorption. Deffieux of France have studied metallocene catalyst [12,13] and α-diimine/nickel catalyst [14,15] for hexene-1 polymerization with UV–VIS spectroscopic system. The variational regularity of active and inactive absorptions were investigated under room temperature. These studies proved that UV–VIS spectroscopic system is an efficient method to study

the catalytic mechanism for single-site catalyst with strong conjugated system.

In order to study the catalytic mechanism of single-site catalyst for ethylene polymerization with UV–VIS spectroscopy, here we have designed and built a set of in situ UV–VIS spectroscopic system for ethylene polymerization under atmospheric pressure, and was successfully used to study late-transition metal catalysts including 2,6-diiminepyridine/iron, 2,6-diiminepyridine/cobalt and α-diimine/nickel catalysts, the increasing and decreasing regularities of active absorptions were investigated for the whole process of ethylene polymerization.

2. Experimental

2.1. Instrument

TU-1221 UV–VIS spectrophotometer.

2.2. General procedure for in situ UV–VIS spectroscopic experiment

In situ UV–VIS spectroscopic system for ethylene polymerization under atmospheric pressure was designed and shown in Fig. 1.

In a N_2 drying box, about 30 ml solution of catalyst precursor in chlorobenzene or tetrahydrofuran(THF) of desired concentration was added into reactor (a). A bladder (d) with (c) was purified with ethylene at least three times and was introduced full of ethylene. Then in the N_2 drying box, (a), (d) and (e) were linked together with latex tube to form a closed system. Before the experiment, pure solvent was swept, and it's absorption was used as background to be deducted when sample was detected.

At the beginning of the experiment, see Fig. 1, valve (c) was in closed state, (a) was raised, (e) was lowered, thus sample flowed into (e) by itself and until to 3/4 volume of (e) cell. Immediately, the UV–VIS spectroscopy was obtained, which was assigned to the complex used as catalyst precursor. Then (e) cell was raised, (a) was lowered, thus the solution flowed back to (a) completely. After desired amount of MAO was added with a syringe, immediately the reactor (a) was shaken and the solution was made to flow into (e) cell with the above described
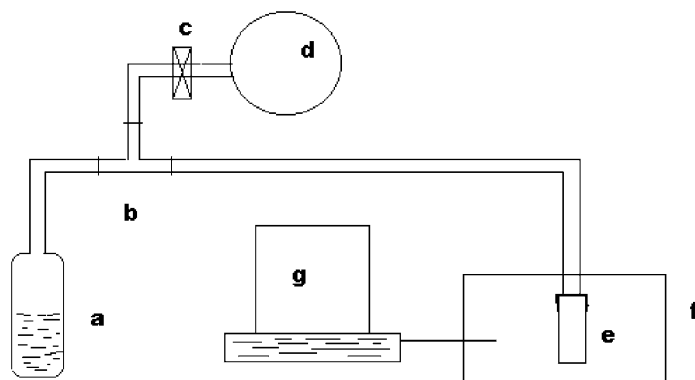
Fig. 1. In situ UV–VIS spectroscopic system for ethylene polymerization under atmospheric pressure: (a) glass reactor (50 ml); (b) three-way pipe; (c) valve; (d) bladder; (e) colorimeter(1 cm thick); (f) UV–VIS spectrophotometer; (g) computer control system. Note: latex tube was used to connect a and b, b and c, b and e.

method, and the sample was swept quickly. Thus, the obtained UV–VIS spectroscopy was assigned to the catalyst activated by MAO. After the solution was made to flow back to reactor (a) by the above described method, valve (c) was opened, ethylene was introduced into the catalyst system, immediately (a) was shaken, solution was made to flow into (e) cell, and the UV–VIS spectroscopy was obtained quickly. Then, the above described operation was repeated after certain period of time. By this way the increasing regularity of active absorption was investigated. After the active absorption grew up and maintained stable, anhydrous ethanol was added in batches to terminate the polymerization. UV–VIS spectroscopy was obtained immediately after ethanol was added for every time, to investigate the decreasing regularity of the active absorption. Finally, a little amount of polyethylene was separated and characterized with FT–IR.

3. Results

Here with in situ UV–VIS spectroscopic technique for ethylene polymerization under atmospheric pressure, four late-transition metal catalysts including 2,6-diiminepyridine/iron, 2,6-diiminepyridine/cobalt and α-diimine/nickel catalysts were investigated as catalyst precursor, which molecular structures are shown in Scheme 1.

For iron and cobalt catalysts the concentration of the solution of complex in chlorobenzene was 0.8 μmol/ml. For nickel catalyst, the concentration was 1.0 μmol/ml in THF. Desired amount of MAO was used as cocatalyst which concentration was 1.5 mol/ml in toluene. Polymerization was performed under room temperature and atmospheric pressure. At the same time UV–VIS absorption spectroscopy was obtained.
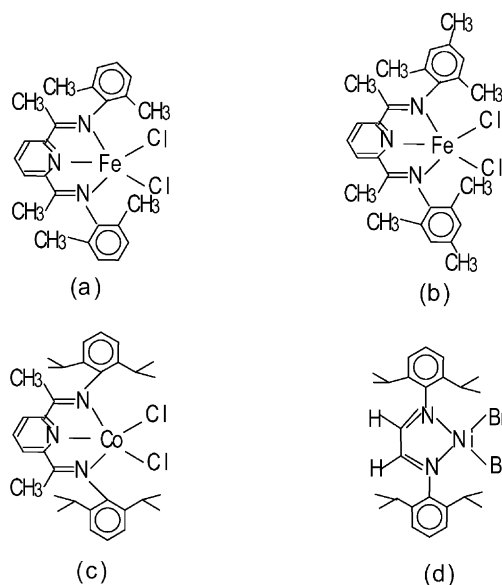
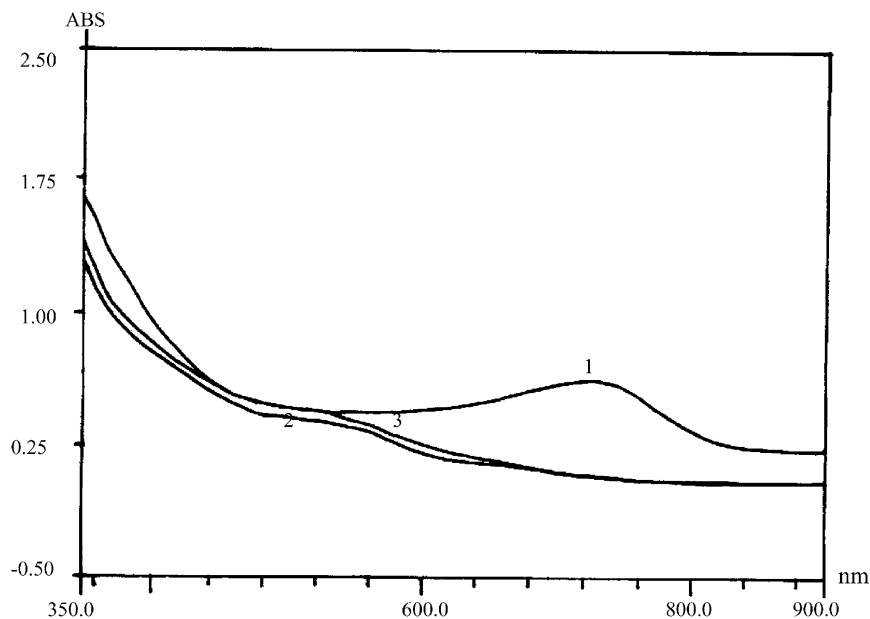Scheme 1. Molecular structures of late-transition metal catalysts.

Fig. 2. UV–VIS absorption spectra before and after ethylene was introduced with complex (a) as catalyst precursor. (1) Solution of complex (a) in chlorobenzene (0.8 μmol/ml); (2) after MAO was added (Al/Fe = 50); (3) after ethylene was introduced.
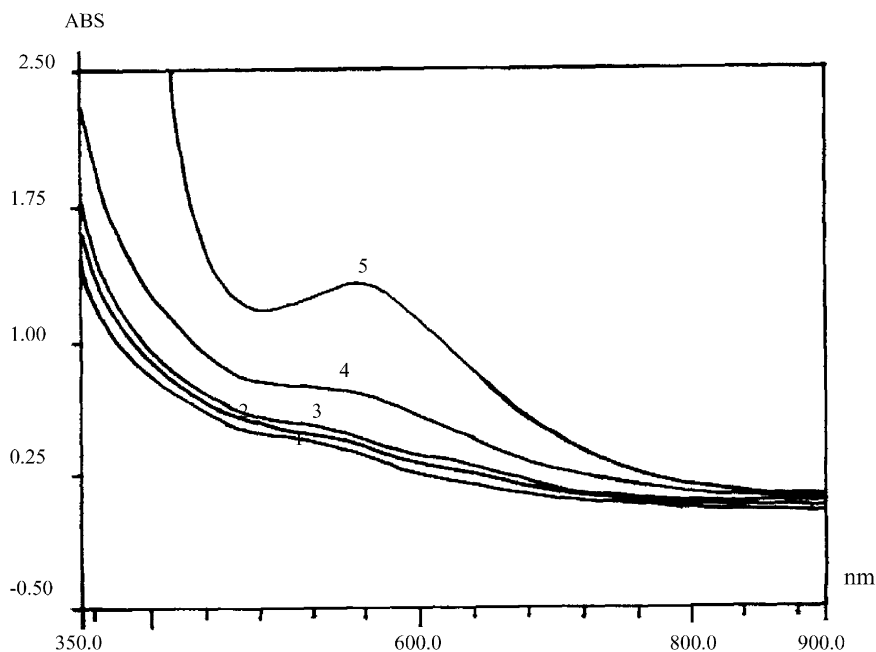

Fig. 3. In situ UV–VIS absorption spectra for ethylene polymerization under atmospheric pressure with complex (a) as catalyst precursor. (1) Immediately after ethylene was introduced; (2) reaction for 12 min; (3) reaction for 27 min; (4) reaction for 40 min; (5) reaction for 62 min.

3.1. Results of complex (a) used as catalyst precursor

To the solution of complex (a) in chlorobenzene, the used amount of MAO was controlled so that Al/Fe molar ratio was 50. Fig. 2 showed the UV–VIS spectra obtained before and after ethylene was introduced. Fig. 3 showed the UV–VIS spectra obtained in the process of the polymerization initiation. Fig. 4 showed the UV–VIS spectra obtained in the polymerization termination process by anhydrous ethanol in batches.

In Fig. 2, complex (a) had an absorption at 730 nm. After MAO was added, the absorption at 730 nm disappeared immediately. In Fig. 3, in the process of the polymerization initiation under ethylene ambi-

ence, new absorption at 560 nm grew up gradually. In Fig. 4, in the process of polymerization termination by batches anhydrous ethanol, absorption at 560 nm decreased gradually and finally disappeared, at the same time, absorption at 730 nm reappeared and strengthened gradually. The final absorption curve was similar to that of the initial UV–VIS spectroscopy of the complex (a).

Little amount of polyethylene was separated and characterized with FT-IR. The FT-IR spectroscopy is shown in Fig. 5, which is a typical IR spectroscopy of linear polyethylene. IR: 2918 cm^{-1}: $v_{as(-CH_2-)}$, 2850 cm^{-1}: $v_{s(-CH_2-)}$, 1470 cm^{-1}: $v_{s(-CH_2-)}$, 718 cm^{-1}: $v_{\gamma(-CH_2-)}$.
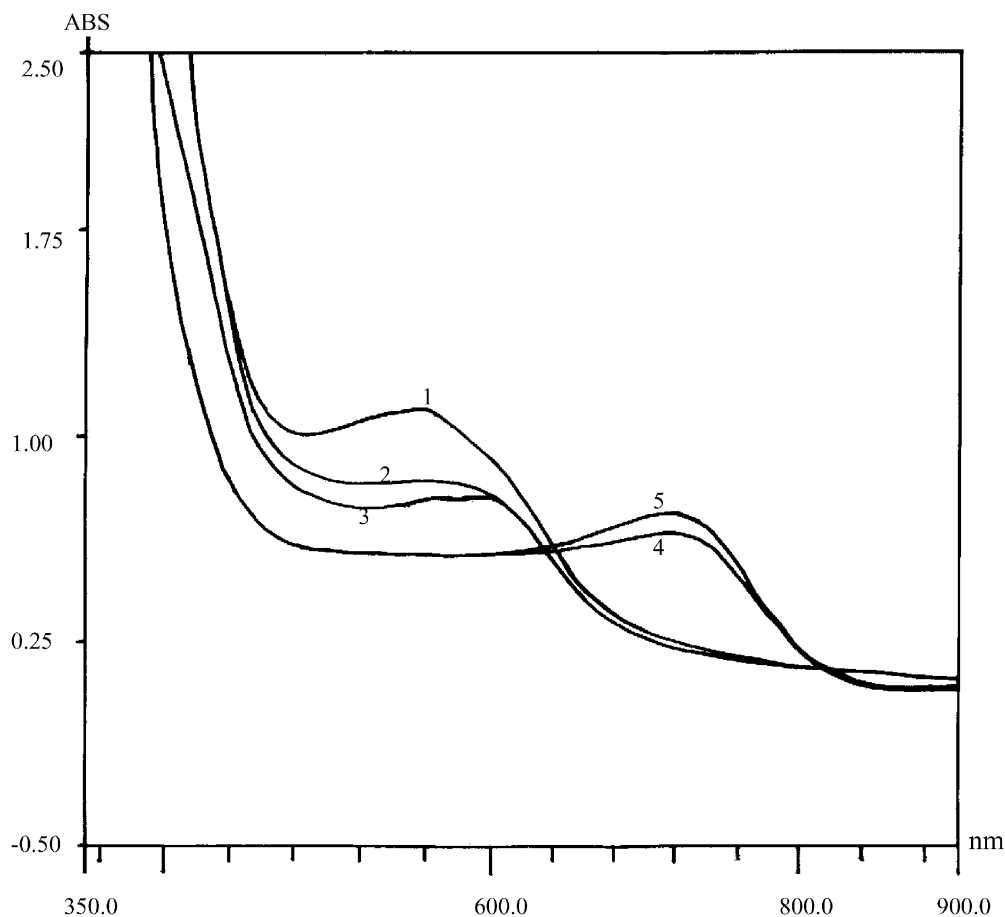

Fig. 4. In situ UV–VIS absorption spectra during the step-termination of the polymerization by addition of anhydrous ethanol with complex (a) as catalyst precursor. (1) Polymerization for 87 min; (2) total amount of added ethanol was 3 µl; (3) total amount of added ethanol was 6 µl; (4) total amount of added ethanol was 15 µl; (5) total amount of added ethanol was 18 µl.
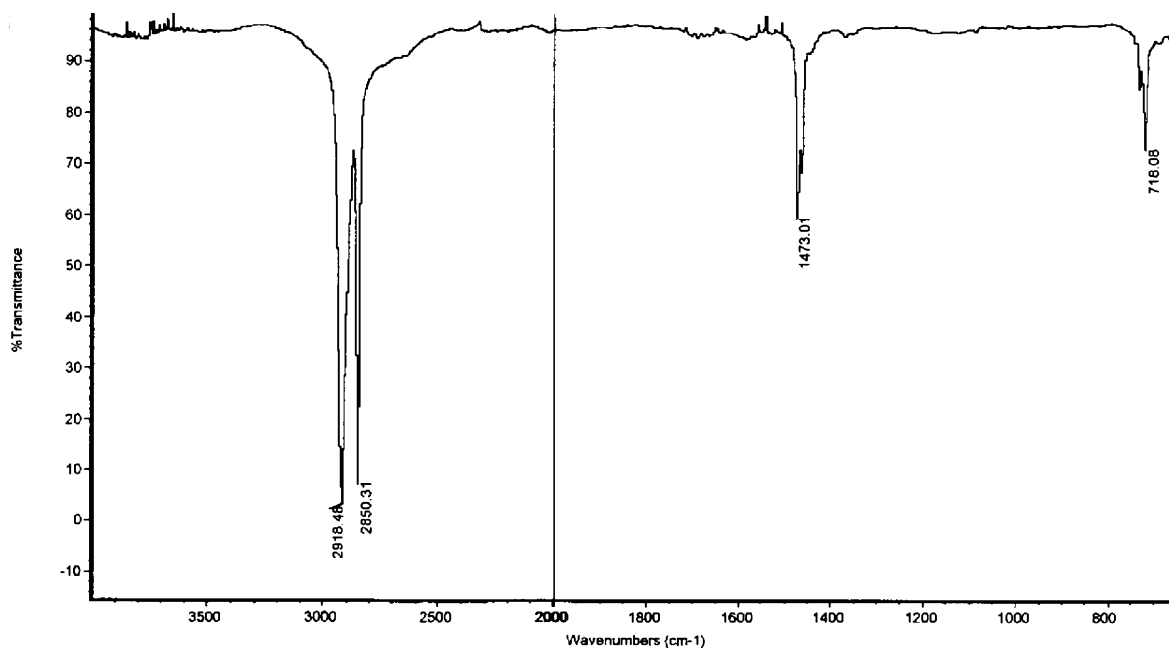
Fig. 5. FT-IR spectroscopy of polyethylene prepared with iron catalyst.
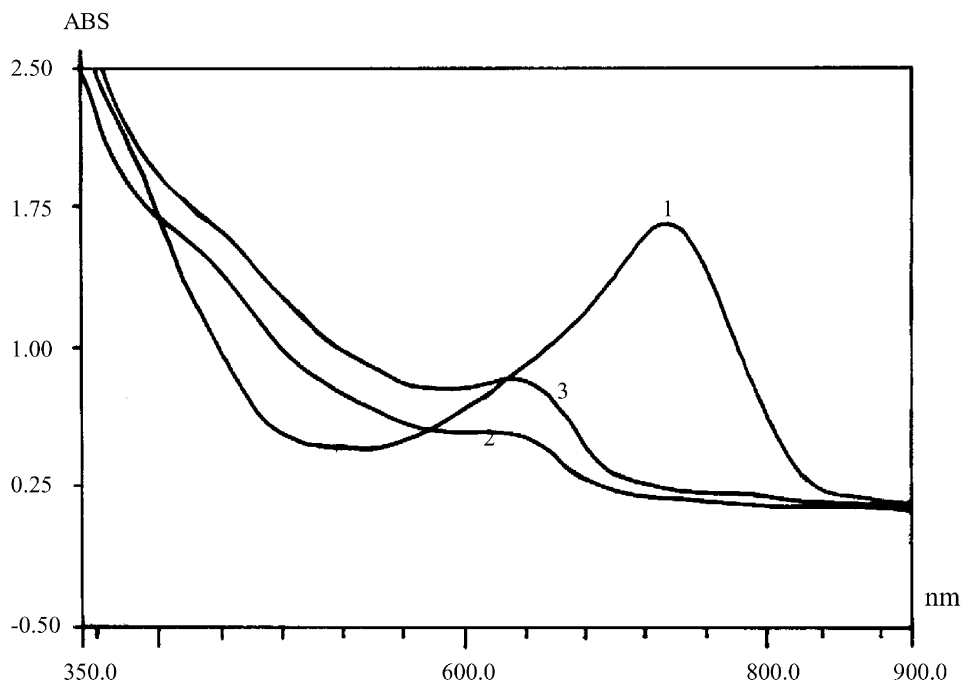
Fig. 6. UV–VIS absorption spectra before and after ethylene was introduced with complex (b) as catalyst precursor. (1) Solution of complex (b) in chlorobenzene (0.8 μmol/ml); (2) after MAO was added. (Al/Fe = 200); (3) after ethylene was introduced.

3.2. Results of complex (b) used as catalyst precursor

To the solution of complex (b) in chlorobenzene, the used amount of MAO was controlled so that Al/Fe molar ratio was 200. Fig. 6 showed the UV–VIS spectra obtained before and after ethylene was introduced. Fig. 7 showed the UV–VIS spectra obtained in the process of the polymerization initiation. Fig. 8 showed the UV–VIS spectra obtained in the polymerization termination process by anhydrous ethanol.

In Fig. 6, complex (b) had a strong absorption at 730 nm. After MAO was added, the absorption at 730 nm disappeared immediately. In Fig. 7, in the process of the polymerization initiation under ethylene ambience, a new absorption at 640 nm grew up gradually. In Fig. 8, when 200 ml anhydrous ethanol was added, absorption at 640 nm decreased quickly and finally disappeared, at the same time, an absorption at 720 nm appeared. The final absorption curve was similar to that of the initial UV–VIS spectroscopy of the complex (b).

3.3. Results of complex (c) used as catalyst precursor

To the solution of complex (c) in chlorobenzene, the used amount of MAO was controlled so that Al/Co molar ratio was 300. Fig. 9 showed the UV–VIS spectra obtained before and after ethylene was introduced. Fig. 10 showed the UV–VIS spectra obtained in the process of the polymerization initiation. Fig. 11 showed the UV–VIS spectra obtained in the reaction termination process by anhydrous ethanol.

In Fig. 9, complex (c) had no evident absorption at between 350 and 900 nm. After MAO was added, two strong absorptions appeared immediately at 580 and 760 nm. In Fig. 10, with the polymerization time was prolonged, absorption at 580 nm increased gradually, meanwhile, absorption at 760 nm decreased gradually and became very weak. In Fig. 11, with the addition of anhydrous ethanol in batches, absorption at 580 nm decreased quickly, and finally both the absorption at 580 and 760 nm disappeared completely, just as that complex (c) has no absorption in this absorption range.
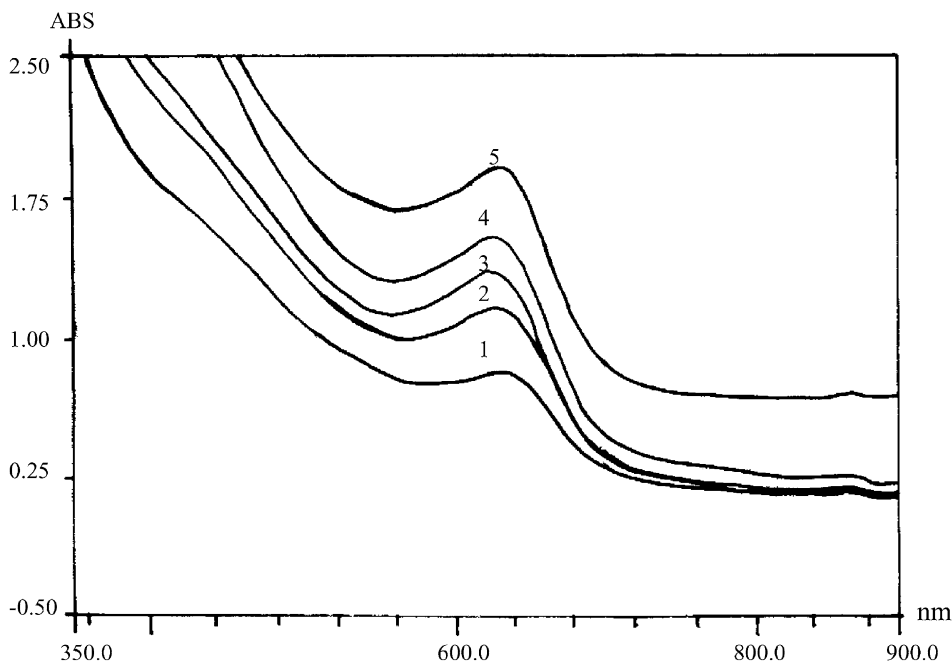

Fig. 7. In situ UV–VIS absorption spectra for ethylene polymerization under atmospheric pressure with complex (b) as catalyst precursor. (1) immediately after ethylene was introduced; (2) reaction for 10 min; (3) reaction for 26 min; (4) reaction for 70 min; (5) reaction for 99 min.
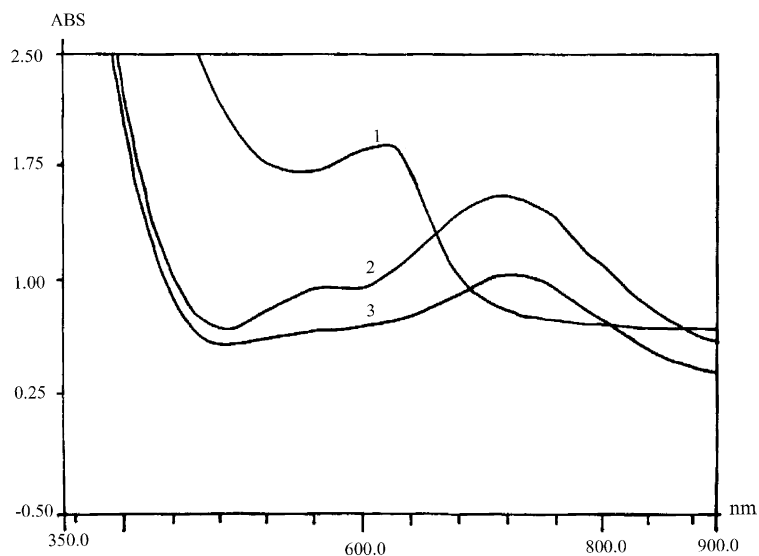
Fig. 8. In situ UV–VIS absorption spectra during the step-termination of the polymerization by addition of anhydrous ethanol with complex (b) as catalyst precursor. (1) polymerization for 120 min; (2) 200 μl ethanol was added; (3) after reaction for 5 min.
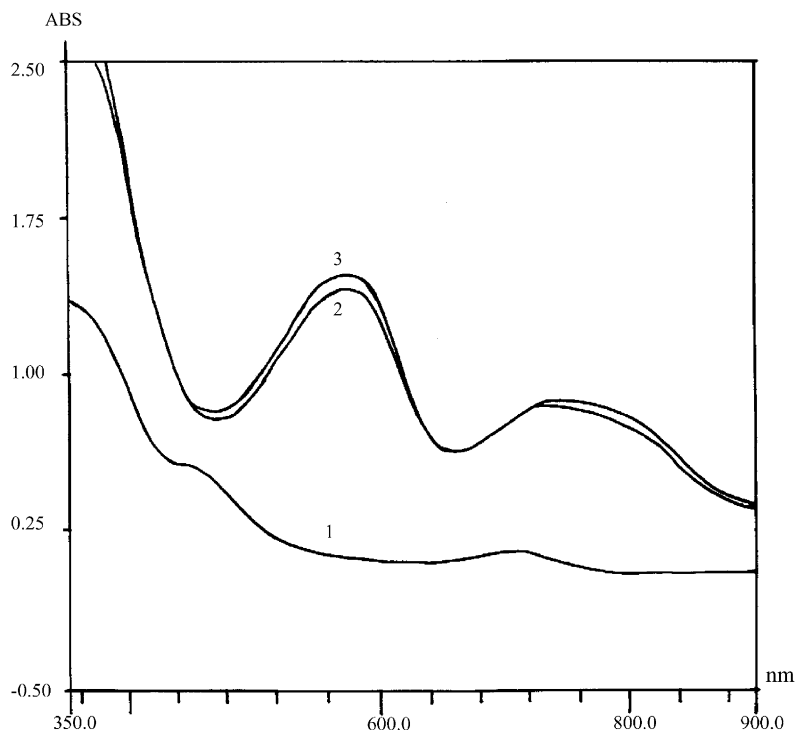

Fig. 9. UV–VIS absorption spectra before and after ethylene was introduced with complex (c) as catalyst precursor. (1) Solution of complex (c) in chlorobenzene (0.8 μmol/ml); (2) after MAO was added (Al/Co = 300); (3) after ethylene was introduced.
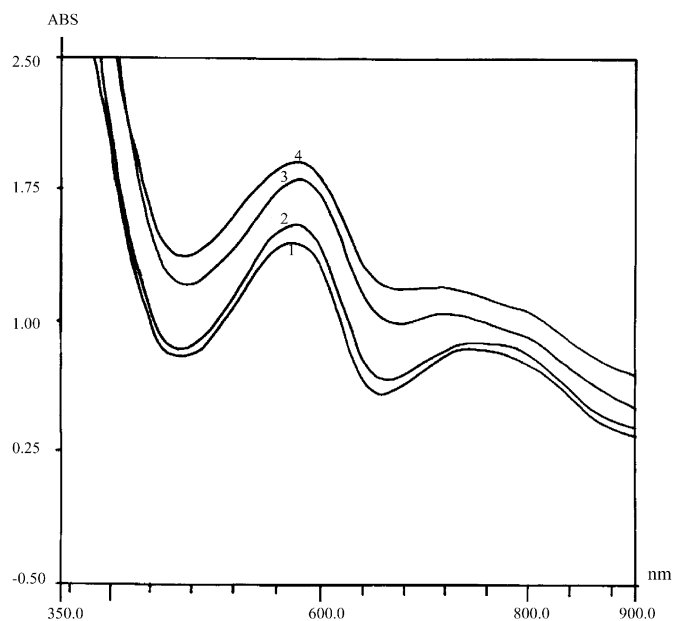
Fig. 10. In situ UV–VIS absorption spectra for ethylene polymerization under atmospheric pressure with complex (c) as catalyst precursor. (1) Immediately after ethylene was introduced; (2) reaction for 10 min; (3) reaction for 15 min; (4) reaction for 82 min.
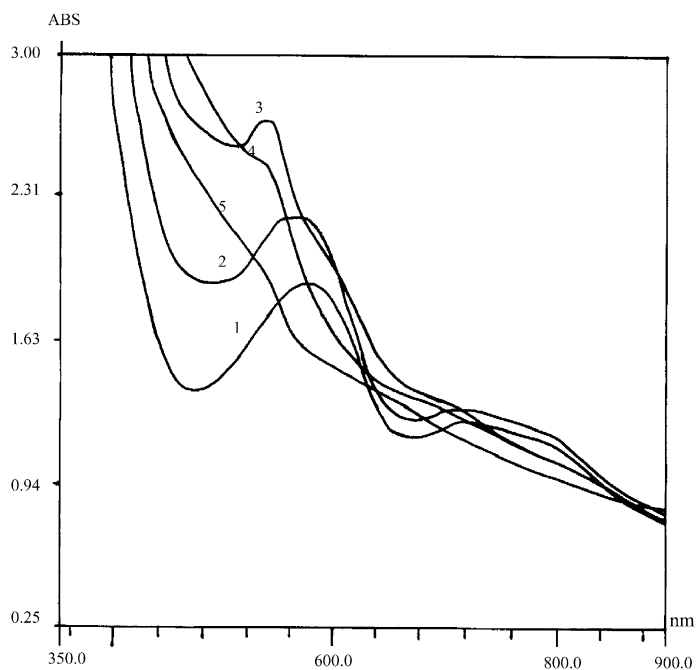

Fig. 11. In situ UV–VIS absorption spectra during the step-termination of the polymerization by addition of ethanol with complex (c) as catalyst precursor. (1) Polymerization for 82 min; (2) total amount of added ethanol was 20 µl; (3) total amount of added ethanol was 40 µl; (4) total amount of added ethanol was 50 µl; (5) total amount of added ethanol was 100 µl.

When Al/Co molar ratio was 200, the same result as above was obtained.

3.4. Results of complex (d) used as catalyst precursor

To the solution of complex (d) in THF, the used amount of MAO was controlled so that Al/Ni molar ratio was 200. Fig. 12 showed the UV–VIS spectra obtained before and after ethylene was introduced. Fig. 13 showed the UV–VIS spectra obtained in the process of the polymerization initiation. Fig. 14 showed the UV–VIS spectra obtained in the polymerization termination process by anhydrous ethanol in batches.

In Fig. 12, complex (d) had no evident absorption at between 350 and 900 nm. After MAO was added, two strong absorptions appeared immediately at 545 and 660 nm. In Fig. 13, with the polymerization time was prolonged, absorption at 545 nm increased gradually, meanwhile, absorption at 660 nm increased firstly, and then decreased greatly, and finally disappeared. In Fig. 14, with the addition of anhydrous ethanol in batches, absorption at 545 nm decreased quickly, and finally disappeared completely, just as that complex (d) has no absorption in this absorption range.

Fig. 13. In situ UV–VIS absorption spectra for ethylene polymerization under atmospheric pressure with complex (d) as catalyst precursor. (1) Immediately after ethylene was introduced; (2) reaction for 7 min; (3) reaction for 13 min; (4) reaction for 31 min; (5) reaction for 87 min.
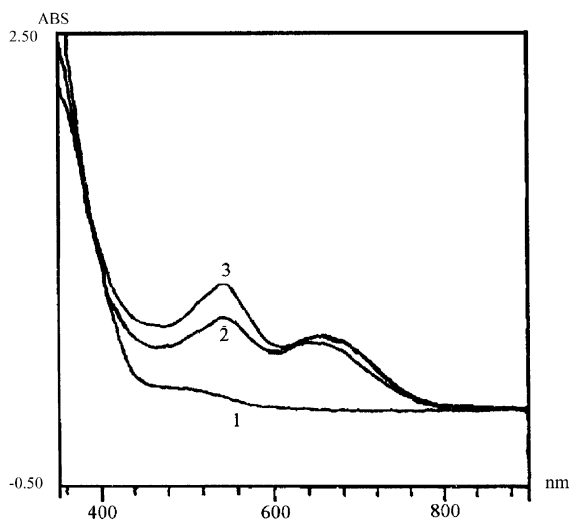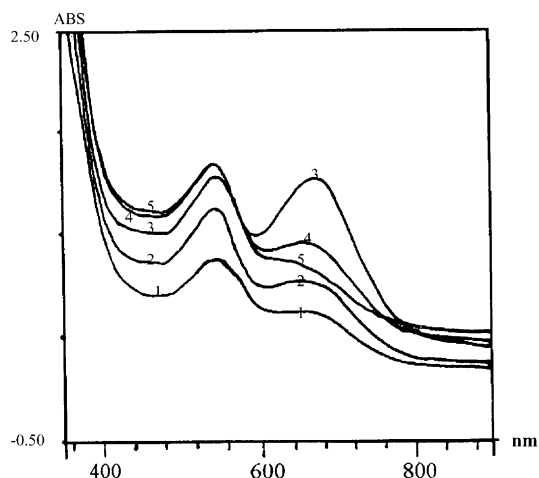

Fig. 12. UV–VIS absorption spectra before and after ethylene was introduced with complex (d) as catalyst precursor. (1) Solution of complex (d) in THF(1.0 μmol/ml); (2) after MAO was added. (Al/Ni = 200); (3) after ethylene was introduced.
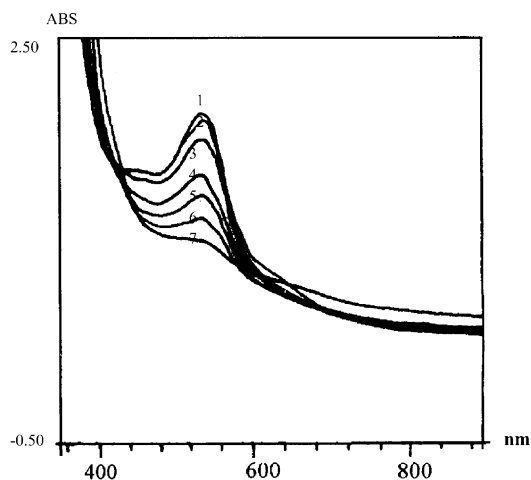

Fig. 14. In situ UV–VIS absorption spectra during the step-termination of the polymerization by addition of ethanol with complex (d) as catalyst precursor. (1) Total amount of added ethanol was 25 μl; (2) total amount of added ethanol was 35 μl; (3) total amount of added ethanol was 40 μl; (4) Total amount of added ethanol was 45 μl; (5) total amount of added ethanol was 50 μl; (6) total amount of added ethanol was 55 μl; (7) total amount of added ethanol was 93 μl.
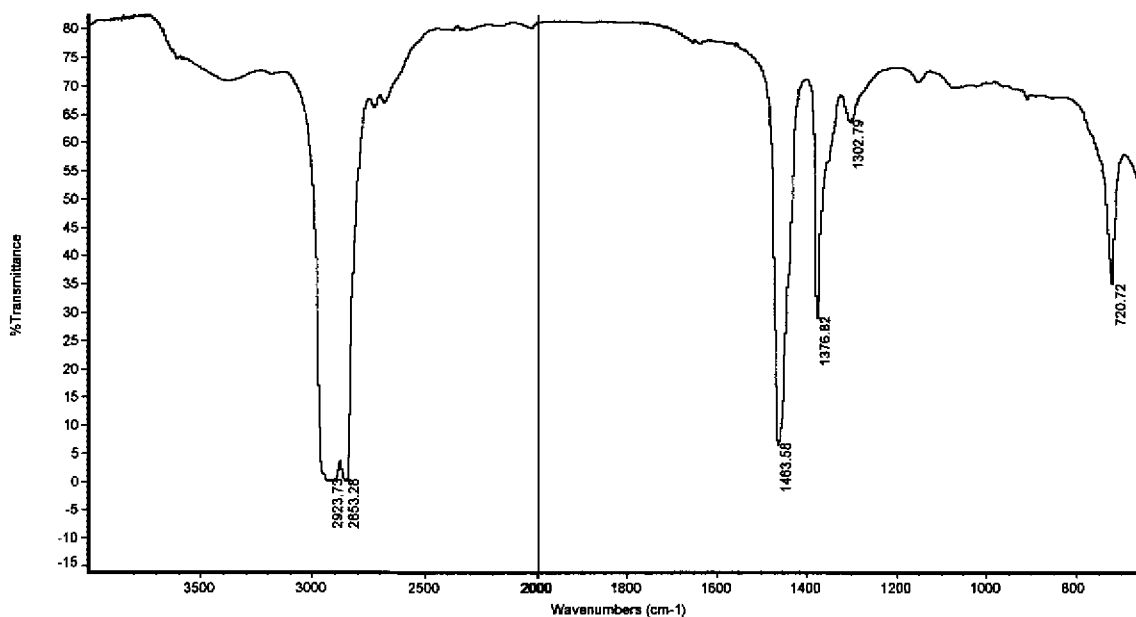
Fig. 15. FT-IR spectroscopy of polyethylene prepared with nickel catalyst.

Little amount of polyethylene was separated and characterized with FT-IR. The FT-IR spectroscopy is shown in Fig. 15, which is a typical IR spectroscopy of highly branched polyethylene. IR: $2924\,\mathrm{cm}^{-1}$: $\upsilon_{\mathrm{as}(-\mathrm{CH_2}-)}$, $2853\,\mathrm{cm}^{-1}$: $\upsilon_{\mathrm{s}(-\mathrm{CH_2}-)}$, $1464\,\mathrm{cm}^{-1}$: $\upsilon_{\mathrm{s}(-\mathrm{CH_2}-)}$, $1377\,\mathrm{cm}^{-1}$: $\upsilon_{(-\mathrm{CH_3})}$, $1303\,\mathrm{cm}^{-1}$: $\upsilon_{(-\mathrm{CH}-)}$, $721\,\mathrm{cm}^{-1}$: $\upsilon_{\gamma(-\mathrm{CH_2}-)}$.

When Al/Ni molar ratio was 200, the same result as above was also obtained.
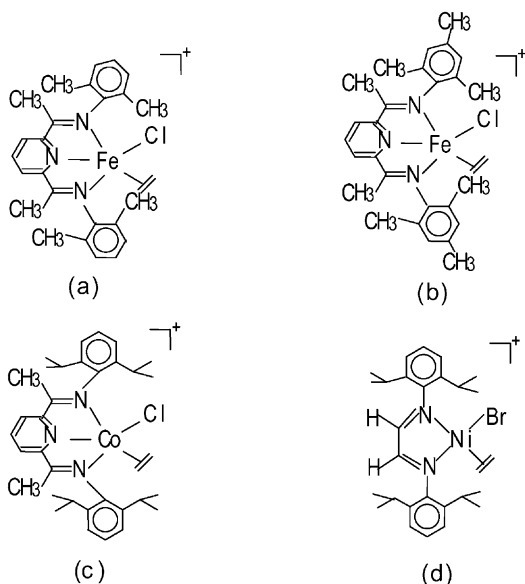
4. Discussion

4.1. The interaction of catalyst precursor with MAO

MAO is the most common cocatalyst for transition metal complex used as single-site catalyst precursor for ethylene polymerization, especially for di-halogen-complexes. Usually, the activation of MAO to complex is believed to be achieved by alkylation and ionization, and the produced active species are coordinatively unsaturated cationic alkyl complexes [1]. Figs. 2, 6, 9 and 12 showed that UV–VIS absorption shifted greatly and immediately after MAO was added. In Fig. 2, the absorption at 730 nm

disappeared immediately after addition of MAO; in the Fig. 6, the absorption at 730 nm also disappeared immediately after addition of MAO; in Fig. 9, two strong absorptions at 580 and 760 nm appeared immediately after addition of MAO; In Fig. 12, two strong absorptions at 545 and 660 nm appeared immediately after addition of MAO. The above described results showed clearly that the reaction of MAO with catalyst precursor is very easily, quickly and completely. Meanwhile it may show that cocatalyst MAO has excellent activation effect to catalyst precursor.

4.2. The catalytic active species

First, the absorption at 560 nm in Fig. 3, the absorption at 630 nm in Fig. 7, the absorption at 580 nm in Fig. 10, and the absorption at 545 nm in Fig. 13, all grew up gradually and existed under real polymerization conditions. Second, when the polymerization was terminated by addition of anhydrous ethanol in batches, the above described four active absorptions all decreased gradually and finally disappeared, the final UV–VIS absorption curve was similar to the initial absorption curve assigned to catalyst precursor shown in Figs. 2, 6, 9 and 11. The above results showed that
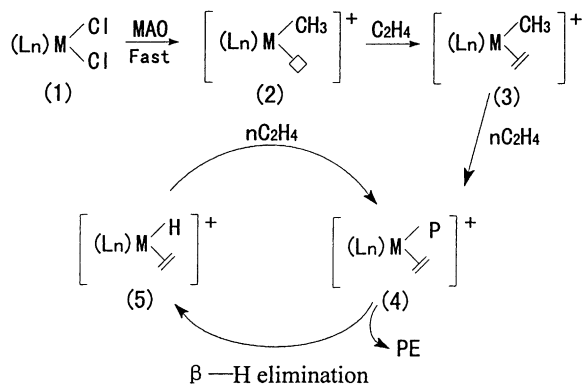
Scheme 2. The possible assigned active species in accordance to the active absorportions.

Scheme 3. Proposed catalytic mechanism for late-transition metal catalyst. Wherein: Ln is 2,6- diiminepyridine or α-diimine: M is Fe, Co, Ni; P the polyethylene chain(linear chain for Fe or Co; branched chain for Ni).

the absorption at 560 nm in Fig. 3, the absorption at 630 nm in Fig. 7, the absorption at 580 nm in Fig. 10, and the absorption at 545 nm in Fig. 13 are all assigned to catalytic active species. But the absorption at 730 nm in Figs. 2 and 4, the absorptions at 730 and 720 nm in Figs. 6 and 8, the absorption at 760 nm in Figs. 9 and 11, and the absorption at 660 nm in Figs. 12 and 13, are all assigned to inactive species.

Because catalytic active species are coordinatively unsaturated cationic alkyl complex, and considering the published works of Deffieux, in this paper, the catalytically active species are probably assigned to ethylene coordination alkyl cationic complexes shown in Scheme 2.

4.3. Proposed catalytic mechanism

The activation of MAO to catalyst precursor (a, b, c, d) is achieved by alkylation and ionization. UV–VIS spectra in Figs. 2, 6, 9 and 12 clearly showed that this interaction is easily, quickly and completely from (1) to (2) in Scheme 3. The produced coordinatively unsaturated cationic alkyl complex (2) transferred to ethylene coordination active species (3) in ethylene ambience. Intermediate (4) was produced after chain

propagation by a number of ethylene insertion. Then polyethylene and active species (5) were produced from intermediate (4) by β-H elimination. Active species (5) returned to intermediate (4) after a number of ethylene insertions. Thus, a complete catalytic recycle was achieved [10,11,16].

4.4. Polymerization termination mechanism by anhydrous ethanol

Alkyl metal compound reacts with alcohol very easily producing corresponding oxylkyl metal compound and alkane. Here, the active species and MAO are all alkyl metal compounds, which could react easily, quickly and completely with ethanol. The possible reactions are shown in Eqs. (1) and (2). So ethanol could not only destroyed active species, but also destroyed the cocatalyst MAO. Thus, the catalyst was caused to be deactivated completely. Therefore, active absorptions in UV–VIS spectra were decreased quickly after addition of ethanol, and finally disappeared completely (see Figs. 4, 8, 11 and 14). By this way, the active absorptions were confirmed to be assigned to alkyl metal active species.

$$(Ln)M\text{–}R^{\urcorner+} + CH_3CH_2OH$$
$$\rightarrow (Ln)M\text{–}OCH_2CH_3^{\urcorner+} + RH \qquad (1)$$

$$(2)$$
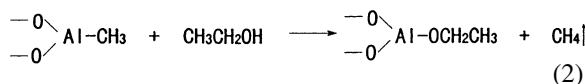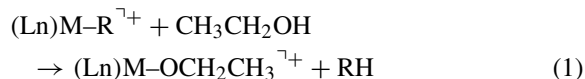
5. Conclusions

1. In situ UV–VIS spectroscopic system for ethylene polymerization under atmospheric pressure was designed and built, and was proved to be an efficient method to mechanistic studies for coordination catalysts with strong conjugated system.
2. Mechanistic studies on late-transition metal catalysts showed that the step of the activation of MAO to procatalyst is very fast, indicating clearly that MAO had very efficient activation to procatalyst.
3. Four catalyst systems with four different iron, cobalt or nickel complexes as catalyst precursor, were studied. The whole process of ethylene polymerization was followed by UV–VIS spectroscopic system. Active absorptions were observed and their variational regularity was investigated, according to which the structures of active species and catalytic mechanism were discussed.

Acknowledgements

References

[1] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem. Int. Ed. 38 (1999) 428–447.
[2] B.L. Small, M. Brookhart, A.M.A. Bennett, J. Am. Chem. Soc. 120 (1998) 4049–4050.
[3] A.M.A. Bennett, WO 98/27124 (1998).
[4] G.J.P. Britovsek, V.C. Gibson, B.S. Kimerley, et al., Chem. Commun. (1998) 849–850.
[5] G.J.P. Britovsek, B.A. Dorer, V.C. Gibson, B.S. Kimerley, WO 99/12981 (1999).
[6] C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 118 (1996) 11664–11665.
[7] L.K. Johnson, C.M. Killian, S.D. Arthur, et al., WO 96/23010 (1996).
[8] Z.-H. Yang, H.-K. Luo, B.-Q. Mao, et al., Petrochem. Technol. 29(6) (2000) 425–427 (in Chinese).
[9] S.A. Svejda, L.K. Johnson, M. Brookhart, J. Am. Chem. Soc. 121 (1999) 10634–10635.
[10] G.J.P. Britovsek, M. Bruce, V.C. Gibson, et al., J. Am. Chem. Soc. 121 (1999) 8728–8740.
[11] L. Deng, P. Margl, T. Ziegler, J. Am. Chem. Soc. 121 (1999) 6479–6487.
[12] D. Coevoet, H. Cramail, A. Deffieux, Macromol. Chem. Phys. 199 (1998) 1451–1457.
[13] D. Coevoet, H. Cramail, A. Deffieux, Macromol. Chem. Phys. 199 (1998) 1459–1464.
[14] F. Peruch, H. Ramail, A. Deffieux, Macromolecules 32 (1999) 7977–7983.
[15] D. Coevoet, H. Ramail, A. Deffieux, et al., Polym. Int. 48 (1999) 257–263.
[16] C. Pellecchia, M. Mazzeo, D. Pappalardo, Macromol. Rapid. Commun. 19 (1998) 651–655.