*Journal of the Chinese Chemical Society*, **2006**, *53*, 1349-1354

# Ethylene Polymerization Catalyzed by Diimine-Palladium(II) Complexes Modified on Silicas

Jung-Hua Lee ( 李榮華 ) and Shiuh-Tzung Liu* ( 劉緒宗 )
*Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, R.O.C.*

Both mesoporous (MCM-41) and spherical silica supported palladium-based diimine catalysts were prepared and their behaviors on ethylene polymerization were studied. The results showed that good catalytic activities could be reached with cocatalyst sodium tetraarylborate. Ethylene polymerization with palladium-based catalysts in mesoporous silicas (MCM-41) gave polymers with less branched chains than those obtained with the corresponding homogeneous catalyst.

**Keywords:** Polymerization; Palladium; Ethylene; Silica.

## INTRODUCTION

Since the discovery of late transition metal complexes on polymerization of α-olefins by Brookhart[1] and Gibson,[2] the interest in developing new catalysts other than metallocenes has greatly increased owing to their unique features, in particular the low oxophilicity of the catalysts.[3] Another characteristic of the late transition metal complexes catalyzed polymerization is to produce highly branched polymers even from ethylene as a monomer. It is known that the microstructure of the polymers can be varied by changing the structural bulkiness of ligands and metal ions and by changing pressure or temperature.[4] In other words, the activity of the metal center would be adjusted along with the environmental change. Thus investigation of supporting metal catalysts on inorganic substrates for the polymerization of olefins has become an attractive subject in this context.[5] For examples, catalysts loaded onto the mesoporous silicas, i.e. MCM-41,[6] SBA-15[7] and MSF (mesoporous silica fiber),[8] have been applied for polymerization.[9] Polymerization reactions carried out inside a pore structure, similar to a nano-scale reactor, influence the process of chain growth, which offers a possibility of searching for a new structure of polymers.[10]

For ethylene polymerization catalyzed by late transition metal complexes, there are numbers of studies on the use of impregnated metal complexes on inorganic supports.[11] However, there are few reports concerning the fixation of metal complexes onto silica[12] and MCM-41.[13] In this work, we prepared the covalent bond linkages of α-diimine complexes onto spherical as well as mesoporous silica and used their palladium complexes as catalysts for the polymerization of ethylene in the presence of suitable activators.

## EXPERIMENTAL SECTION

### General Information

All reactions, manipulations, and purifications steps were performed under a dry nitrogen atmosphere. Tetrahydrofuran was distilled under nitrogen dried over sodium with dibenzophenone as an indicator. Dichloromethane was dried with $CaH_2$ and distilled under nitrogen. Other chemicals and solvents were of analytical grade and were used as received unless otherwise stated. Silica was purchased from Merck Chemicals (70-230 mesh; surface area, 489 $m^2/g$) and pretreated by heating under vacuum at 150 °C for 12 h to remove the water absorbed before use. Nuclear magnetic resonance spectra were recorded in $CDCl_3$ on either a Bruker AM-300 or AVANCE-400 spectrometer and TMS as internal standard. Infrared spectra were measured on a Perkin-Elmer 983G spectrometer (Series-II) as KBr pellets, unless otherwise noted. Palladium content in the modified catalysts was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The spectrometer is Allied Analytic System (Jarrell-Ash), Model ICAP 9000. All samples were dissolved in $HNO_3$/

---

This article is dedicated to the late Professor Tong-Ing Ho, who passed away on Dec. 14, 2005.

HF mixed acid. And the elemental analyses of C, H, and N were performed with a Perkin-Elmer 240C spectrometer. Surface areas and pore size distribution of each sample were determined by $N_2$ adsorption-desorption isotherms performed at -196 °C with a Micromeritics ASAP 2010 instrument. Prior to adsorption, each sample (approx. 50 mg) was degassed at 100 °C for at least 6 h under $10^{-3}$ Torr. The specific surface areas were calculated according to the BET method, and the pore size distribution curves were obtained from the analysis of the adsorption branch of the isotherms using the BJH (Barrett-Joyner-Halenda) method. DSC measurements were performed with an LT-Modulate DSC 2920 and differential scanning calorimeter at a rate of 10 °C/min. GPC measurements of the polyethylene were conducted at 40 °C with a POLYMER LABORATORIES chromatograph equipped with a Plgel 5 µm MIXED-D 300 × 7.5 mm column. THF was used as the solvent at a flow rate of 1.0 mL/min. The calibration was made with a polystyrene standard.

### Preparation of (ArN=C(Me)-C(Me)=NAr) (Ar = 4-(HO)-2,6-$(Me)_2C_6H_2$) (1)

To a stirred solution of 2,6-dimethyl-phenylhydroxylamine (0.75 g, 5.5 mmol), which was prepared starting from 1-nitro-2,6-xylene,[14] in methanol (10 mL) was added 2,3-butadione (0.24 g, 2.8 mmol) at room temperature. A few drops of glacial acetic acid were added to the above mixture, and the resulting solution was stirred overnight. The desired product was precipitated and crystallized from methanol. Upon filtration, the yellow solid was washed with cold methanol and dried under vacuum overnight (0.45 g, 50%). $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 8.88 (s, 2H, 2 OH), 6.50 (s, 4H, 4 $H_{aryl}$), 1.90 (s, 6H, each, N=C($CH_3$)-C($CH_3$')=N), 1.96 (s, 12H, ArMe). $^{13}$C NMR (100 MHz): δ 168.9, 153.4, 140.6, 125.6, 114.9, 18.0, 16.0. Anal. Calcd for $C_{20}H_{24}N_2O_2\cdot H_2O$: C, 70.15; H, 7.65; N, 8.18. found: C, 69.95; H, 7.96; N, 8.02.

### Preparation of [ArN=C(Me)-C(Me)=NAr]PdMeCl, [Ar = 4-(HO)-2,6-$(Me)_2C_6H_2$] (1C)

Diimine ligand **1** (50 mg, 1.5 × $10^{-1}$ mmol) and (COD)PdMeCl (41 mg, 1.5 × $10^{-1}$ mmol) were mixed in $CH_2Cl_2$ (10 mL) at room temperature for 2 h. After vaporization of solvents, the red solid was washed with ether and dried under vacuum. (43 mg, 60%). $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 9.38 (s, 1H, OH), 9.16 (s, 1H, OH'), 6.55 (s, 2H, 2 $H_{aryl}$), 6.46 (s, 2H, 2 $H'_{aryl}$), 2.04 (s, 6H, each, N=C($CH_3$)-C($CH_3$')=N), 1.99 (s, 12H, ArMe), -0.02 (s, 3H, PdMe). $^{13}$C NMR (100 MHz): δ 178.3, 173.0, 155.6, 155.0, 136.9, 136.4, 129.6, 128.9, 114.8, 114.6, 19.8, 18.8, 18.3, 17.9, -0.14. Anal. Calcd for $C_{21}H_{27}ClN_2O_2Pd$: C, 52.40; H, 5.65. found: C, 52.25; H, 5.26.

### Modification of ligand onto the silica surface of particles

To diimine ligand **1** (0.5 g, 1.5 mmol) in DMF (25 mL) was added 3-(glycidoxy)-propyltrimethoxysilane (0.75 g, 3.4 mmol) at room temperature. The resulting solution was heated to 110 °C for 24 h. Then the dehydroxylated silica (4.6 g) was added to the above solution, and the suspension was stirred at 110 °C for another 24 h. The silicate solid was separated via filtration and washed with THF (20 mL × 3), acetone, dichloromethane and methanol to remove the impurities. The obtained materials were dried under vacuum at room temperature for 24 h. $^{13}$C CP MAS NMR: δ 8, 21, 28, 52, 63, 71, 114, 128, 168. IR: 3436.5, 2945.9, 2886.2, 1646.4, 1480.7, 1414.4, 1096.1, 956.9, 811.0, 472.9 $cm^{-1}$. Anal found: C, 7.76; H, 1.67, N, 0.57. BET surface: 376 $m^2$ $g^{-1}$.

### Modification of Pd(II) onto modified silica

The ligand modified silica (0.32 g) and (COD)PdMeCl (0.05 g, 1.5 × $10^{-1}$ mmol) were mixed in $CH_2Cl_2$ (10 mL). The solution was stirred at room temperature for 24 h. After vaporization of solvents, the residue was washed with THF and $CH_2Cl_2$ to remove the impurities. The metal complexes of silicas were dried under vacuum at room temperature for 24 h. The palladium content was determined to be 0.47% by ICP Mass analysis. BET surface: 337 $m^2$ $g^{-1}$.

### Modification of ligand and metal onto the MCM-41

The procedures for the modification are similar to those for the silica surface of particles. Physical data for the ligand modification: $^{13}$C CP MAS NMR: δ 8, 21, 28, 52, 63, 71, 114, 128, 168. IR: 3436.5, 2945.9, 2886.2, 1646.4, 1480.7, 1414.4, 1096.1, 956.9, 811.0, 472.9 $cm^{-1}$. Anal found: C, 16.72; H, 3.34; N, 0.37. BET surface: 658 $m^2$ $g^{-1}$. pore size 2.2 nm. Physical data for the metal complex: Pd content = 0.78%. BET surface: 705 $m^2$ $g^{-1}$. pore size 2.2 nm.

### Polymerization

The general procedure for the polymerization of ethylene was conducted in an autoclave (100 mL). Catalyst and cocatalyst sodium tetrakis[3,5-bis(trifluoromethyl)-

phenyl]borate were placed into the reactor. After purging with nitrogen three times, $CH_2Cl_2$ (20 mL) was introduced under nitrogen atmosphere and ethylene gas was then pressurized. After completion of the reaction, the excess of ethylene was vented and the solvents were removed under reduced pressure. The obtained polymer was collected, washed with methanol and then dried under vacuum at 30 °C overnight. The polymers were characterized by GPC and NMR spectroscopy. The branching numbers for polyethylene can be determined by $^1H$ NMR spectroscopy using the ratio of the methyl groups (terminal groups) to the overall number of carbons and are reported as branches per thousand carbons. The type of branched side-chains can be identified by the study of $^{13}C$ NMR spectra of polymers.[16]

## RESULTS AND DISCUSSION

### Preparation and Characterization of Polymerization Catalysts

Condensation of 2,6-dimethyl-phenylhydroxylamine with 2,3-butadione in methanol yielded the ligand **1**,[14] which was subsequently reacted with the epoxide **2** to provide the desired silylated diimine ligands. This coupling agent is extremely moisture sensitive, which tends to undergo self-condensation. Therefore we used it right after the preparation for the following step without the purification. Modification on the silica surface was achieved through Si-O bond formation as shown in Scheme I. From the FTIR spectra, some characteristic features can be distinguished: for instance, the band at 1096 $cm^{-1}$ indicates the presence of Si–C bonds in the Si–O–Si stretching region,[12d,15] the occurrence at both 2955 and 2870 $cm^{-1}$ is attributed to the stretching of C-H ($-CH_3$ and $-CH_2-$), and the band at 1648 $cm^{-1}$ designates the presence of C=N. For the modification on spherical silica, the surface area decreased from 489 $m^2\ g^{-1}$ to 376 $m^2\ g^{-1}$. From the elemental analysis of nitrogen, the amount of the loading ligand was estimated to be 0.14 mmol per gram of silica. On the other hand, the ligand modified in the mesoporous MCM-41 caused the decrease of the pore diameter from 3.6 nm to 2.2 nm and the reduction of the surface area from 958 to 705 $m^2\ g^{-1}$. The ligand was loaded to be 0.13 mmol per gram of silica.

Complexation of palladium ions was attained by the substitution reaction of $(COD)PdCl(CH_3)$ with the anchored diimine ligands. The palladium content was found to be 0.044 mmol per gram of spherical silica [denoted as catalyst **a**] by ICP Mass analysis, whereas the loading of palladium in the MCM41 was 0.074 mmol per gram of silica [denoted as catalyst **b**]. The larger amount of loading in the MCM41 is presumably due to the larger surface area of the porous structure.

### Catalytic Polymerization

Palladium complexes developed in this work were used to test their activities on ethylene polymerization. It

**Scheme I**

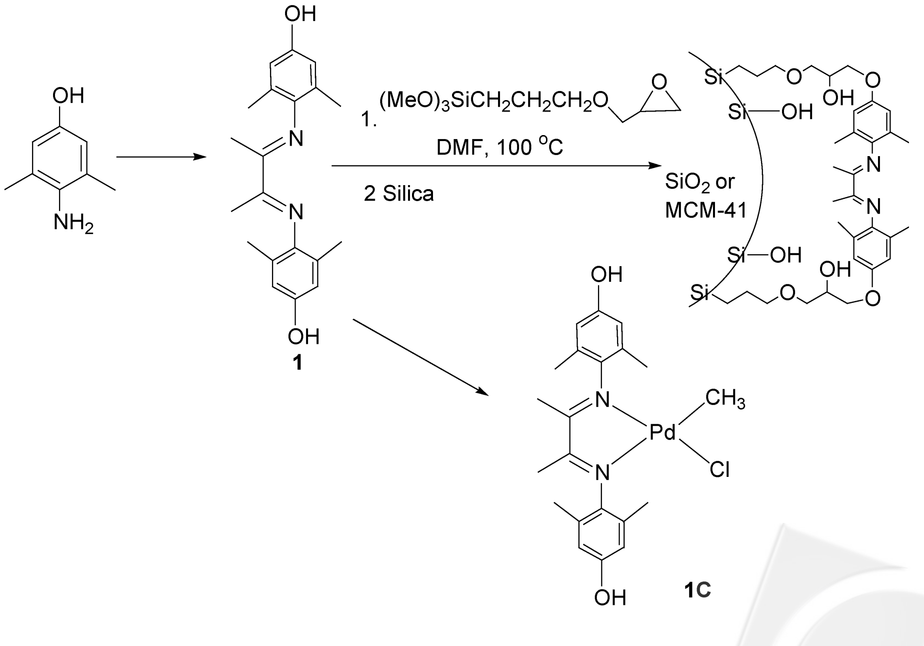

Table 1. Ethylene polymerization catalyzed by the diimine complexes

| Entry | cat.[a] | ethylene (psi) | t (h) | Yield (mg) | Productivity (g/mol cat) | Mw (× $10^4$) | PDI | Branched number[b] |
|---|---|---|---|---|---|---|---|---|
| 1 | **1C** | 400 | 5 | 1400 | $2.6 \times 10^4$ | 15 | 2.3 | 118 |
| 2 | **a** | 550 | 12 | 274 | $2.1 \times 10^5$ | 8.8 | 2.25 | 107 |
| 3 | **a** | 550 | 24 | 490 | $3.7 \times 10^5$ | 9.0 | 2.7 | 117 |
| 4 | **a** | 550 | 72 | 1000 | $7.6 \times 10^5$ | 9.2 | 2.45 | 108 |
| 5 | **a** | 50 | 24 | 252 | $1.9 \times 10^5$ | 8.6 | 2.3 | 120 |
| 6 | **a** | 100 | 24 | 369 | $2.8 \times 10^5$ | 8.8 | 2.64 | 136 |
| 7 | **a** | 400 | 24 | 455 | $3.4 \times 10^5$ | 9.1 | 2.27 | 92 |
| 8[c] | **a** | 400 | 14 | 78 | $5.9 \times 10^4$ | - | - | - |
| 9[d] | **a** | 400 | 24 | 161 | $1.2 \times 10^5$ | 8.1 | 1.82 | 101 |
| 10 | **b** | 400 | 24 | 327 | $1.47 \times 10^5$ | 7.9 | 1.89 | 72 |
| 11 | **b** | 400 | 12 | 298 | $1.40 \times 10^5$ | 8.0 | 1.97 | 78 |
| 12 | **b** | 400 | 2 | 74 | $6.13 \times 10^4$ | 9.3 | 1.82 | 80 |

[a] Catalyst a: catalyst **a** ($1.32 \times 10^{-3}$ nmmol); catalyst **b** ($2.22 \times 10^{-3}$ mmol); reaction temperature: 30 °C, 20 mg of NaBAr'$_4$, 20 mL of $CH_2Cl_2$. [b] Determined by $^1H$ NMR (per thousand carbon chains). ° 0 °C. [d] 80 °C. [e] > $C_8$ carbon chain.

was found that complexes modified on both spherical and MCM-41 did catalyze the polymerization of ethylene. In a typical experiment for the reaction, palladium catalyst ($1.32 \times 10^{-3}$ mmol) and cocatalyst sodium tetrakis[3,5-bis-(trifluoromethylphenyl)borate (20 mg) in dichloromethane were placed in an autoclave, followed by pressurizing ethylene gas (500 psi). The mixture was stirred at room temperature for a specified period of time. After the reaction was stopped, the reaction mixture was diluted with dichloromethane, and the solid product was obtained by filtration. The obtained polymers were characterized by NMR spectroscopy and GPC analysis. Results of the polymerization study are summarized in Table 1.

Table 1 shows that the molecular weight of the obtained polyethylene is generally similar for the supported catalyst as well as the homogeneous catalyst, i.e. the molecular weights are in the range of $8.0 \sim 9.5 \times 10^5$. However, the polydispersity (PDI) of the polymers depends on the catalyst used. PDI values of the polyethylene obtained from catalyst **b** appear to be smaller than those from other catalysts.

The branching number of the obtained polymers is in the range 70 to 120 branches per 1000 carbon atoms. Both catalyst **a** (immobilized on spherical silica) and catalyst **1C** (homogeneous system) catalyzed the ethylene polymerization to provide similar branching chain numbers. Nevertheless, there is a significant difference on the type of the branch chains on the polyethylene (Fig. 1). A $^{13}C$ NMR spectrum of the polymer of entry 7, through a protocol reported by Cotts,[16b] indicated that methyl and ethyl branches are present in the polymer. The methyl resonance corresponding to $C_8$ and longer branches integrated to approximately the same intensity as the methyl resonance for the methyl and ethyl branch. For the catalyst **1C**, the ratio of the long branching chains versus the short ones appears to be greater than 1. On the other hand, the obtained polymers from the supported catalyst tend to yield a shorter branch chain, i.e., the chain-walking process is slower (see below).

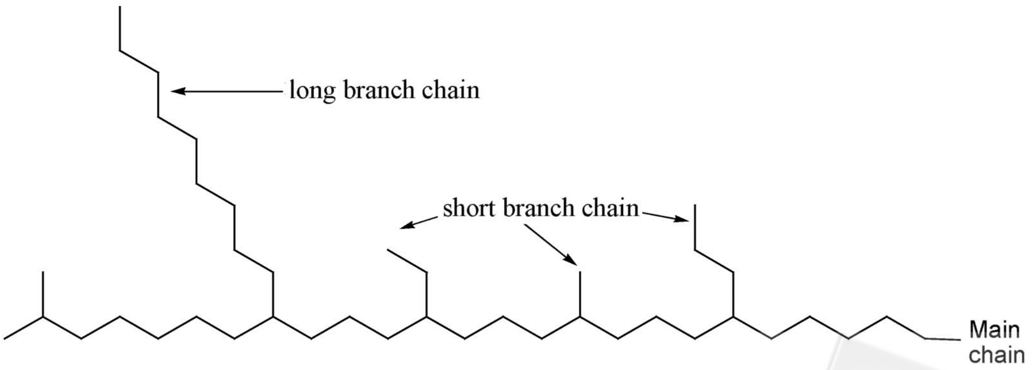

Fig. 1. Structure of polyethylene with branches.

By increasing the reaction time (entries 2-4), the activity of the catalyst slowly decreases, but the obtained polymers are in the same molecular weights ($M_w$) along with the branch numbers of the polyethylene. The pressure of ethylene adopted for the reactions does not influence the polymerization process. By varying the temperature, the activity decreased at 0 °C (entry 8). The polyethylene produced at 80 °C is made of a higher number of long branched chains, but with the similar molecular weights as others (entry 9).

The polymer produced via the homogeneous Pd-diimine catalyst **1C** was an oil product, which did not illustrate any melting point. The thermal behavior of the resulting polyethylene prepared by catalyst **a** was evaluated by differential scanning calorimetry (DSC) (Fig. 2). The DSC profiles were achieved at a heating rate of 10 °C $min^{-1}$ in a nitrogen atmosphere. Bimodal melting behavior observed in the first heating cycle exhibited the $T_m$ of 50 and 85 °C. In the second heating cycle, there was only one $T_m$ of 62 °C observed. We believe that the difference between these two heating cycles was caused by the effect of constrained geometry on the surface during the polymerization process.

Due to the chain walking mechanism of late transition metal catalysts,[1a] the hyperbranched polyethylene is generally found. In this work, the polymers obtained still have a fair number of branched chains, even with the catalyst **b**. However, the types of the branched chain and melting behaviors were quite different. The numbers of the long-chain branches of the polymers produced with our supported system decreased relevant to the homogeneous system as evidenced by $^{13}C$ NMR study. The supported catalyst with the steric bulkiness exerted by the support surface exhibited lower chain walking rates, which lower the production of the long-chain branches along the polymer main chain. Furthermore, the decreasing branch numbers of polymers obtained from catalyst **b** indicates that the chain-walking process is substantially suppressed in a confined space.

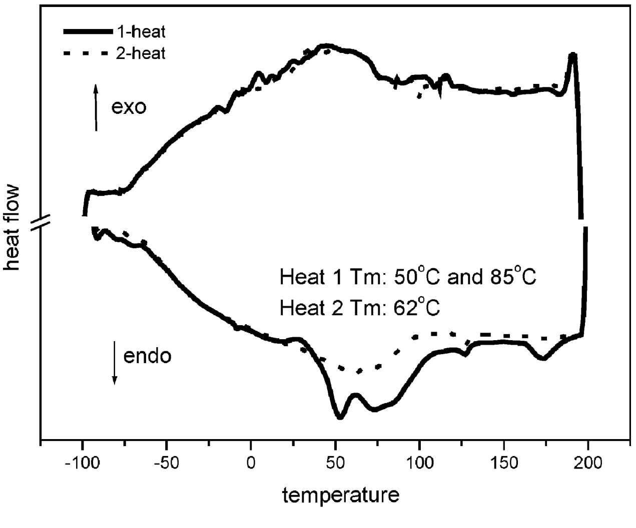

Fig. 2. DSC chart of polyethylene.

## CONCLUSION

We have demonstrated the synthetic approach to prepare the palladium diimine complexes anchored onto the surface of silicas through covalent bonding. Ethylene polymerization was investigated in the presence of sodium tetraarylborate under various conditions employing these types of catalytic systems. In general, the catalytic activity of this supported catalyst is similar to that of the homogeneous catalytic system **1C**, but the morphology of polymers is different, which offers the possibility of searching for new materials. The support of other late transition metal catalysts using the same method and the recycled uses of the catalysts are under investigation.

## ACKNOWLEDGEMENTS

This work was supported by the National Science Council, ROC (NSC94-2113-M002-035).

Received June 19, 2006.

## REFERENCES

1. (a) Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414. (b) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000,** *100*, 1169. (c) Killian, C. M.; Tempel, D. J.; Johnson L. K.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 11664. (d) Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120,* 4049. (e) Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143. (f) Gates, D. P.; Svejda, S. A.; Onate, E.; illian, C. M.; Johnson, L. K.; White, P. S.; Brookhart, M. *Macromolecules* **2000**, *33*, 2320.
2. Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem. Int. Ed. Engl.* **1999**, *38*, 429.

3. (a) Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *18*, 267. (b) Mecking, S.; Johnson, L. K.; Wang, L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 888. (c) Younkin, T. R.; Connor, E. F.; Henderson, J. I.; Friedrich, S. K.; Grubbs, R. H.; Bansleben, D. A. *Science* **2000**, *287*, 460.
4. (a) Tempel, D. J.; Brookhart, M. *Organometallics* **1998**, *17*, 2290. (b) Jurkiewicz, A.; Eilerts, N. W.; Hsieh, E. T. *Macromolecules* **1999**, *32*, 5471. (c) Guan, Z.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**, *283*, 2059. (d) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945.
5. (a) Abbenhuis, H. C. L. *Angew. Chem. Int. Ed.* **1999**, *38*, 1058. (b) Hlatky, G. G. *Chem. Rev.* **2000**, *100*, 1347. (c) Fink, G.; Steinmetz, B.; Zechlin, J.; Przybyla, C.; Tesche, B. *Chem. Rev.* **2000**, *100*, 1377.
6. (a) Huo, Q.; Zhao, D.; Feng, J.; Weston, K.; Buratto, S. K.; Stucky, G. D. Schacht, S.; Schuth, F. *Adv. Mater.* **1997**, *9*, 974. (b) Cai, Q.; Lin, W.-Y.; Xiao, F.-S.; Pang, W.-Q.; Chen, X.-H.; Zou, B.-S. *Microporous Mesoporous Mater.* **1999**, *32*, 1. (c) Mokaya, R.; Zhou, W.; Jones, W. *Chem. Commun.* **1999**, 51.
7. (a) Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredickson, G. H.; Chmelka, B. F.; Stucky, G. D. *Science* **1998**, *279*, 548. (b) Zhao, D.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *J. Am. Chem. Soc.* **1998**, *120*, 6024. (c) Zhao, D.; Yang, P.; Melosh, N.; Feng, J.; Chmelka, B. F.; Stucky, G. D. *Adv. Mater.* **1998**, *10*, 1380.
8. Marlow, F.; Spliethoff, B.; Tesche, B.; Zhao, D. *Adv. Mater.* **2000**, *12*, 961.
9. (a) Van Looveren, L. K.; Geysen, D. F.; Vercruysse, K. A.; Wouters, B. H.; Grobet, P. J.; Jacobs, P. A. *Angew. Chem. Int. Ed.* **1998**, *37*, 517. (b) Dong, X.; Wang, L.; Wang, W.; Yu, H.; Wang, J.; Chen, T.; Zhao, Z. *Eur. Polym. J.* **2005**, *41*, 797. (c) Chen, S.; Guo, C.; Liu, L.; Xu, H.; Dong, J.; Hu, Y. *Polymer.* **2005**, *46*, 11093. (d) Miller, C. J.; O'Hare, D. *Chem. Commun.* **2004**, 1710. (e) Chan, S.-H.; Lin, Y.-Y.; Ting, C. *Macromolecules* **2003**, *36,* 8910. (f) Tajima, K.; Ogawa, G.; Aida, T. *J. Polym. Sci. Part A*: *Polym. Chem.* **2000**, *38*, 4821. (g) Craymer, J. F.; Kasi, R. M.; Coughlin, E. B. *Polyhedron* **2005**, *24*, 1347.
10. (a) Ko, Y. S.; Woo, S. I. *Macromol. Chem. Phys.* **2001**, *202*, 739. (b) Tudor, J.; O'Hare, D. *Chem. Commun.* **1997**, 603. (c) O'Brien, S.; Tudor, J.; Maschmeyer, T.; O'Hare, D. *Chem. Commun.* **1997**, 1905. (d) Kageyama, K.; Tamazawa, J.; Aida, T. *Science* **1999**, *285*, 2113. (e) Rao, R. R.; Weckhuysen, B. M.; Schoonheydt, R. A. *Chem. Commun.* **1999**, 445. (f) Kaminsky, W.; Strübel, C.; Lechert, H.; Genske, D.; Woo, S. I. *Macromol. Rapid. Commun.* **2000**, *21*, 909.
11. (a) Yea, Z.; Alsyouri, H.; Zhua, S.; Lin, Y. S. *Polymer* **2003**, *44*, 969.
12. (a) Kaul, Franz A. R.; Puchta, G. T.; Schneider, H.; Bielert, F.; Mihalios, D.; Herrmann, W. A. *Organometallics* **2002**, *21,* 74. (b) Preishuber-Pflugl, P.; Brookhart, M. *Macromolecules* **2002**, *35*, 6074. (c) Wang, Q.; Liu, P. *J. Polym. Sci. Part A*: *Polym Chem.* **2005**, *43*, 5506. (d) Zheng, Z.; Liu, J.; Li, Y. *J. Catal.* **2005**, *234*, 101.
13. (a) Zhang, M.; Xu, H.; Guo, C.; Ma, Z.; Dong, J.; Ke1, Y.; Hu1, Y. *Polym. Int.* **2005**, *54*, 274. (b) Guo, C.; Jin, G. X.; Wang, F. *J. Polym. Sci. Part A*: *Polym. Chem.* **2004**, *42*, 4830.
14. Kjaer, A. M.; Ulstrup, J. *J. Amer. Chem. Soc*. **1988**, *110*, 3874.
15. Evans, J.; Zaki, A. B.; EI-Sheikh, M. Y.; EI-Safty, S. A. *J. Phys. Chem. B* **2000**, *104*, 10271.
16. (a) Escher, E. F. N.; Galland, G. B.; Ferrira, M. *J. Polym. Sci. Part A*: *Polym. Chem*. **2003**, *41*, 2531. (b) Cotts, P. M.; Guan, Z.; McCord, E.; McLain, S. *Macromolecules* **2000**, *33*, 6945.