Investigation of Styrene/1-Hexene Copolymerization by Homogeneous and Heterogeneous Bisindenyl Ethane Zirconium Dichloride Catalyst System

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ABSTRACT: Homogeneous copolymerization of styrene and 1-hexene was carried out in toluene at room temperature using bisindenyl ethane zirconium dichloride/methylaluminoxane (MAO). The supported catalyst was prepared with immobilization of $Et(Ind)_2ZrCl_2$/MAO on silica (calcinated at 500°C) with premixed method. Heterogeneous copolymerization of styrene/1-hexene with different mole ratios was carried out in the presence of supported catalyst system. The copolymers obtained from homogeneous and heterogeneous catalyst system were characterized by ^{1}H NMR and ^{13}C NMR. Composition of the resulting copolymers was determined by ^{1}H NMR data. Analysis of ^{13}C NMR spectra of obtained copolymers by homogeneous and heterogeneous catalyst systems present isotactic olefin-enriched copolymers. Molecular weight and thermal behavior of resulting copolymers was investigated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 4008–4014, 2007

Key words: copolymerization; isotactic; metallocene catalysts; polystyrene; supported catalyst

INTRODUCTION

The commercial interest of using metallocene catalysts and methylaluminoxane (MAO) as a cocatalyst for olefin polymerization has led to extensive efforts to utilize metallocene catalysts efficiently.[1–3] The single-site character of the active species allows predicting and controlling properties of the resulting polyolefins, such as the content of comonomer, molar mass, molar mass distribution, microstructure, and tacticity. Styrene polymerization and its copolymerization with other styrene-deriving monomers as well as with 1-alkenes and dienes, initiated by metallocene catalysts, have been studied by a number of researchers. The main objective of such studies has been to improve the certain properties of polystyrene.[4,5] Most of styrene–olefin copolymerization studies deal with the styrene–ethylene pair and some of them with styrene–propylene, whereas those dealing with the styrene–(α-olefin) system are rare.

Commercial polystyrene has very reliable properties. It is a good electrical insulator, has excellent optical clarity, and is easy to process making it a suitable material for many and diverse applications. However, it is brittle, has poor impact resistance, has a low upper temperature limit, poor weatherability, and is attacked by organic solvents. With the aim to overcome these deficiencies, some efforts have been made through copolymerization with other monomers, blending with other polymers, and stereoregular polymerization. Both isotactic and syndiotactic polystyrene, with melting temperature $T_m = 240$ and 270°C, respectively, have been obtained, raising considerably the ceiling temperature of amorphous polystyrene, which is limited by its glass-transition temperature T_g of 100°C.[6–9] Isotactic polystyrene has very low crystallization rates, which make it of no commercial interest, whereas syndiotactic polystyrene has a fast crystallization rate. Beside its high melting temperature, syndiotactic polystyrene has high crystallinity and high thermal resistance. However, due to its rigidity, syndiotactic polystyrene is still a brittle material with low impact resistance and its processing requires a rather high temperature. With the aim of overcoming the deficiencies of syndiotactic polystyrene, recently our research group and other groups have been working on stereoregular styrene polymerization and on its copolymerization with various monomers.[10–13]

In this article, we describe the homogeneous copolymerization of styrene and 1-hexene with different mole ratios by bisindenyl ethane zirconium dichloride/MAO and also we immobilized this catalyst on silica and then copolymerization was performed by supported catalyst system. The copolymers obtained from homogeneous and heterogeneous catalyst system were characterized by ^{1}H NMR and ^{13}C NMR. Composition of the resulting copolymers was determined by ^{1}H NMR data and compared in both catalyst systems.

EXPERIMENTAL

All experiment was performed under inert atmosphere using Schlenk technique.

Materials

MAO (10% in toluene) was provided by Aldrich (Steinheim, Germany) and used without further purification. Styrene (Tabriz Petrochemical, Iran) was purified by distillation under reduced pressure over CaH_2. 1-Hexene (96%) was purchased from Merck (Hohenburn, Germany) and purified by distilling over sodium/benzophenone under argon atmosphere prior to use. Silica (pore volume = 1.6 mL/g, powder surface area = 300 m^2/g) was purchased from Alfa (Karlsruhe, Germany) and calcinated under argon atmosphere for 12 h at 500°C.

Preparation of bisindenyl ethane zirconium dichloride

Bisindenyl ethane zirconium dichloride was synthesized by modification of the literature methods.[14] A brief description of this method is as follows:

1,2-Bisindenyl ethane

Indene (6 mL, 46 mmol, 90% grade) was dissolved in 50 mL of dry tetrahydrofuran (THF) under argon atmosphere. n-Buthyllithium (30 mL of 1.6M solution in hexane) was added dropwise to the solution over 30 min at −78°C with stirring. Then the mixture was warmed to room temperature and stirred for additional 1 h. The solution was cooled to −78°C and 1,2-dibromoethane (1.8 mL, 20.8 mmol) in 20 mL of THF was added dropwise over 0.5 h by addition funnel. The resulting purple solution was warmed slowly to room temperature and quenched at 0°C by the addition of saturated NH_4Cl solution (50 mL). The two-phase mixture was diluted with petroleum ether (30-60) and the organic layer was washed with water and dried over $MgSO_4$, filtered, and concentrated in vacuum to provide an oily solid. Crystallization from acetone and ethanol provided 4.5 g (76% yields).

Bisindenyl ethane zirconium dichloride

A degassed solution of bisindenylethane (2.0 g, 7.74 mmol) in 80 mL of dry THF was treated with solution of n-buthyllithium in hexane (9.67 mL of 1.6M) at −78°C. The mixture was warmed to room temperature. $ZrCl_4$ (1.8 g, 7.74 mmol) was placed in two-necked flask under argon atmosphere, cooled to −78°C, and a precooled THF was added dropwise via jacket dropping funnel. After formation of $ZrCl_4$/2THF adduct, additional THF was added until the total volume reached 80 mL. The content of both flasks was simultaneously added at the same rate to a third flask, containing 50 mL of THF, by two cannular, with vigorous stirring. After the addition was completed, the orange-yellow solution was stirred overnight at room temperature. Then the solution was cooled to 0°C and HCl gas passed through the mixture for about 50 s with stirring. A bright canary yellow solution was obtained. The solvent was concentrated in vacuum, and then the precipitation of the complex was completed by addition of ether. The yellow precipitates was quickly filtered and dried in vacuum. The yellow powder was soxhlet by dichloromethane under argon atmosphere for separation of pure compound from LiCl, dried in vacuum, and stored in Schlenk tube (50% yield). For removing the minor amount of its mesoisomer from final product, washing of product with hot toluene was performed.

Polymerizations

Homogeneous polymerization

Into 100-mL two-necked round bottom flask equipped with magnetic stirring bar and argon inlet and outlet was injected 20 mL toluene, followed by injection of styrene and 1-hexene mixture, followed by injection of 2 mL MAO. Then the catalyst solution (previously prepared by dissolving of 2.8 μmol $Et(Ind)_2ZrCl_2$ in 2 mL toluene) was injected to the aforementioned flask. The reaction was carried out at room temperature and was quenched after 24 h by addition of 15 mL methanol containing 1.5 mL of HCl. The organic layer was separated and aqueous suspension was extracted three times with 20 mL methylenechloride. The combined organic phases were dried over Na_2SO_4. The solvent was removed under vacuum. Copolymer samples were extracted with solvents using acetone, cyclohexane, and chloroform in that order.[15]

Preparation of supported catalyst

Into a 50 mL vial equipped with a magnetic stirring bar, 1 g silica dehydrated at 500°C was added. The vial was evacuated under vacuum for 10 min. At the end of vacuum evacuation, the pressure of the vial was reduced to ambient pressure by argon atmosphere, and then 6 mL dry toluene was added. Into another 50 mL vial, 0.043 g (0.109 mmol) Ind_2ZrCl_2, followed by 8 mL 10 wt % MAO in toluene solution was added. The mixture was stirred at 25°C for 15 min. The metallocene/MAO mixture was then transferred into the silica-containing vial through a syringe while the silica was under constant stir. The mixture was stirred for 4 h, then the solid was separated from the solvent by decantation and was washed with 6 mL of dry toluene and the solvent was again decanted. The washing process was

repeated until the filtrate solvent was colorless. The solid support was dried at vacuum evacuation to give a free-flowing powder.

The zirconium and aluminum contents in the catalysts were determined by the technique of inductively coupled plasma-atomic emission spectroscopy (ICP-AES), from samples dissolved in fluoridric acid. The results for the Zr and Al measurements were as follows: $Zr = 0.26\%$ and $Al = 10.3\%$.

Heterogeneous polymerization

100 mg of the supported catalyst (2.8 μmol $Et(Ind)_2ZrCl_2$) was transferred in to 50-mL two-necked round bottom flask equipped with magnetic stirring bar and argon inlet and outlet, and then 22 mL toluene was injected. Polymerization was initiated by injection of either the styrene or 1-hexene or simultaneously the required amount of styrene and 1-hexene on the supported catalyst. Polymerization reaction was followed by an analogous procedure explained in the previous section.

Polymer analysis

The NMR samples were prepared by dissolving the polymers in a $CDCl_3$ and measured at 25°C on a Brucker 400 MHz NMR instrument. Differential scanning calorimetry (DSC) analyses were performed by using a Mettler Toledo instrument model DSC 822 with samples placed in a nitrogen athmosphere and were used for the measurements; exotherms of nascent polymers were obtained by scanning from an initial temperature of −100°C to a final temperature of 200°C at a rate of 10°C/min. Calibration of the instrument was done with an indium standard. The molecular weight of the resulting polymers was obtained with a maxima 820 GPC analysis instrument using PS (10^6, 10^5, and 10^4 Å) calibration standards with a THF mobile phase.

RESULTS AND DISCUSSION

The selection of the transition metal in the metallocene catalysts is of significant importance for the

TABLE I
Homopolymerization of 1-Hexene and Styrene in the Presence of the Catalytic System Based on $Et(Ind)_2ZrCl_2$-MAO

Run	Styrene (mmol)	1-Hexene (mmol)	Conversion (%)
1	86.5	–	8.04
2	–	79.7	88[a]

Polymerization conditions: [zr] = 2.8 × 10^{-6} mol; Al/Zr = 1000; polymerization time t_p = 24 h; polymerization temperature T_p = room temperature; Conversion (%) = (weight of polymer/weight of monomer) × 100.
[a] Amorphous and viscous.

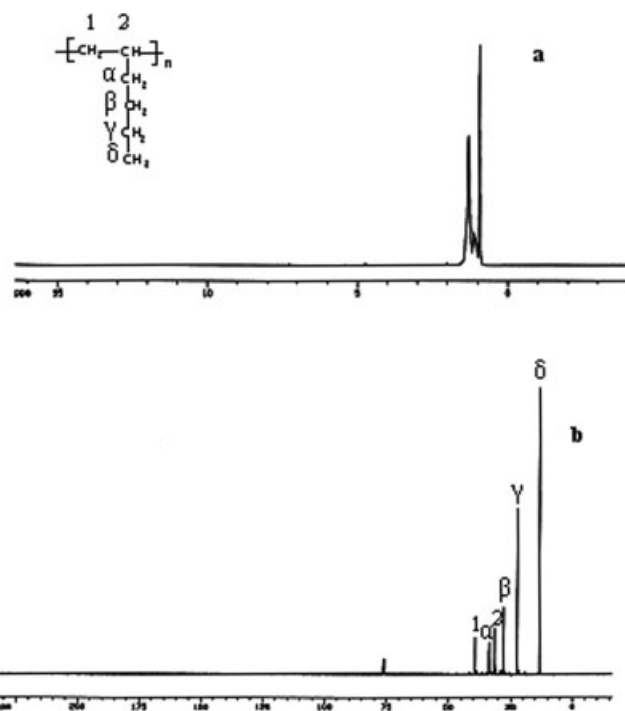**Figure 1** (a) ^{1}H NMR and (b) ^{13}C NMR spectra of poly(1-hexene) obtained using the $Et(Ind)_2ZrCl_2$/MAO catalyst system.

catalyst activity and stereoselectivity in the sydiotactic polystyrene. Titanocenes such as CP_2TiCl_2, n-$BuCP_2TiCl_2$, and $CPTiCl_3$ give rise to almost pure syndiotactic polystyrene, whereas zirconocenes such as Ind_2ZrCl_2, CP_2ZrCl_2, and related others produce mostly atactic polystyrene with a low content of syndiotactic polystyrene. Also the constrained geometry catalyst, which is based on titanium, is able to homopolymerize styrene, whereas the equivalent catalyst based on zirconium is not.[10]

In the present study, we report the copolymerization of styrene/1-hexene in the presence of $Et(Ind)_2ZrCl_2$ in homogeneous and heterogeneous system. The obtained copolymers showed that the amount of 1-hexene in copolymers is higher than styrene with respect to the initial feed composition. In other word, the $Et(Ind)_2ZrCl_2$ catalyst and supported type of this catalyst is highly active for 1-hexene, whereas both catalyst system are less effective for styrene polymerization.

Table I shows the obtained results for the homopolymerization of 1-hexene and styrene by $Et(Ind)_2ZrCl_2$/MAO.

This catalyst is highly active for 1-hexene and led to isotactic poly(1-hexene), but the catalyst system is less effective for styrene polymerization and produce atactic polystyrene, in agreement with previously reported results for zirconocene type.[11] Figure 1 shows the ^{1}H NMR and ^{13}C NMR spectra of poly(1-hexene). In the ^{13}C NMR spectra, the chemical

TABLE II
Hemogeneous Copolymerization of Styrene with 1-Hexene in the Presence of the Catalytic System Based on Et(Ind)$_2$ZrCl$_2$-MAO

Run	Styrene (mmol)	Initial feed S/1-hexene (mol/mol)	Conversion (%)[a]	Styrene units in copolymer (mol %)	1-Hexene units in copolymer[b] (mol %)
1	32.19	1	33.7	38.84	61.52
2	42.40	2	29.5	56.50	43.5
3	48.46	3	12.86	59.17	40.83

Polymerization conditions: total volume = 30 mL; [zr] = 2.8 × 10^{-6} mol; Al/Zr = 1000; [S + 1-hexene] = 2.1 mol/L; polymerization time t_p = 24 h; polymerization temperature T_p = room temperature.
[a] Conversion (%) = (weight of polymer/weight of monomer) × 100.
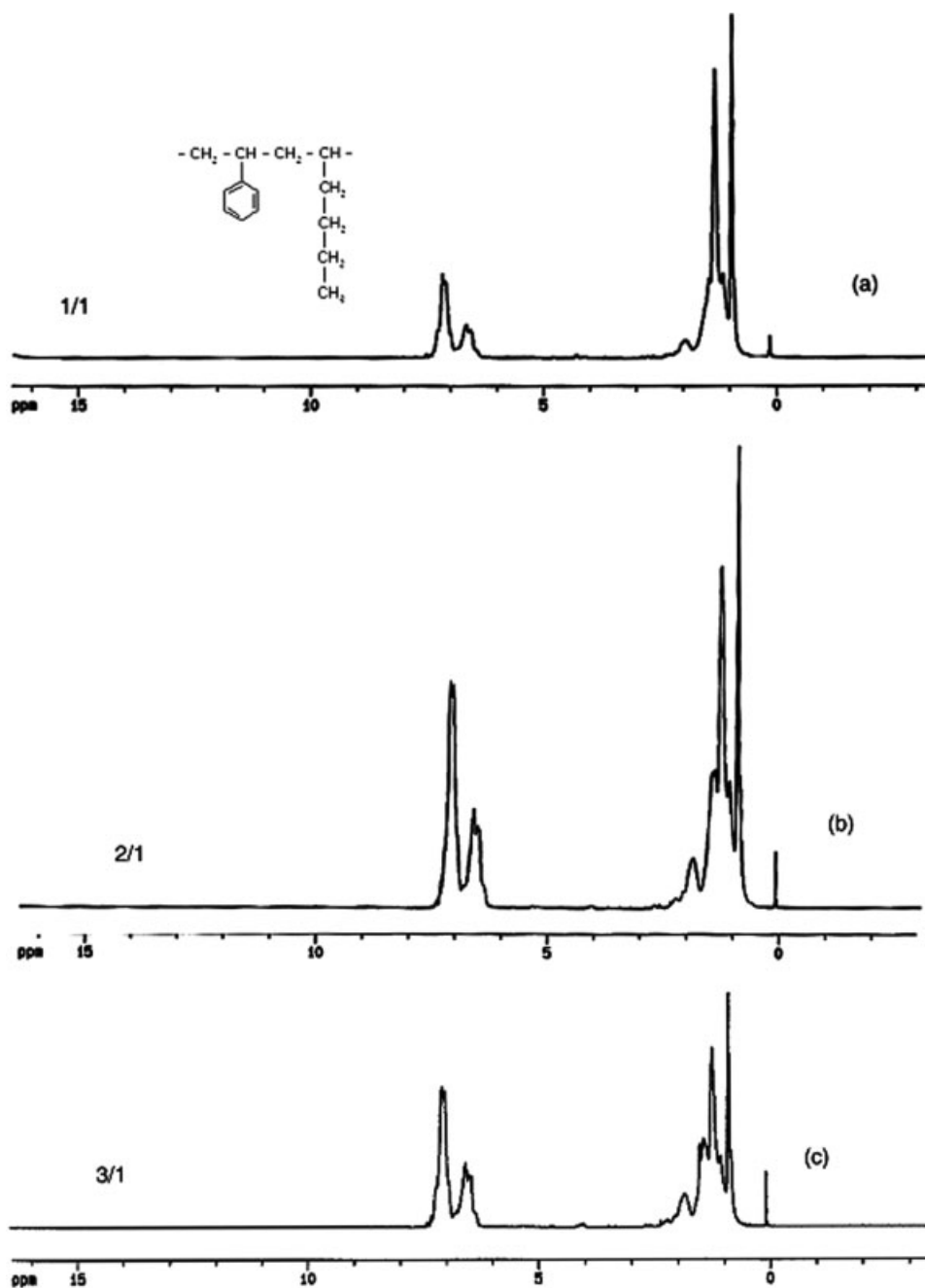[b] Calculated from NMR data.

Figure 2 (a–c) The ^{1}H NMR spectra of styrene/1-hexene copolymers at various initial molar ratios using Et(Ind)$_2$ZrCl$_2$/MAO catalyst system.

shifts of the signals are in agreement with an isotactic microstructure. Therefore it is seen that the structure of poly(1-hexene) obtained from this system is isotactic.[16]

Table II shows the results of copolymerization of styrene and 1-hexene in a 1/1, 2/1, and 3/1 mol ratios using Et(Ind)$_2$ZrCl$_2$/MAO catalyst system.

The results showed that the incorporation of styrene in the copolymers is considerable. These values also indicate that the total conversion decreases with increasing amount of styrene in the initial feed composition. The influence of the presence of styrene on polymerization rates is complex and involves chemical effects, e.g., changes in propagation rate constants, as well as physical changes to the catalyst, e.g., different fragmentation, and changes to the structure of the polymer, i.e., changes in polymer crystallinity.[17,18]

The copolymer composition was calculated by integration of the ^{1}H NMR signals corresponding to the aliphatic CH, CH$_2$, and CH$_3$ signals (0.8–2.5 ppm) and aromatic protons (6.3–7.4 ppm) of styrene

units. Table II shows the copolymer composition calculated for these copolymers. These values indicate that the copolymers are enriched in 1-hexene with respect to the initial feed composition. This is an expected result in agreement with the higher reactivity of 1-hexane compared with the styrene monomer.

Figure 2(a–c) shows the ^{1}H NMR spectra of styrene/1-hexene copolymers with 1/1, 2/1, and 3/1 mol ratios obtained using Et(Ind)$_2$ZrCl$_2$/MAO. The results show the presence of signals corresponding to both styrene and 1-hexene units and the amount of styrene unit increase according to the initial feed.

The ^{13}C NMR spectra, which are shown in Figure 3(a,b), confirmed the isotacticity of 1-hexene sequence in the copolymers. The signal centered at 33.7 ppm could be straightforwardly assigned to the α-CH$_2$ of the side chain. This signal was attributed to the mmmm pentads and broadens as the styrene content in the copolymer increases. The broadening of this signal can be attributed to the 1-hexene sequence effects.[16]
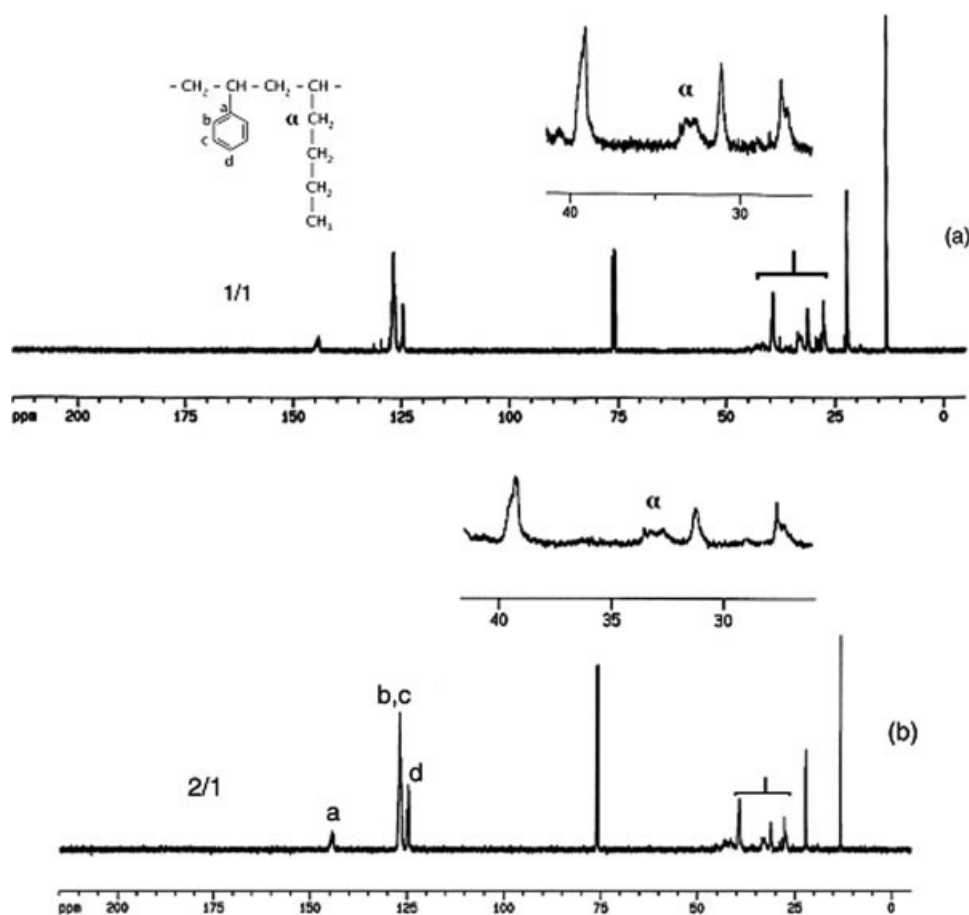

Figure 3 (a,b) The ^{13}C NMR spectra of styrene/1-hexene copolymers at various initial molar ratios using Et(Ind)$_2$ZrCl$_2$/MAO catalyst system.

Heterogeneous Copolymerization of Styrene with 1-Hexene in the Presence of the Catalytic System Based on Et(Ind)$_2$ZrCl$_2$/MAO/SiO$_2$

Run	Styrene (mmol)	Initial feed S/1-hexene (mol/mol)	Conversion (%)[a]	Styrene units in copolymer[b] (mol %)	1-Hexene units in copolymer[b] (mol %)	M_n[c]
1	80.4	1	16.06	25.7	74.3	3138
2	107.2	2	10.43	50.58	49.42	–
3	121.5	3	3.09	54.3	45.7	2716

Polymerization conditions: total volume = 30 mL; [zr] = 2.8 × 10^{-6}; Al/Zr = 130; Zr/Silica = 0.26%; [S + 1-hexene] = 2.1 mol/L; polymerization time t_p = 24 h; polymerization temperature T_p = room temperature.
[a] Conversion (%) = (weight of polymer/weight of monomer) × 100.
[b] Calculated from NMR data.
[c] Determined by GPC.

Silica is used commonly as support for metallocene immobilization. The supported catalyst behavior depends on both support and supporting technique.

Different methods of heterogenization are possible. In this work the premixing method has been used. In this method the bisindenyl ethane zirconium dichloride and MAO have to be premixed to form an activated zirconocene species suitable for anchoring onto silica. In methylated metallocene species ([Et(Ind)$_2$ZrCH$_3$]$^+$ [MAO]$^-$), MAO binds stronger to the silica than the zirconocene and the active species is Et(Ind)$_2$ZrMe$^+$ electrostatically bound to the MAO-grafted silica.[19]

Table III shows the results of heterogeneous copolymerization of styrene/1-hexene with 1/1, 2/1, and 3/1 mol ratios using Et(Ind)$_2$ZrCl$_2$/MAO/SiO$_2$ catalyst system.

The results showed that the conversion and styrene content in copolymers were decreased in this system, but the aluminum consumption was decreased toward homogeneous system. Figure 4(a,b) shows the ^{1}H NMR spectra of styrene/1-hexene copolymers with 1/1 and 2/1 mol ratios using Et(Ind)$_2$ZrCl$_2$/MAO/SiO$_2$ catalyst system.

These spectra confirmed the decreasing of the styrene content in copolymers. DSC thermograms of the copolymers obtained for the initial feeds styrene/1-hexene = 1/1 and 3/1 mol/mol are shown in the Figure 5. These thermograms are indicative of the crystalline nature of the copolymers. Also these thermograms showed that the glass-transition temperature of copolymers increase with increasing the styrene content of the copolymers.

CONCLUSIONS

From this work we can conclude that the Et(Ind)$_2$ZrCl$_2$/MAO system is highly active for 1-hexene and produce isotactic poly(1-hexene), but the system is less effective for styrene polymerization and produce atactic polystyrene. Copolymerization of styrene/1-hexene with this catalyst gave isotactic olefin-enriched copolymers. The conversion and styrene content in copolymers were decreased in heterogeneous catalyst system [Et(Ind)$_2$ZrCl$_2$/MAO/SiO$_2$]. The DSC thermograms showed that the glass-transition temperature of copolymers increase with increasing the styrene content of the copolymers.
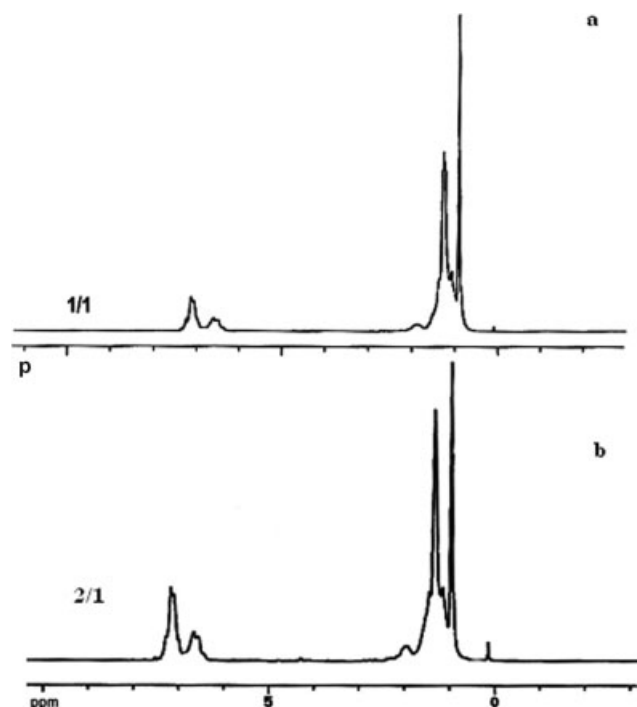

Figure 4 (a,b) The ^{1}H NMR spectra of styrene/1-hexene copolymers at various initial molar ratios using Et(Ind)$_2$ZrCl$_2$/MAO/SiO$_2$ catalyst system.
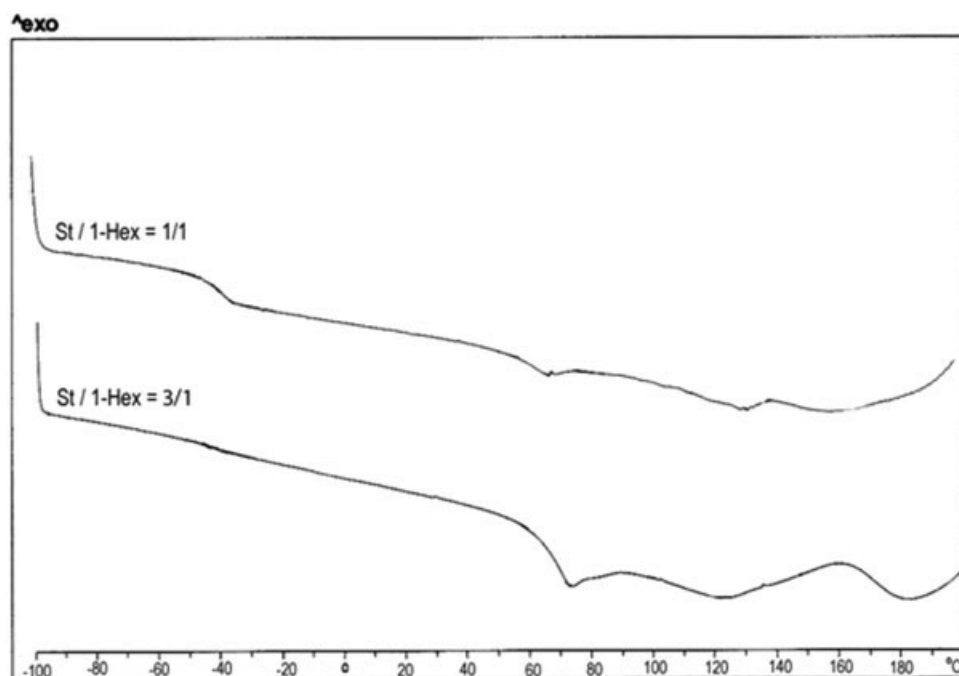
Figure 5 DSC thermograms for styrene/1-hexene copolymers obtained using the Et(Ind)$_2$ZrCl$_2$/MAO/SiO$_2$ catalyst system at various styrene/1-hexene initial molar ratios.

References

1. Brintzinger, H. H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. Angew Chem 1995, 107, 1255.
2. Kaminsky, W. Macromol Chem Phys 1996, 197, 3907.
3. Entezami, A.; Moghadam, P. N. Polym Int 2005, 54, 1326.
4. Po, R.; Cardi, N. Prog Polym Sci 1996, 21, 47.
5. Schellenberg, J.; Tomotsu, N. Prog Polym Sci 2002, 27, 1925.
6. Ntta, G.; Pino, P.; Corradini, P.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. J Am Chem Soc 1955, 77, 1708.
7. Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. Macromolecules 1986, 19, 2464.
8. Pellechia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. Makromol Chem Rapid Commun 1987, 8, 277.
9. Kaminsky, W. Catal Today 2000, 62, 23.
10. Rabaglita, F. M.; Cancino, R. A.; Perez, M. A.; Rodriguze, F. J. Macromol Symp 2004, 21, 655.
11. Rabaglita, F. M.; Cancino, R. A.; de Ilarduya, A. M.; Munoz-Guerra, S. Eur Polym J 2005, 41, 1013.
12. Entezami, A.; Agaalipour, M.; Moghadam, P. N. J Iran Chem Soc 2005, 2, 149.
13. Abbasian, M.; Rahmani, S.; Mohammadi, R.; Entezami, A. A. J Appl Polym Sci, to appear.
14. Lee, I. M.; Gauthier, W. J.; Ball, J. M.; Iyenger, B.; Collins, S. Organometallics 1992, 11, 2115.
15. Chiellini, E.; Raspolli-Galletti, A. M.; Solaro, R. Macromolecules 1984, 17, 2212.
16. Asakura, T.; Demura, M.; Nishiyama, Y. Macromolecules 1991, 24, 2334.
17. Wester, T. S.; Ystenes, M. Macromol Chem Phys 1997, 198, 1623.
18. Jongsomjit, B.; Kaewkrajang, P.; Praserthdam, P. Eur Polym J 2004, 40, 2813.
19. Line, C. H.; Sheu, C. Y. Macromol Rapid Commun 2000, 21, 1058.