

POLYMERIZATION OF ETHYLENE WITH UNSYMMETRIC 2,6-BIS(IMINO)PYRIDINE IRON(II) COMPLEX*

Zhi Ma, Wen-hua Sun**, Zi-long Li, Chang-xing Shao and You-liang Hu

State Key Laboratory of Engineering Plastics and the Center for Molecular Sciences
Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Abstract An unsymmetric 2,6-bis(imino)pyridine iron(II) complex **1'** was synthesized. The relationship between catalyst structure and its activity in ethylene polymerization is discussed. The kinetic behavior of ethylene polymerization and the effects of polymerization conditions such as temperature, aluminum/iron molar ratio on the activity of catalyst and the characteristics of polyethylene were reported. The unsymmetric catalyst **1'** has a good catalytic performance of 3.47×10^6 gPE $\cdot$ mol⁻¹ $\cdot$ Fe $\cdot$ h⁻¹ at 40 °C with aluminum/iron molar ratio = 2500. A dependence of catalyst activity on the methylaluminoxane (MAO) concentration and reaction temperature was found. The molecular weight (MW) of polyethylene with broad dispersity is about 10^4 – 10^5 g/mol. The melting temperature and branching of polyethylenes vary with changing reaction temperature and aluminum/iron molar ratio.

Keywords Unsymmetric 2,6-bis(imino)pyridine iron(II) complex, Ethylene polymerization, Catalyst structure, Catalytic activity

INTRODUCTION

Development of new catalysts with early transition metals has played an important role in the fast-growing polyolefins industry^[1]. Following Ziegler-Natta catalysts, metallocene catalysts appeared in the 1980s and resulted in numerous industrial processes for improving the properties of polyolefinic materials along with performance parameters. For designing the microstructure and properties of polyolefins and extending their application range, general screening of new catalysts is very helpful for discovering novel polyolefin catalysts. In contrast to the huge number of early transition metal catalysts, there are relatively fewer reports on the late transition metal catalysts for olefin polymerization, because the late transition metal complexes commonly undergo β -hydride elimination with the formation of oligomers^[2] which could hinder the chain growth of olefin insertion for polymerization. In 1990s, Brookhart and his colleagues discovered a new class of catalysts known as late transition metal complexes for ethylene polymerization and copolymerization of ethylene and α -olefins^[3], which has attracted great interest from academic and industrial circles. This achievement was induced by the impact of bulky substituted ligands for preventing β -hydride elimination. Successively, in 1998, Brookhart and Gibson reported the highly active ethylene polymerization catalysts based on iron (II) and cobalt (II) complexes bearing tridentate 2,6-bis(imino)pyridyl ligands^[4]. These publications boosted the investigation of polymerization catalyzed with well-defined late transition metal catalysts and promised a bright future for the copolymerization of polar monomers^[5].

The catalyst activity, the polymeric product as well as its molecular weight and microstructure are greatly

* This work was financially supported by the National Natural Science Foundation of China (No. 29734141, 50103012); Core Research for Engineering Innovation KG CX2-203; the Foundation of "One Hundred Talents" program for W-H Sun, Chinese Academy of Sciences.

** Corresponding author: Wen-hua Sun (孙文华), E-mail: whsun@infoc3.icas.ac.cn

Received April 28, 2001; Revised June 25, 2001; Accepted June 27, 2001

dependent on the structure of the catalyst associated with the ligands' structure. As showed in other homogeneous catalyses, the stereo-chemistry of the catalyst will influence the selectivity of reactions, while the electronic factor of the ligands will affect its activity. Therefore, it would be interesting for us to modify the Brookhart-Gibson catalyst with different symmetric and unsymmetric ligands comprising various amines for olefin polymerization. The effect of catalyst structure is discussed.

EXPERIMENTAL

Materials

Polymer grade ethylene was provided by Yanshan Petro-Chemical Co. MAO (1.4 mol/L solution in toluene) was purchased from Arbemarle Co. and 2,6-diacetylpyridine and all the amines were purchased from Aldrich and Acros Chemical Co. Other chemicals were available commercially and used as received unless stated otherwise. Solvents were refluxed over appropriate drying agents and degassed prior to use. All manipulations were carried out under Ar atmosphere using Schlenk techniques.

Measurements

Elemental analyses were determined using Carlo Erba 1106 and ST02 apparatuses. ^1H - and ^{13}C -NMR spectra were recorded on Bruker DMX spectrometer (300 MHz; CDCl_3 as the solvent for ligands, *d*-dichlorobenzene as the solvent for polyethylene at 135 °C). Mass spectra were obtained using an electron impact (EI) instrument (Kratos AEI MS-50). The molecular weight of polymers was determined by gel permeation chromatography (GPC Waters 300) at 135 °C with *o*-dichlorobenzene as the solvent. The melting temperatures (T_m) of polyethylene were determined by a DSC-7 differential scanning calorimeter (Perkin-Elmer Co.) operating at a heating rate of 10 K/min from 40 °C to 150 °C, and T_m was determined in the second scan. The degree of crystallinity was calculated from the DSC thermograms from the enthalpy of fusion. The pressed films of polyethylene were used to determine the degree of branching via infrared spectroscopy with a System 2000 FT-IR (Perkin-Elmer Co.).

Synthesis of Ligands

Generally, these ligands were synthesized by the Shiff base reaction.

Synthesis of 2-[1-(2-Isopropylimino)ethyl]-6-[1-(2,6-diisopropylimino)ethyl]pyridine (1)

Under an Ar atmosphere, 2,6-diacetylpyridine (1.00 g, 6.13 mmol) and 2,6-diisopropylaniline (1.23 g, 6.40 mmol) were dissolved in 100 mL anhydrous methanol in a flamed Schlenk flask. 0.2 mL formic acid was added via a syringe, and the solution was stirred for 48 h at 60 °C. The product (yellow solid) was collected by filtration and washed with cold methanol. Then it was extracted in a Soxhlet apparatus with isopropyl alcohol to remove the diimine product. The solution was cooled to give the monoimine. Monoimine (500 mg, 1.55 mmol) and 4 equivalents (equiv.) 2-isopropylaniline were dissolved in 20 mL isopropyl alcohol in a Schlenk flask. 0.1 mL formic acid was added, and the solution was stirred in the flask under an inert atmosphere at reflux temperature for 48 h. The solution was allowed to cool, and the impure product was isolated by filtration. The filtrate was cooled to -30 °C, and 0.0880 g product were collected (Yield: 43.05%). ^1H -NMR (CDCl_3 , δ): 8.86 (d, H, Py-Hm); 8.20 (d, 1H, Py-Hm), 8.03 (t, 1H, Py-Hp), 7.22–7.27 (m, 7H, Ar-H), 2.80 (septet, 3H, $-\text{CHMe}_2$), 2.49 (s, 1H, $\text{CH}_3\text{C}=\text{N}$), 2.38 (s, 1H, $\text{CH}_3\text{C}=\text{N}$), 1.23 (m, 18H, $(\text{CH}_3)_2\text{CH}-$). ^{13}C -NMR (CDCl_3 , δ): 167.90, 154.50, 136.95, 136.12, 132.28, 129.48, 127.10, 124.12, 123.07, 29.69, 28.30, 23.00 and 17.20. EI-MS (70 eV): $m/z = 439$. Elemental analysis: Calc. (%): C 81.96, H 8.48, N 9.56, Found (%): C 81.71, H 8.61, N 9.68.

Synthesis of ligand 2 and 3

Ligands 2 and 3 were synthesized according to the method in the literature^[6, 7]. The results of ^1H -, ^{13}C -NMR, EI-MS and elemental analysis identify their structure as the same as those reported in the literature.

Synthesis of Complexes

Appropriate ligand (1.05 equiv.) and 1.0 equiv. of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were added to a flame-dried Schlenk flask equipped with a magnetic stirrer. The flask was purged three times with Ar. Then under an argon atmosphere, an

appropriate amount of THF was added via a syringe. Stirring was started at room temperature for 2 h, resulting in the formation of a deep blue (or green) solution or suspension. Pentane was added to the reaction flask, and the solids were filtered and washed with ether and pentane. The products were vacuum dried. Catalyst **1'** EI-MS (70 eV): $[M^+-Cl] = 531$. Elemental analysis: Calc. (%): C 63.62, H 6.58, N 7.42, Found (%): C 63.39, H 6.87, N 7.14. Data of EI-MS and elemental analysis for catalyst **2'** and **3'** are the same as those reported in the literatures^[6, 7].

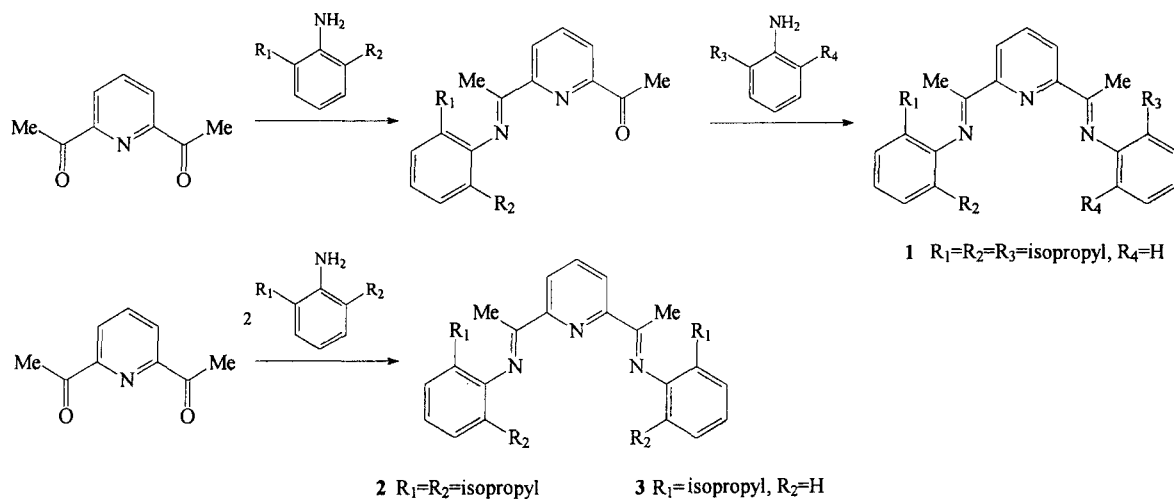
Polymerization Procedure

A flame-dried three-neck flask was purged three times with nitrogen and filled twice with ethylene, then 50 mL of purified toluene was added and stirred. When the temperature was raised to a definite value, alumoxane cocatalyst was added via a syringe. After several minutes, the precatalyst complex dissolved in dichloromethane or 1,2-dichloroethane was added to the flask via a syringe. The polymerization was quenched with acidified ethanol, and the polymer was filtered, washed with ethanol several times and dried in vacuum at 60°C. Taking catalyst **1'** as an example a typical polymerization condition was as follows: 2 μ mol catalyst **1'** (in 1 mL dichloroethane), Al/Fe molar ratio = 2000, 50 mL toluene, $T = 40^\circ\text{C}$, $t = 30$ min, pressure of ethylene = 1.013×10^5 Pa.

RESULT AND DISCUSSION

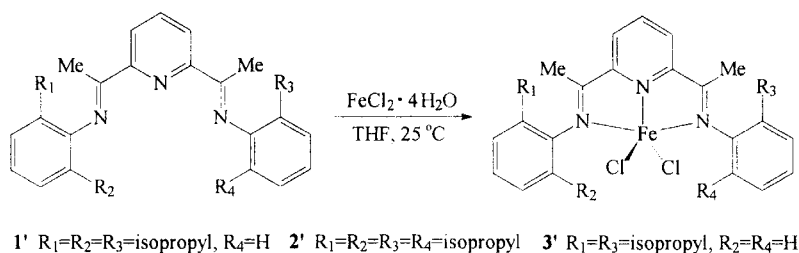
Synthesis of Unsymmetrical 2,6-Bis(imino)pyridine Iron Complexes

The synthesis procedure of unsymmetrical 2,6-bis(imino)pyridine iron complexes includes the preparation of corresponding ligands and complexes. Different from the one step method to obtain symmetric ligands, the unsymmetric ligands were stepwise synthesized with one equivalent of two kinds of aryl amines (Scheme 1).



Scheme 1 Synthesis of ligands

The precatalyst complexes (**1'**–**3'**) were made by coordinating iron (II) dichloride with a slight excess of the ligand in tetrahydrofuran (THF) (Scheme 2).



Scheme 2 Synthesis of complexes

Relationship between Catalyst Structure and Activities in Ethylene Polymerization

The catalytic activities of the three catalysts for ethylene polymerization are presented in Table 1. The polymerizations were carried out in toluene using MAO as cocatalyst under 1.013×10^5 Pa of ethylene.

Table 1. Results of polymerization of ethylene

Precatalyst	Loading (μmol)	Al/Fe ratio (mol/mol)	T ($^{\circ}\text{C}$)	Activity ($10^6 \text{ gPE} \cdot \text{mol}^{-1}\text{Fe} \cdot \text{h}^{-1}$)
1' ^a	2	2000	40	3.22
2' ^a	2	2000	40	4.46
3' ^b	1.7	-	25	8.4×10^5 (Oligomerization) ^c

^a The two runs were done using 1.013×10^5 Pa ethylene and 50 mL toluene with MAO as cocatalyst.

Each polymerization was run for 30 min.

^b The data are cited from reference 6.

^c The unit of activity is $\text{kg oligomer} \cdot \text{mol}^{-1}\text{Fe} \cdot \text{h}^{-1}$.

The results in Table 1 show that catalysts 1' and 2' have good activities for ethylene polymerization while catalyst 3' has oligomerization activity. In the tridentate N—N—N ligands, the conjugated system is present due to the double bond of the imino group and aryl rings in the structure of catalysts 1'–3'. Additionally, substituents in two *ortho*-positions on the aryl ring provide bulky steric effects which inhibited β -hydride elimination and benefit the propagation of polymer chain^[7]. Therefore, the combination of these two effects resulted in good catalytic activity of catalyst 1' and 2'. In the structure of catalyst 3', due to the free rotation of C—N bond, the steric contribution of one isopropyl in the aryl *ortho*-position to protecting the active site is less than those of the other two. This less bulky effect resulted in the ethylene oligomerization. Accordingly, it is understandable that catalyst 1' has lower activity than catalyst 2'. It is necessary to undertake more work in order to gain a clear idea about the role of the *ortho*-position substituents in unsymmetric catalysts.

Kinetic Behavior of Ethylene Polymerization with Catalyst 1'

In order to understand the kinetic behavior of ethylene polymerization, the ethylene absorption was measured. In the polymerization process with catalyst 1' (Fig. 1), the catalytic activity rises quickly to its maximum at the beginning of the ethylene polymerization. After that, its activity drops sharply and keeps relative stable for 10 to 30 min. In contrast to the kinetic curve of catalyst 2'^[8], there is no time delay for its activity to reach the maximum. We consider that there is some smaller steric effect in catalyst 1', which benefits polymer chain propagation around the active site.

Effect of Molar Ratio Between MAO and Precatalyst on Catalyst Activities

The cocatalyst MAO also plays an important role in olefin polymerization^[9]. Catalyst 1' was chosen as example, and the effect of MAO concentration on catalyst activity is shown in Fig. 2.

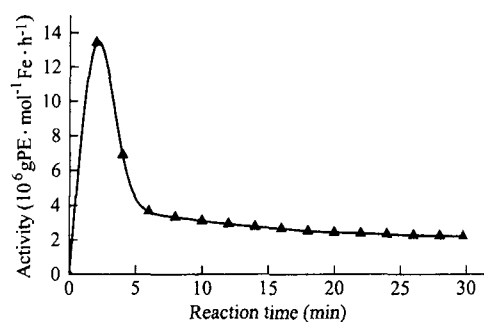


Fig. 1 Relationship between the activity of catalyst 1' and reaction time

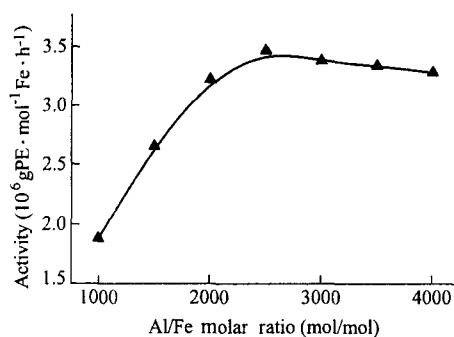


Fig. 2 Relationship between catalyst activity and Al/Fe molar ratio

With increasing MAO concentration, the catalytic activity of catalyst 1' is increasing at the beginning, and the highest activity up to $3.47 \times 10^6 \text{ gPE} \cdot \text{mol}^{-1} \text{Fe} \cdot \text{h}^{-1}$ appears at 2500 Al/Fe molar ratio. Afterwards, the activity decreases slightly. This result can be ascribed to the two effects of MAO. The increase of MAO concentration results in the elimination of impurity in the polymerization system, and the appropriate proportion of MAO probably leads to the creation of active sites of the precatalyst. However, excess MAO will inhibit the coordination of monomer with the active center and result in a slight decrease in catalytic activity. The optimal Al/Fe molar ratio is 2500 to 4000.

Effect of Polymerization Temperature on Catalyst Activity

During polymerization, temperature is the critical factor, so is the homogeneous catalysis. The study on the dependence of catalyst activity on polymerization temperature reveals that there is an optimal temperature for catalyst 1' to reach its highest activity (Fig. 3). Generally, an increase in temperature often results in higher chain-propagation and chain-transfer rates, and the catalyst activity would be increased. However, there are two counteracting effects, as the temperature increases. The solubility of ethylene in toluene decreases with increasing temperature^[10]. This causes a lowering of monomer concentration in the polymerization system. Moreover, higher temperature is favorable for the deactivation of catalyst. This combined effect is likely to account for the dependence of catalyst on temperature.

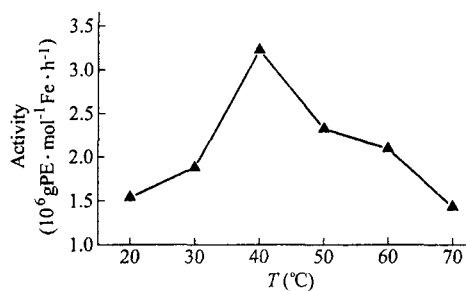


Fig. 3 Relationship between catalyst activity and temperature

Effect of Reaction Conditions on Polymer Products

The characteristics of polyethylene obtained with catalyst 1' are shown in Table 2.

It reveals that the MW of polyethylene is dependent on both MAO concentration and polymerization temperature. With increasing Al/Fe molar ratio, the MW of the corresponding polyolefin decreases. An increase of the MAO concentration will enhance the rate of chain-transfer to aluminum which, in conjunction with a constant rate of chain propagation, will result in even shorter polymer chains. Moreover, the melting temperature of polyethylene decreases with an increase in the proportion of the lower MW fraction. In addition, the reaction temperature has a great influence on polymer characteristics. Elevated temperature will result in catalyst

activation and a higher rate of propagation. Inversely, this will result in a higher chain-transfer rate and leads to shorter chains. These two effects are likely to reflect the observed dependences of MW and melting temperature on variations in the temperature parameter. The polymers produced have a crystallinity ranging from 72.7% to 80.1%.

Table 2. Characteristics of polyethylene obtained with catalyst **1'**^a

Sample	T_r (°C)	Al/Fe (mol/mol)	M_n (10^4)	M_w (10^4)	D^b	T_m (°C)	X_c^c (%)	Degree of branching CH ₃ /1000C
1	40	1000	0.28	12.59	45.07	133.52	73.5	14.8
2	40	2000	0.23	11.58	49.73	129.90	72.7	16.8
3	40	3000	0.17	8.44	48.28	127.22	77.5	17.6
4	40	4000	0.13	3.76	29.58	126.30	75.6	22.0
5	30	2000	0.68	7.97	11.68	132.74	74.7	12.1
6	50	2000	0.68	5.28	7.75	132.04	77.0	15.2
7	60	2000	0.51	2.84	5.56	131.30	80.1	13.5
8	70	2000	0.36	1.18	3.30	129.45	74.9	11.4

^a All reactions were conducted using 2 μ mol catalyst and 50 mL toluene at 1.013×10^5 Pa ethylene pressure with MAO as cocatalyst. Each polymerization was run for 30 min.

^b D : Molecular weight distribution

^c X_c : Crystallinity

Additionally, as shown in Figs. 4 and 5, chain branching can be observed in polyethylene obtained with catalyst **1'** in contrast to polymers obtained with typical symmetric catalysts **2'**. Therefore, control of the degree of branching of polyethylene is possible by changing the polymerization conditions so as to yield various polyethylenes with different structure and physical characterization. Research on the relationship between the formation of branched chains and catalyst structure is underway.

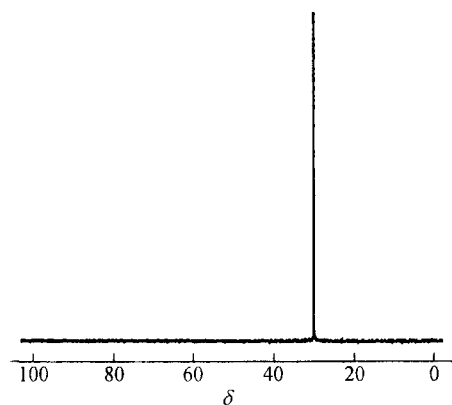


Fig. 4 ^{13}C -NMR spectrum of PE obtained with catalyst **2'**

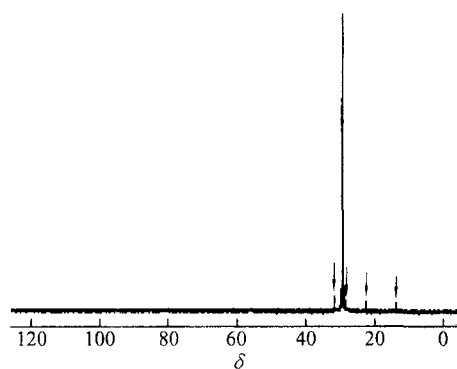


Fig. 5 ^{13}C -NMR spectrum of PE obtained with catalyst **1'**

CONCLUSIONS

The unsymmetric 2,6-bis(imino)pyridine iron (II) complexes have good catalytic performances in ethylene polymerization. The polymerization activities of catalysts **1'** and **2'** were found to be 3.22 and 4.46×10^6 gPE $\cdot$ mol⁻¹Fe $\cdot$ h⁻¹, respectively. However, 8.4×10^5 kg ethylene oligomer mol⁻¹ $\cdot$ Fe $\cdot$ h⁻¹ oligomerization activity is shown for catalyst **3'**. Different steric effects on the active site give different activities. For catalyst **1'**, a dependence of catalytic activity on MAO concentration and reaction temperature was found. The catalyst has an optimal value at which activity attains its maximum. By using catalyst **1'**, the MW of the obtained

polyethylene with a broad dispersity is 10^4 – 10^5 g/mol. The melting temperature and branches of polyethylenes could be varied with the changing reaction temperature and Al/Fe molar ratio.

Acknowledgment Thanks are due to Mr. Ke-yue Hou and Ms. Ge Li for help in NMR and DSC measurements. We are indebted to Dr. He-kuan Luo (Beijing Institute of Chemical Engineering) and Dr. Ji-jun Zeng for helpful discussions.

REFERENCES

- 1 (a) Brinzingger, H.H., Fisher, D., Mülhaupt, R., Rieger, R. and Waymouth, R.M., *Angew. Chem. Int. Ed. Engl.*, 1995, 34: 1143
(b) Reddy, S.S. and Sivaram, S., *Prog. Polym. Sci.*, 1995, 20(2): 309
- 2 (a) Peuckert, M. and Keim, W., *Organometallics*, 1983, (2): 594
(b) Mohring, V.M. and Fink, G., *Angew. Chem. Int. Ed. Engl.*, 1985, 24: 1001
(c) Wilke, G., *Angew. Chem. Int. Ed. Engl.*, 1988, 27: 185
- 3 Johnson, L.K., Killian, C. M. and Brookhart, M., *J. Am. Chem. Soc.*, 1995, 117: 6414
- 4 (a) Small, B.L., Brookhart, M. and Bennett, A.M.A., *J. Am. Chem. Soc.*, 1998, 120: 4049
(b) Britovsek, G.J.P., Gibson, V.C., Kimberley, B.S., Maddox, P.J., McTavish, S.J., Solan, G.A., White, A.J.P. and Williams, D.J., *Chem. Commun.*, 1998, 849
- 5 Johnson, L.K., Mecking, S. and Brookhart, M.J., *Am. Chem. Soc.*, 1996, 118: 267
- 6 Small, B.L. and Brookhart, M., *J. Am. Chem. Soc.*, 1998, 120: 7143
- 7 Britovsek, G.J.P., Bruce, M., Gibson, V.C., Kimberley, B.S., Maddox, P.J., Mastroianni, S., McTavish, S.J., Redshaw, C., Solan, G.A., Strömberg, S. White, A.J.P. and Williams, D.J., *J. Am. Chem. Soc.*, 1999, 121: 8728
- 8 Qiu, J.M., Li, Y.F. and Hu, Y.L., *Polym. Int.*, 2000, 49: 5
- 9 Chen, Y-X.E. and Marks, T.J., *Chem. Rev.*, 2000, 100: 1391
- 10 Atiqullah, M., Hammawa, H. and Hamid, H., *Eur. Polym. J.* 1998, 34: 1511