Preparation of Polymer-Supported Zirconocene Catalysts and Olefin Polymerization

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Received 18 March 1998; accepted 12 September 1998

ABSTRACT: A novel polymer-supported metallocene catalyst with crosslinked poly(styrene-co-acrylamide) (PSAm) as the support has been prepared and characterized. The probability of long sequences of acrylamide (Am) in PSAm is still low even at an Am amount of 32.8 mol %, implying the relatively homogeneous distribution of Am. The infrared spectra of PSAm and the supported catalyst substantiate that an amide group in PSAm coordinates with methylaluminoxane through both oxygen and nitrogen atoms. Ethylene/ α -octene copolymerization showed that the catalytic activity is not markedly affected by adding α -octene. ¹³C NMR analysis of the ethylene/ α -octene copolymer indicated that the composition distribution of the copolymer is uniform. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 2253–2258, 1999

Key words: polymer-supported catalysts; ethylene polymerization; homogeneous distribution; methylaluminoxane; copolymerization

INTRODUCTION

The discovery of soluble metallocene catalyst by Kaminsky and Sinn^{1,2} highlighted interest in the area of Ziegler-Natta (Z-N) polymerization. Unfortunately, these catalysts require a large excess of methylaluminoxane (MAO) to realize the maximum catalytic activity, which, to some extent, may impair its value in commercial applications. One way to overcome this problem that has met with some success involves the preparation of cationic $(d^0,$ 14e⁻) metallocene compounds^{3,4} that do not require any cocatalyst for polymerization. Another approach involves absorbing metallocene compounds on a support, such as SiO_2 , Al_2O_3 , or other supports of a high surface area.^{5–7} Because many polyolefin manufacturing plants are based on fluidized bed technology, the supported metallocene catalysts would add new dimensions to their usefulness.

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Journal of Applied Polymer Science, Vol. 71, 2253-2258 (1999)

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Until now, most of the supported metallocene catalysts are based on inorganic support materials, and catalysts with polymeric materials as the carrier are rarely reported.^{8,9} This type of catalyst should have great interest in industry and academic research because the content of inorganic impurities in this catalyst is significantly limited.

Recently, on the basis of long experience in polymer-supported rare-earth catalysts for diene polymerization,¹⁰ we successfully developed a series of novel polymer-supported metallocene catalysts for olefin polymerization. This article reports the preparation and characterization of poly(styrene*co*-acrylamide) (PSAm)-supported zirconocene catalysts, as well as the results on its use in ethylene polymerization and copolymerization with α -octene.

EXPERIMENTAL

Materials

Ethylene, polymerization-grade from Liaoyang Chemical Corporation, was used without further treatment. Toluene as the solvent was dried with 4A molecular sieves and then distilled in the presence of Na/K alloy. Cp₂ZrCl₂ (Cp : η^5 -cyclopentadienyl) (from Boulder Scientific Company) and MAO in 30 wt % toluene solution (from Ethyl Corporation) were used as received. α -Octene was purified by distillation before use.

Preparation of Support

Crosslinked PSAm was prepared by radical copolymerization of styrene with acrylamide (Am) and a calculated amount of divinylbenzene as crosslinking agent in the presence of azobisisobutyronitrile as the initiator. Polymerization temperature was 80°C. The conversion was $\sim 10\%$. The product was washed several times with the mixture of hexane and water to remove the residual comonomer, followed by drying in vacuum at 60°C for 48 h. Finally, the dried polymer was ground by pulverizer and then the product through 60 mesh sieve was chosen as catalyst support. The nitrogen content of the support was determined by elementary analysis method.

Preparation of Supported Catalysts

Preparation of the PSAm-supported catalyst was conducted in a specially designed vessel. A described amount of MAO was dropped to a 3.00 g PSAm suspension in toluene under stirring and allowed to react for 1 h at room temperature. It was filtered and washed three times with toluene, then 50 mL of toluene containing 0.15 g of Cp_2ZrCl_2 was injected slowly into the reactor and reacted for 2 h at 40°C. It was washed with plenty of toluene for several times to remove the zirconocene compound not bound to the support. The catalyst was dried under reduced pressure at 40°C for 24 h. SiO_2 -supported Cp_2ZrCl_2 catalyst was prepared according to the literature.⁷

Catalyst Characterization

The contents of zirconium (Zr) and aluminum (Al) in the supported catalyst were determined by plasma photoelectron element analysis (Baird-P-SIII). Infrared (IR) spectra were recorded on a BIO-RAD FTS-7 spectrometer.

Polymerization

Polymerization of ethylene was conducted with stirring in a 300 mL glass reactor. Ethylene was continuously fed in so as to keep pressure constant. Diluent, monomer, MAO, and supported catalyst were added in the stated order. After a specific polymerization time, an ethanol solution of hydrochloric acid was injected into the reactor to quench the polymerization. The polymer was washed several times with ethanol and dried under vacuum at 50°C for 24 h.

Polymer Characterization

Compositions of the copolymer were determined by 13 C NMR 11 obtained on a pulsed Fourier transform FX-100 NMR spectrometer. Melting points and crystallinity of the polymers were determined using a Perkin–Elmer DSC-7 calorimeter at a scanning rate of 10°C min⁻¹.

RESULTS AND DISCUSSION

Preparation and Characterization of PSAm-Supported Catalysts

The distribution and the sequence length of functional group Am in PSAm are important factors of

Am (mol %)				P(Am,n) (%)		
	n	n = 1	n = 2	n = 3	n = 4	n = 5
8.6	1.011	98.88	1.104	0.0123	0.0001	
13.7	1.018	98.13	1.834	0.0343	0.0006	
19.1	1.028	97.24	2.679	0.0738	0.0020	
22.5	1.035	96.63	3.253	0.1095	0.0037	0.0001
32.8	1.058	94.47	5.227	0.2892	0.0160	0.0008

Table I Am Distribution Function of the Sequence of Different Lengths in PSAm

Note: n is the number-average sequence length of Am units; P(Am, n) is the probability of occurrence of a sequence of Am units of length n.

		Reactant				Catalysts	
No.	PSAm (g)	MAO (g)	Al/N	$Cp_2ZrCl_2(g)$	Zr (wt %)	Al (wt %)	
Cat-4	3.00	0	0	0.15	ND	0	
Cat-5	3.00	0.78	4	0.15	0.35	6.03	
Cat-6	3.00	2.32	12	0.15	0.41	7.92	
Cat-7	3.00	2.90	15	0.15	0.48	10.08	

Table II Preparation of PSAm-Supported Catalysts

Note: ND, not detected.

the PSAm-supported catalyst. The relativity ratio r_1 and r_2 of styrene (M_1) and Am (M_2) determined by the Fineman–Ross method¹² were 0.72 and 0.12, respectively. The number-average sequence length of Am units and the number distribution function are calculated according to the literature.¹³

$$n \equiv 1/P_{21}, P(Am,n) = P_{22}^{n-1} P_{21}$$

where \boldsymbol{n} is the number-average sequence length of Am units, and P(Am,n)—the number distribution function for Am units—is the odds of occurrence of a sequence of Am units of length n. P_{22} and P_{21} are the respective probabilities of reactions $\sim \sim m_2^* + M_2$ and $\sim \sim m_2^* + M_1$.



Figure 1 IR spectra of PSAm (a) and the supported catalyst (b).

$$P_{22} = r_2[M_2]/(r_2[M_2] + [M_1]),$$

$$P_{21} = 1 - P_{22} = [M_1]/(r_2[M_2] + [M_1])$$

where, as usual, $r_1 = k_{11}/k_{12}$, $r_2 = k_{22}/k_{21}$, and $[M_1]$, $[M_2]$ are respective monomers (styrene, Am) concentrations in the original feed. Calculated results are shown in Table I. Even at Am = 32.8 mol %, the probability of long sequences of Am in PSAm is still low, and the number-average sequence length \boldsymbol{n} is 1.058, which implies the relatively homogeneous distribution of Am.

Crosslinking degree of the support plays an important role in the preparation of supported catalyst. The support with high crosslinking degree is not easy to be pulverized, whereas for the support of low crosslinking degree the metallocene compound unabsorbed on the carrier is difficult to be removed because of the swelling effect of PSAm in toluene. In this article, PSAm with a crosslinking degree of 5% and a nitrogen content of 1.93 wt % was chosen as support.

Different preparations of PSAm-supported catalysts are shown in Table II. When preparing PSAm · Ti catalyst for syndiotactic polymerization of styrene,¹⁴ it was found that TiCl₄ coordinated easily with amide groups in PSAm. But, for Cp_2ZrCl_2 , as in the case of Cat-4, the bare PSAm carries so little Zr that cannot be detected, probably because Cp₂ZrCl₂ is less electron-deficient than TiCl₄; and Zr atoms do not coordinate directly with functional groups in PSAm. When PSAm was first treated with MAO and then reacted with Cp₂ZrCl₂, the Zr/MAO/PSAm-supported catalysts were obtained. This MAOtreated, PSAm-supported catalyst (Cat-5) has a dramatic increase in Zr loading from almost 0 to 0.35 wt % by just adding a little MAO (0.78 g). It is also noted that the contents of Zr and Al in the

No.	Al/Zr (molar ratio)	<i>T</i> (°C)	Activity $(10^{6} \text{ g mol}^{-1} \text{ Zr}^{-1} \text{ h}^{-1})$			
1	400	50	0.85			
1	400	50	0.00			
2 2	1000	50	1.27			
0 4	1000	50	2.30			
4	2000	50	2.60			
Э С	2000	00 20	2.81			
6	1000	30	1.81			
7	1000	40	2.70			
8	1000	60	2.12			

 Table III
 Results of Ethylene Polymerization

 with the Zr/MAO/PSAm Catalyst

Polymerization conditions: Zr, 1.20 μ mol; ethylene pressure, 140 KPa; toluene, 100 mL; 1 h.

supported catalysts increased with increments of MAO from 0.78 to 2.90 g in the reactants.

To make a point of the interplay between MAO and PSAm, comparison of the IR spectrum of the supported catalyst (Cat-6) with that of PSAm (Fig. 1) was studied. The characteristic peaks of N—H stretching vibrations at 3476 and 3392 cm⁻¹ in the spectrum of PSAm disappear, and a new peak at 3453 cm⁻¹ is observed in that of the supported catalyst. In addition, in the amplified part of the IR spectra, the shift of the characteristic peak of γ (C=O) from 1686 cm⁻¹ of the support polymer to 1676 cm⁻¹ of the supported catalyst can be detected. This infers that Am in PSAm coordinates with MAO through both the oxygen and nitrogen atoms.

Of the three possible modes of binding of MAO with the amide in the case of PSAm \cdot MAO (a-c), structure c is postulated to be probable on the above IR evidence.



A significant advantage in using polymeric materials as support is that the distribution of functional groups in the macromolecule chains can be controlled by choosing suitable copolymerization conditions, not attainable with inorganic carriers. As previously stated, distribution of Am is relatively even. Accordingly, the Cp_2ZrCl_2 is also dispersed homogeneously on the support.

Polymerization of Ethylene

To study behavior of this supported catalyst, the influence of Al/Zr molar ratio and temperature on polymerization activity of the Zr/MAO/PSAm catalyst in toluene solvent with MAO as cocatalyst was investigated (see Table III). Although the activity increases with the increase in the Al/Zr molar ratio, and reaches a high activity of 2.36 $\times 10^{6} \text{ gPE mol}^{-1} \text{ Zr}^{-1} \text{ h}^{-1}$ at an Al/Zr = 1000, it is not markedly affected by further increment of MAO beyond the Al/Zr molar ratio of 1000, differing much from the behavior of soluble zirconocene catalytic systems, and also from some other polymer-supported catalyst whose typical is the sharp increment of activity at Al/Zr (molar ratio) of 400, and then leading to an almost constant fair activity.¹⁵ Table III also shows that the activity is

				Copolymer Properties	
No.	Octene Concentration (M)	$\begin{array}{c} & Activity \\ (10^6 \ g \ mol^{-1} \ Zr^{-1} \ h^{-1}) \end{array}$	Octene Incorporation (mol %)	χ_c (%)	T_m (°C)
9	0	2.68	0	61.2	136.4
10	0.1	2.45	ND	58.0	117.7
11	0.2	2.50	1.54	47.2	112.5
12	0.3	2.58	2.20	42.4	102.5
13	0.5	2.36	4.65	31.3	95.1
14	1.0	2.20	8.11	4.3	74.8

Table IV Copolymerization of Ethylene and Octene

Polymerization conditions: Zr, 1.20 μmol; Al/Zr, 1040; ethylene pressure, 150 KPa; 40°C; 1 h. ND, not detected.

No.	Cat. System	Octene in Copolymer (mol %)	[000]	[EOE]	[EOO]	[EEE]	[OEO]	[OEE]
15 16	Zr/MAO	4.00 7.10	ND ND	4.00 7.10	ND ND	91.61 87.60	ND ND	$4.39 \\ 5.30$
$\begin{array}{c} 13\\14 \end{array}$	Zr/MAO/PSAm	$\begin{array}{c} 4.65\\ 8.11\end{array}$	ND ND	$\begin{array}{c} 4.65\\ 8.11\end{array}$	ND ND	90.66 86.60	ND ND	$4.69 \\ 5.29$

Table V Triad Sequence Distribution of Ethylene/a-Octene Copolymers

Note: ND, not detected.

highest at a polymerization temperature of 40°C, and further increasing temperature impairs polymerization activity.

Copolymerization of Ethylene and α -Octene

Copolymerization of ethylene and α -octene was investigated for Zr/MAO/PSAm catalyst. Enhancement of ethylene polymerization activity by α -olefin in traditional Z-N catalysis is a well-



Figure 2 DSC curves of ethylene/ α -octene copolymers with the Zr/MAO/PSAm catalyst.

known phenomenon of considerable technological and scientific interests.¹⁶ The enhancement factor could be quite sizeable, as much as a factor of 10 for certain low activity Z-N catalysts.¹⁷ Table IV shows that the activity of ethylene polymerization is not significantly affected by the addition of α -octene, and the activity of copolymerization is always a little lower than that of ethylene polymerization. The melting point and crystallinity decrease markedly with an increase in octene content in the copolymers. This little influence of comonomer or even "negative" comonomer effect was observed by other researchers as well.^{18,19} Maybe all the Zr atoms are catalytically active in the zirconocene/MAO catalytic system, and addition of α -olefin does not lead to the enhancement in active center concentration. The possible expla-



Figure 3 DSC curves of ethylene/ α -octene copolymers with the Zr/MAO/SiO₂ catalyst.

nation for the above results is that, although addition of octene results in lower crystallinity of the product favoring the diffusion of ethylene to the active centers, the polymerization activity of octene is far lower than that of ethylene.

Characterization of Ethylene/ α -Octene Copolymers

From the triad sequence distributions of ethylene/ α -octene copolymers produced by soluble and polymer-supported catalysts (Table V), it is noted that [OOO], [EOO], and [OEO] are not detected for both polymer-supported catalyst and soluble catalyst. (The detection limit for triad sequence distribution is 0.1 mol %). So, the composition distribution of the copolymers obtained with the Zr/MAO/PSAm catalyst maintains the significant advantage of soluble catalytic system.

It is generally believed that the origin of the T_m peak is attributed to the lamellar thickness, which is governed by copolymer composition distribution and thermal history. Comparing the differential scanning calorimetry (DSC) curves of two types of ethylene/ α -octene copolymers with Zr/MAO/PSAm and Zr/MAO/SiO₂, one can see that only one peak is found in the DSC curve of the ethylene/ α -octene copolymer with the Zr/MAO/PSAm catalyst (Fig. 2), whereas for $Zr/MAO/SiO_2$ catalyst, three T_m peaks at 84.4, 95.9, and 103.6°C, respectively, in sample 75 and two peaks at 96.4 and 102.4°C in sample 76 under the same thermal history (Fig. 3). This indicates that the comonomer distribution of ethylene/ α -octene copolymer with this polymer-supported catalyst is more even than that of copolymer with SiO₂-supported catalyst. Probably the complexity of hydroxyl groups on the surface of SiO₂ is circumvented.

This project was supported by the National Natural Science Foundation of China.

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