

Study on Ethylene (Co)Polymerization and Its Kinetics Catalyzed by a Reversible Crosslinked Polystyrene-supported Metallocene Catalyst

Wenqin Wang, Li Wang, Jianfeng Wang, Zhenli Ma, Jianjun Wang

The State Key Laboratory of Polymer Reaction Engineering, College of Materials Science and Chemical Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: A well-defined linear polystyrene with cyclopentadienes groups was prepared and characterized. The cyclopentadienes groups performed a Diels–Alder reaction to form the reversible crosslinking of the support. In olefin polymerization the crosslinked active species transformed noncrosslinked active species via MAO. The influence of the reversibility of network on olefin polymerization was investigated.

The polystyrene-supported metallocene catalyst showed high activity and stable polymerization process in olefin polymerization. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 1632–1636, 2005

Key words: polystyrene; crosslinking; network; metallocene catalyst; olefin

INTRODUCTION

Recently a large amount of research dealing with heterogenization of metallocene using inorganic materials^{1–3} or organic materials^{4–6} as carriers has been published. However, despite the evident advantage of heterogeneous metallocenes systems compared to homogeneous metallocenes systems, heterogeneous metallocene catalyst systems still remain an unsolved problem. The main aim is to find a method to support the metallocene to the carrier, while retaining the advantages of homogeneous catalysts to meet the requirements for industrial application. Organic materials provide a much closer analogue to the environment prevailing in homogenous polymerization as opposed to inorganic supports with a rigid and polar surface structure^{4,6}. Furthermore, organic materials can be easily functionalized to satisfy certain requirements. Yang et al.⁷ studied the polymer-bound Cp anion, which reacted with $\text{Ti}(\text{O}-\text{Bu})_3\text{Cl}$ to form polystyrene-bound $\text{Ti}(\text{O}-\text{Bu})_3$. However, the catalyst was not characterized in detail. In this article, a well-defined linear polystyrene carrier containing cyclopentadienes groups was synthesized and was used to immobilize metallocene. The ethylene polymerization and ethylene/ α -olefin copolymerization were studied using the resultant polystyrene-supported metallo-

cene catalyst and its (co)polymerization kinetic was investigated.

EXPERIMENTAL

Materials

All of the operations were carried out under dry argon atmosphere using the standard Schlenk techniques. Hexamethylphosphoramide (HMPA) (from Aldrich), 1-nitropropane (from ACROS), dicyclopentadiene (from ACROS), chloromethyl methyl ether (from TCI), CpZrCl_3 (from Strem), BuLi (1.6M in hexane, from ACROS) and MAO (w/w10% in toluene from Albetmarle) were purchased and used without further purification. Tetrahydrofuran (THF) and toluene were distilled from Na/K alloy under argon atmosphere. Cyclopentadiene was obtained by cracking dicyclopentadiene under argon atmosphere and styrene was distilled prior to use. Polymerization-grade ethylene was further purified by passing over 4 Å molecular sieves. 1-Hexene and 1-dodecene were purified by refluxing over Na under nitrogen atmosphere. Cyclopentadienylsodium (CpNa) was synthesized according to the literature.⁸

Preparation of the linear polystyrene

The linear polystyrene was prepared by suspension polymerization. 2 g of polyvinyl alcohol was dissolved in 500 mL of deionized water. Subsequently, 100 g of styrene and 3 g of benzoyl peroxide were added. The mixed solution was warmed to 80°C and stirred vig-

Correspondence to: L. Wang (opl_wl@diel.zju.edu.cn).

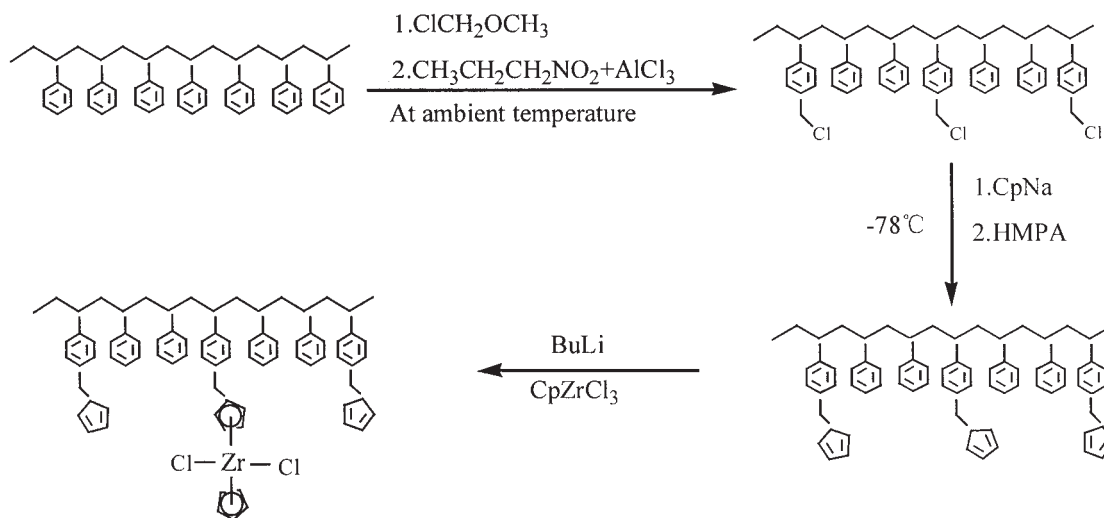


Figure 1 The preparation of polystyrene-supported metallocene catalyst.

orously for 3 h. The product was dried under vacuum overnight.

Synthesis of polystyrene with 8.4% chloromethyl content per polystyrene unit

5 g of polystyrene was dissolved in 450 mL of CCl_4 and 5 mL of chloromethyl methyl ether (65.83 mmol) was added. Subsequently a catalytic solution containing 1.33 g of anhydrous AlCl_3 (9.97 mmol), 21 mL of 1-nitropropane (0.235 mol), and 170 mL of CCl_4 was added. The reaction was performed for 1 h at room temperature and quenched using 10 mL of glacial acetic acid. The resultant product was precipitated using anhydrous methanol and then washed and filtrated. Finally the product was dried under vacuum overnight.

Synthesis of polystyrene with cyclopentadienes groups

1.46 g of chloromethylated polystyrene containing 1.15 mmol chloromethyl units was dissolved in 30 mL THF; subsequently, 10 mL of HMPA (57.47 mmol) and CpNa (23 mmol, in 30 mL of THF) were added at -78°C . The mixture was gradually warmed to 0°C and reacted for 3.5 h. The reaction was quenched using 10 mL of saturated solution of NH_4Cl . Finally, the resultant product was precipitated using anhydrous methanol and dried under vacuum for 12 h at 0°C .

Synthesis of polystyrene-supported catalyst

0.796 g of polymer containing 0.62 mmol cyclopentadienes units was dissolved in 40 mL toluene and 7.2 mL of *n*-BuLi solution (11.52 mmol) was added at

-78°C . The temperature was gradually warmed to -10°C and reacted for 1 h. The product was precipitated and washed using hexane and dried under vacuum at 0°C . The above product was dissolved in 50 mL of THF followed by the addition of 0.162 g of CpZrCl_3 (0.617 mmol). The reaction was carried out for 6 h at 0°C . Finally the catalyst was precipitated using hexane, washed with hexane/THF mixed solution (4 : 1 v/v), and dried in vacuum at 0°C .

Polymerization procedure

Ethylene polymerization and ethylene/ α -olefin copolymerization were carried out in a 100-mL glass flask equipped with an ethylene inlet, a magnetic stirrer, and a vacuum line outlet. The reactor was filled with 50 mL of dry toluene and certain quantities of MAO. The mixture was stirred at fixed temperature and then saturated with ethylene (1 atm). Certain quantities of α -olefin were added into the above-mentioned system in ethylene/ α -olefin copolymerization. The reaction was initiated by adding the catalyst. The ethylene consumption was continuously recorded using a magnetic valve. After 30 min the polymerization was terminated by the addition of acidified ethanol. The resulting polymer was separated by filtration and dried at 70°C for 12 h.

Characterization

The molecular weight and molecular weight distribution of the linear polystyrene were measured at 20°C by gel permeation chromatography (GPC) using THF as solvent. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) spectra were recorded by Bruker AVANCE DMX500. The differential scanning calorimetry (DSC) analysis of the copol-

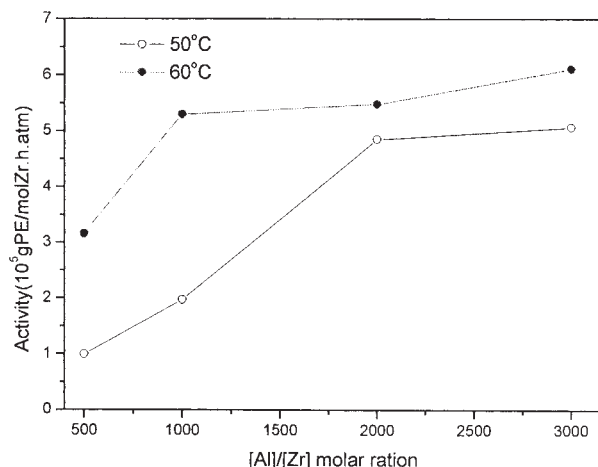


Figure 2 Influence of [Al]/[Zr] ratio on polymerization activity. Polymerization conditions: 50 mL toluene, ethylene pressure = 1 atm.

mer was carried out on Perkin–Elmer DSC-7 calorimeter at a heating rate of $10^\circ\text{C}/\text{min}$ and the second scan was recorded. The previous thermal history in the polymer samples was eliminated by the specimen being heated to 150°C , maintained at this temperature for 1 min and then cooled to 50°C .

RESULTS AND DISCUSSION

Synthesis and characterization of polystyrene-supported metallocene catalyst

Figure 1 outlined the preparation of the polystyrene-supported catalyst: The molecular weight of the linear polystyrene, $M_w = 34,600$, and the polydispersity, $M_w/M_n = 1.88$, were determined by GPC analysis. Subsequently, polystyrene was chloromethylated and the content of chloromethyl groups of the chloromethylated polystyrene was determined by $^1\text{H-NMR}$ spectroscopy by comparing the integral of the methylene signal at $\delta = 4.50$ ppm with the integral of the aromatic region. An excessive amount of CpNa was used to react with chloromethylated polystyrene to cause chlorine groups transform completely into cyclopentadiene groups. After the reaction $^1\text{H-NMR}$ spectroscopy showed the change of the methylene signals from $\delta = 4.50$ to $\delta = 3.75$ ppm, which indicated the conversion of chlorine groups was complete. Polystyrene with cyclopentadiene was metallated by addition of *n*-BuLi and the resultant product followed by addition of cyclopentadienylzirconium trichloride in THF to form the polymer-supported catalyst. The content of zirconocene of the polystyrene-supported metallocene catalyst was determined according to the literature⁹ and it was found that the catalyst contained 0.3866 mmol zirconocene per g polymer.

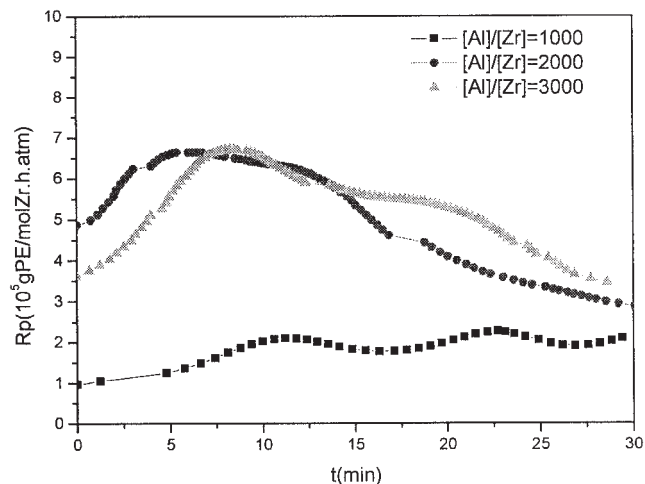


Figure 3 The influence of [Al]/[Zr] molar ratio on the ethylene polymerization rate. Polymerization condition: $T_p = 50^\circ\text{C}$, 50 mL toluene.

Polymerization of ethylene

The influence of [Al]/[Zr] molar ratio and temperature on ethylene polymerization catalyzed by polystyrene-supported catalyst are shown in Figure 2.

Figure 2 revealed that increasing [Al]/[Zr] molar ratio increases the catalyst activity; however, the effect on catalyst activity was minor as we increased [Al]/[Zr] greater than 2,000. In addition, the polymerization temperature had great influence on the activity. The activity increased with the increase of temperature evidently. The influence of [Al]/[Zr] molar ratio and temperature on the ethylene polymerization rate are shown in Figures 3 and 4. The rate of polymerization increased and reached the maximum in a few minutes then decayed slowly.

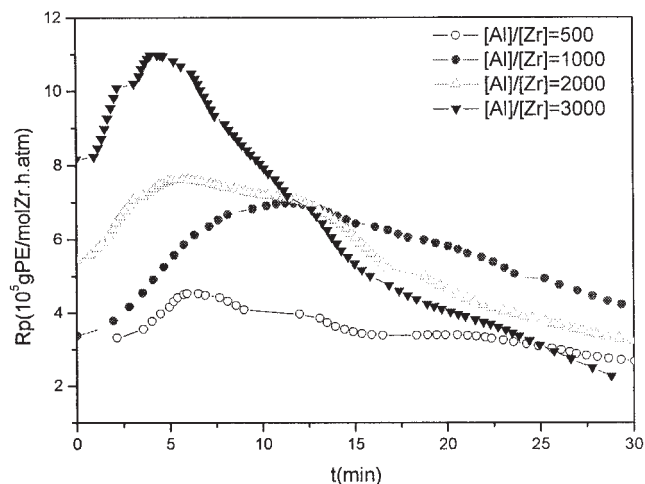


Figure 4 The influence of [Al]/[Zr] molar ratio on the ethylene polymerization rate. Polymerization condition: $T_p = 60^\circ\text{C}$, 50 mL toluene.

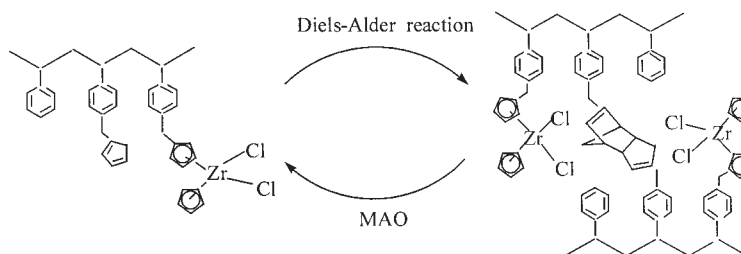


Figure 5 The possible conversion between noncrosslinked catalyst and crosslinked catalyst.

The polystyrene-supported metallocene was insoluble in toluene because the excessive cyclopentadienes groups in the polystyrene chains performed a Diels–Alder reaction.^{10,11} However, the literature indicates that the crosslinked polystyrene-supported metallocene was totally shifted to noncrosslinked species due to the retro-Diels–Alder reaction via MAO.¹² The model of fragmentation of catalyst was shown in Figure 5. The reversible crosslinking of this catalyst system facilitated carrier fragmentation during polymerization. The fragmentation allowed the further permeation of MAO and monomer into the inner part of the catalyst, leading to a successive fragmentation of the catalyst particle. By the fragmentation of carrier, more active species were exposed to monomer. The mechanism was supported by polymerization rate curves (Figures 3 and 4). When the polymerization started, the polymerization rate increased continuously, which hinted at an increase in the number of active species owing to the successive fragmentation of carrier. The mild initiation and stable polymerization process of the polystyrene-supported metallocene catalyst adapted to industrial processes compared with the strong initiation and rapid loss of activity of conventional metallocene catalyst.

TABLE I
Results of the Ethylene/ α -Olefin Copolymerization

Ru <i>n</i>	α -olefin in the feed (mol/L)	Activity (10^5 g Polymer/mol Zr.h.atm)	T_m ($^{\circ}$ C) ^a	ΔH_f (J/g) ^b
1	0	1.97	134.0	152.0
2 ^c	0.1	3.95	116.0	108.7
3 ^c	0.2	6.96	108.7	87.2
4 ^c	0.4	5.83	97.4	49.5
5 ^c	0.6	5.26	88.9	34.1
6 ^d	0.1	4.01	116.5	111.6
7 ^d	0.2	5.19	108.5	86.2
8 ^d	0.4	5.47	100.7	64.5
9 ^d	0.6	3.56	95.1	45.6

^a Melting temperature as determined by DSC.

^b Heat of fusion as determined by DSC.

^c 1-Hexene, $t = 0.5$ h, $P_{\text{ethylene}} = 1$ atm, $[A1]/[Zr] = 1,000$, $T_p = 50^{\circ}\text{C}$, 50 mL toluene.

^d 1-Dodecene, $t = 0.5$ h, $P_{\text{ethylene}} = 1$ atm, $[A1]/[Zr] = 1,000$, $T_p = 50^{\circ}\text{C}$, 50 mL toluene.

Copolymerization of ethylene/ α -olefin

The result of ethylene/ α -olefin copolymerization is shown in Table I. The activities of ethylene/ α -olefin copolymerization were higher than that of ethylene homopolymerization and the obvious positive “comonomer” effect happened. Several authors^{13,14} have observed this effect when comparing the results obtained with ethylene homopolymerization. The phenomena were attributed to an increase in the polymer solubility because an increase in monomer diffusion through the reaction medium would increase its concentration around the active centers.¹⁵ Moreover, the presence of the comonomer in the polyethylene chain would make difficult the formation of a crystalline shell of polyethylene around the active sites.¹⁶ The activities of ethylene/ α -olefin copolymerization increased with the increase of the comonomer concentration until the maximum was reached and then started to decrease with further increase of comonomer concentration. It can be seen also in Table I that the effects of increasing α -olefin concentration include a decrease in the melting temperatures of copolymers and the continuous decrease in the crystallinity of the copolymer (as reflected by the value of ΔH_f). The length of chain of the comonomer had little effect on the activity of copolymerization.

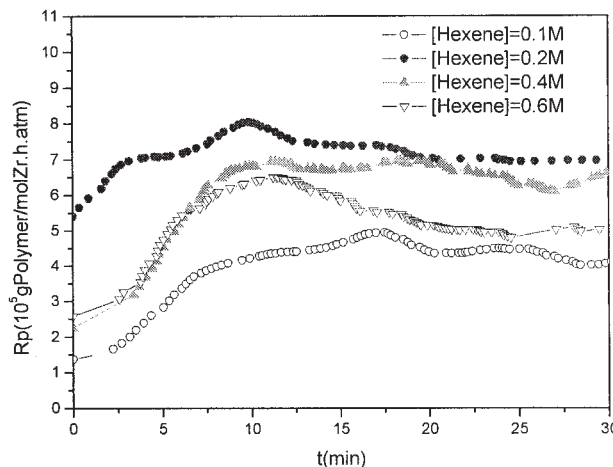


Figure 6 The influence of comonomer concentration on the rate of ethylene/1-hexene copolymerization. Polymerization condition: $T_p = 50^{\circ}\text{C}$, 50 mL toluene.

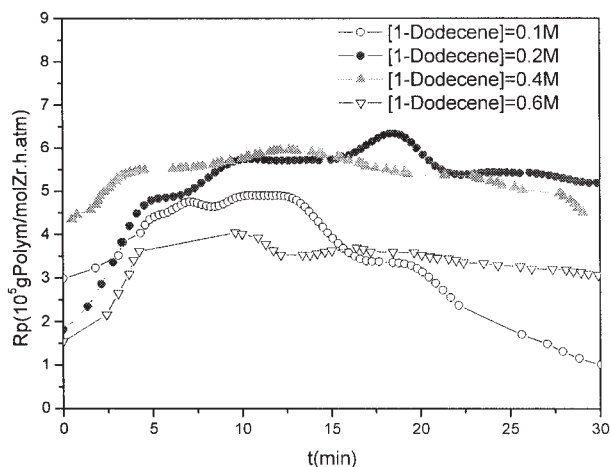


Figure 7 The influence of 1-dodecene concentration on the ethylene/1-dodecene copolymerization rate. Polymerization condition: $T_p = 50^\circ\text{C}$, 50 mL toluene.

The influence of the comonomer concentration on the rate of ethylene/1-hexene copolymerization is shown in Figure 6. The rate of copolymerization increased in the first reaction period and then remained stable. The rate of ethylene/1-dodecene copolymerization was shown in Figure 7. It was obvious that the type of rate–time plots of ethylene/1-dodecene copolymerization was almost the same as that of ethylene/1-hexene copolymerization. The stable polymerization process implied that the fragmentation of carrier had great influence on the copolymerization kinetic. According to Figure 5, with the fragmentation of carrier, active species were exposed gradually to comonomer, which led to little deactivation of copolymerization.

CONCLUSIONS

In this work, a polystyrene-supported metallocene catalyst was synthesized and used to catalyze ethylene

homopolymerization and ethylene/ α -olefin copolymerization. The conversion between noncrosslinked catalyst and crosslinked catalyst significantly influenced the polymerization. (Co)polymerization rate profiles of the polystyrene-supported metallocene catalyst exhibited slow initiation and a stable increase in (co)polymerization activity, which indicated the catalyst was fit to industrial processes. In ethylene/ α -olefin copolymerization, the positive “comonomer effect” was observed also.

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References

- Soga, K.; Kim, H. J.; Shiono, T.; *Macromol Chem Phys* 1994, 195, 3347.
- Soga, K.; Uozumi, T.; Saito, M.; Shiono, T.; *Macromol Chem Phys* 1994, 195, 1503.
- Satyanarayana, G.; Sivaram, S. *Macromolecules* 1993, 26, 4712.
- Hong, S. C.; Ban, H. T.; Kishi, N.; Jin, J.; Uozumi, T.; Soga, K. *Macromol Chem Phys* 1998, 199, 1393.
- Hong, S. C.; Teranishi, T.; Soga, K. *Polymer* 1998, 39, 7153.
- Nishida, H.; Uozumi, T.; Arai, T.; Soga, K.; *Macromol Chem Rapid Commun* 1995, 16, 821.
- Yang, L. Y.; Wang, Y. X.; Wang, J. X. *J Mol Catal (China)* 2001, 15, 56.
- Stone, F. G. *Adv Organomet Chem* 1964, 2, 365.
- Ji, B.; Wang, L.; Feng, L. X. *Chem Online* 2000, 7, 66.
- Stork, M.; Koch, M.; Klapper, M.; Müllen, K.; Gregorius, H.; Rief, U.; *Macromol Rapid Commun* 1999, 20, 210.
- Koch, M.; Stork, M.; Klapper, M.; Müllen, K. *Macromolecules* 2000, 33, 7713.
- Nenov, N.; Koch, M.; Klapper, M.; Müllen, K. *Polym Bull* 2002, 47, 391.
- Santos, J. H. K.; Uozumi, T.; Teranishi, T.; Sano, T.; Soga, K. *Polymer* 2001, 42, 4517.
- Marques, M. D. F. V.; Marinha, A. B. A. S. *J Polym Sci Polym Chem Ed* 2004, 42, 3038.
- Köppl, A.; Babel, A. I. *J Mol Catal A* 2000, 153, 109.
- Marques, M. D. F. V.; Anunciata, C.; Resende, F. C.; Chaves, É G. *J Appl Polym Sci* 2001, 82, 724.