

PREPARATION OF NOVEL POLYETHYLENE-*graft*- POLY(4-VINYLPYRIDINE)-SUPPORTED METALLOCENE CATALYSTS FOR ETHYLENE POLYMERIZATION*

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Abstract Polyethylene (PE) grafting 4-vinylpyridine copolymers has been produced as powders of different rushes by the irradiation method. After treatment with methylaluminoxane (MAO), the copolymers were used as supports for Cp_2ZrCl_2 catalyst. Results of X-ray photoelectron spectroscopy, Fourier transforms infrared spectroscopy, ultraviolet spectroscopy and scanning electron microscope measurements show that the catalytic sites have been linked through MAO on the PE-*graft*-4-vinylpyridine (PEVP). The percentages of grafting 4-vinylpyridine and supported Cp_2ZrCl_2 depend on the size of polyethylene powder. The smaller the polyethylene powder, the more percent of 4-vinylpyridine groups and Cp_2ZrCl_2 exist on the polyethylene chains, and the PEVP-supported catalyst has a relatively high activity for ethylene polymerization.

Keywords Polyethylene grafting 4-vinylpyridine, Copolymer, Irradiation, Supported catalyst, Cp_2ZrCl_2 , Ethylene polymerization

INTRODUCTION

Compared to the inorganic supports for polyolefin catalysts, polymers are also important because there are so many functional groups that can be easily selected in the polymer chains, and they produce fewer residues in the final product compared to the inorganic support. Recently, a number of polymer materials, such as non-interacting polystyrene blends^[1], Psalm^[2, 3], PS4VPy^[4], poly(ethylene-*co*-acrylic acid)^[5], cyclodextrin (CD)^[6, 7], commercial 2% cross-linked poly(4-vinylpyridine)^[8], even modified PP^[9, 10] and EPDM^[11], *etc.*, were applied as supports for polyolefin catalysts, and all these polymer supports should be modified or include some function groups, such as amine, hydroxyl, pyridine, *etc.*, to prevent leaching of the cationic catalysts from the support^[1–11].

Herein we have prepared a supported metallocene catalyst by using polyethylene-*graft*-poly(4-vinylpyridine) (PEVP) as a new polymer support through the irradiation method. After being treated by methylaluminoxane (MAO), the Cp_2ZrCl_2 catalyst could be easily immobilized on the support, and the percentages of grafting 4-vinylpyridine and supported Cp_2ZrCl_2 depend on the size of polyethylene (PE) powder. The application of this supported catalyst to ethylene polymerization was investigated in the presence of MAO co-catalyst.

EXPERIMENT PARTS

Materials

MAO in toluene (10 wt%) used in this study was purchased from the Albemarle Co. (USA). The polymerization

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grade ethylene produced by Beijing Yanshan Petrochemical Co. (China), was used as monomer without further purification. Toluene and hexane were dried with 4 Å molecular sieves and then refluxed over Na/K alloy in the presence of benzophenone. High-density polyethylene (HDPE) powder was obtained from the Second Additive Factory in Beijing as Z-I type. 4-Vinylpyridine, A.R. grade, Aldrich Co., was distilled before used in the presence of CaH_2 . Cp_2ZrCl_2 , A.R. grade, was purchased from Aldrich Co..

Characterization

The X-ray photoelectron spectra (XPS) were measured on an ESCALab220i-XL spectrometer using a monochromatic Al $K\alpha$ X-ray radiation (1486.6 eV) with the source operated at 15 kV and 20 mA. Binding energy (BE) values in all the figures were corrected for eventual surface charging and the peak positions were corrected by referring to the contaminated C_{1s} peak after setting its BE to 284.6 eV. A symmetrical Gaussian-Lorentzian sum function was used to fit peaks of the C_{1s} region as well as the N_{1s} and Zr_{3d5} peaks. The chemical composition of supported catalyst was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Plasma-Spec (I) of the American Leeman Lab. The Fourier transform infrared spectra of the samples were recorded on a Perkin-Elmer system 2000 FTIR spectrometer. Differential scanning calorimeter (DSC) was carried out using a Perkin-Elmer 7 Series Thermal Analysis System in nitrogen atmosphere with the heating rate of 10 K/min in the range of 30–180°C. A well-defined procedure was used for comparing the data of DSC as following: the first scanning run of sample was from 30°C to 180°C; the sample was then quickly quenched to 30°C (at a rate of 200 K/min) and the second scanning run to 180°C followed. The data measured in the second scanning run were collected. Molecular weight (M_w) and polydispersity index of produced polyethylene were determined with a Waters Alliance GPCV 2000 system at 135°C in 1,2,4-trichlorobenzene, and the data were analyzed using a polystyrene calibration curve. The Carlo Erba 1106 Element analysis instrument was used to analyze the grafting of 4-vinylpyridine on the PE powder. A Shimadzu UV-2501PC was used to record the ultraviolet-visible spectra of the samples. The morphology of the polymer powder surface was observed with a JEOL JAX-840 scanning electron microscope after being coated with gold by sputtering.

Radiation Grafting Reaction

The PE powder grafting 4-vinylpyridine copolymer was prepared by irradiation with $\text{Co } \gamma^{60}$ rays (Department Technical Physics, Peking University) in N_2 according to a reported method^[12]. PE powders were graded and dried in vacuum at 60°C prior to use. Appropriate amounts of PE powder, hexene, and 4-vinylpyridine were added in a Schlenk tube and degassed by freeze thawing three times under vacuum. The reactants were then sealed under N_2 by finally releasing the vacuum. The total dose was 2 Mrad at rate of 300 krad/h. After irradiation, the powder was filtered off immediately to minimize post-irradiation effects then Soxhlet extracted with hexane/chloroform (1/3, *V/V*) for 24 h, and with methanol for 24 h to remove unreacted monomer and homopolymer. After extraction, PEVP was dried in vacuum for 12 h. The resulting PEVP was determined by XPS (Table 1).

Preparation of PEVP Supported-Catalysts

All following operations were carried out in a dry nitrogen atmosphere. 15 mL MAO was added into the reaction apparatus containing 60 mL toluene and the PEVP for pre-treatment. The resulting PEVP/MAO support was collected by filtration and washed several times with toluene and an appropriate amount of Cp_2ZrCl_2 was then added into the reactor. After stirring for 12 h at 60°C, the resulting catalyst was collected by filtration and washed with toluene several times, dried in vacuum to yield the light yellow PEVP supported catalyst. Both PEVP/MAO support and resulting supported catalyst were investigated by XPS, and their nitrogen contents were measured (Table 2).

Polymerization of Ethylene

Ethylene polymerization was carried out in a 200 mL Schlenck-type glass reactor equipped with a stirrer bar. After carefully heating and evacuating air and moisture from the reactor for about 30 min, ethylene, 50 mL toluene and MAO were passed into the reactor sequentially. Polymerization started when the appropriate amount

amount of the suspension of PEVP supported catalyst was introduced. After the polymerization reaction had proceeded for a certain time, an acidic ethanol solution (5 wt%) was quickly injected to terminate it. The precipitated polymer was collected and washed with ethanol several times and dried under vacuum at 60°C for 24 h. The catalytic activities are listed in Table 2.

Table 1. The XPS results of PEVP, PEVP/MAO and PEVP/MAO/Cp₂ZrCl₂

	PEVP (eV)	PEVP/MAO (eV)	PEVP/MAO/Cp ₂ ZrCl ₂ (eV)	Cp ₂ ZrCl ₂ (eV)
N 1s	398.90	399.40	400.40	
C 1s	284.60	284.60	284.60	284.60
Zr 3d ₅			182.70	181.75
Al 2p		73.90	74.10	

Table 2. The component of the PEVP supported catalyst and their activities

Entry No	Mesh of PE powder	N ^a (wt%)	Loading Al ^b (wt%)	Loading Zr ^b (wt%)	Activity ^c (10 ⁻⁵ g PE/mol • Zr • h)
Cat1	> 40	0.75	2.66	1.05	0.97
Cat2	40–80	0.80	6.14	2.59	1.39
Cat3	80–120	1.22	9.66	2.70	2.42
Cat4	120–140	1.34	4.30	4.18	5.67

^a Measured by element analysis; ^b Measured by ICP-AES;

^c Polymerization conditions: Al/Zr (mol/mol) = 500, *T* = 25°C, 50 mL toluene, 30 min, 0.1 MPa

RESULTS AND DISCUSSION

UV and FTIR Results of Supported Catalyst

In order to further understand the supporting behavior of metallocene and PEVP/MAO, the FTIR spectrum of supported catalyst was recorded and compared with those of PEVP/MAO and parent PEVP (Fig. 1). In the fingerprint region, the FTIR spectrum of PEVP (line a) displays the deformation vibrations of C–H bonds at 1219 and 719 cm⁻¹, and the C–H twisting vibration at 818 cm⁻¹. In the higher frequency region, there appear three peaks at 1596, 1557 and 1415 cm⁻¹ assigned to the stretching vibrations of C–C and C–N bonds. These phenomena indicate that the 4-vinylpyridine groups are grafted onto the PE chain. Upon treatment with MAO, a new broad peak appears at 721 cm⁻¹ of the spectrum of PEVP/MAO (Fig. 1 line b). This may be assigned to the Al–N vibration, which generally locates at the range of 400–1500 cm⁻¹ and appears as a broad band attributed to the complicated electronic environment decreasing the combination ability of Al–N bond^[13]. Additionally, a new peak assigned to the stretching vibration of C–N–Al bond^[14] appears at 1619 cm⁻¹, along with the significant decrease of original intensity of absorption peaks at 818 and 1415 cm⁻¹. These indicate that the

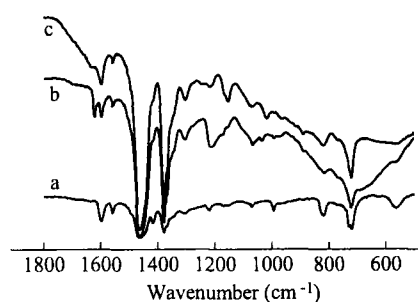


Fig. 1 FTIR spectra of PEVP (a), PEVP/MAO (b) and PEVP/MAO/Cp₂ZrCl₂ (c)

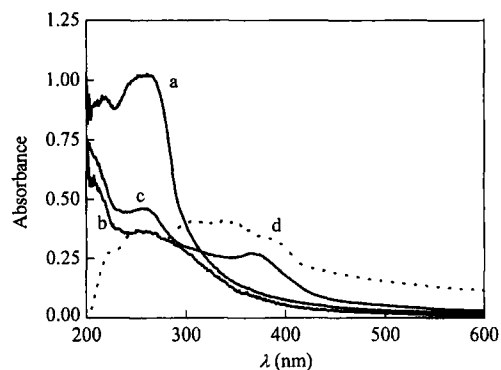
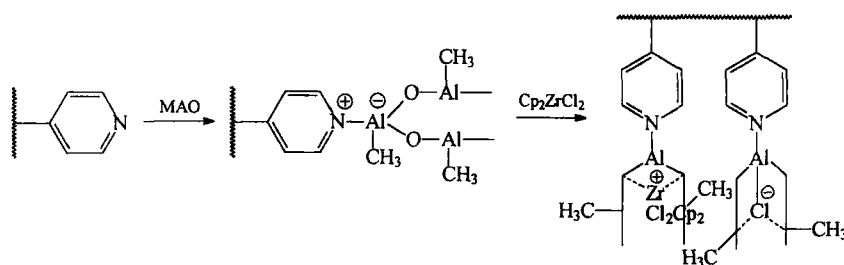


Fig. 2 Ultraviolet and visible spectra of PEVP (a), PEVP/MAO (b) and PEVP/MAO/Cp₂ZrCl₂ (c), Cp₂ZrCl₂ (d)

MAO units are bound to PEVP through association with the pyridine group. In the line c of Fig. 1, the C—N—Al stretching vibration band at 1619 cm^{-1} becomes broader, along with the appearance of a new peak at 1155 cm^{-1} assigned to the C—C vibration of Cp_2ZrCl_2 group. Apart from the FTIR experiment, UV investigation also gives structural information about the supported catalyst. As seen in Fig. 2, PEVP displays a characteristic peak at 261.5 nm assigned to the pyridine chromophore. Ontreatment with MAO, this peak becomes broader, along with a slightly bathochromic shift (1 nm) and a decrease of a absorption intensity, which indicates interactions, such as the electron transfer, between pyridine group on the PEVP chain and associated MAO. Upon supporting the metallocene, the absorption intensity of relevant the peak at 260 nm is obviously enhanced accordingly. Additionally, a new peak assigned to the Cp_2ZrCl_2 appears at 365.5 nm. Further evidence comes from the XPS results, as listed in Table 1; the N_{1s} binding energy of PEVP is enhanced by 0.5 eV upon treated with MAO. In addition, on subsequent support of Cp_2ZrCl_2 , this value is further enhanced by 1.0 eV as compared with PEVP/MAO. These phenomena, accompanying the FTIR and UV data, jointly indicate the formation of the Cp_2ZrCl_2 supported catalyst. Moreover, the $\text{Zr}_{3d/5}$ binding energy of supported catalyst is 0.95 eV higher than that of parent Cp_2ZrCl_2 , which indicates the Zr in the supported catalyst as cation to be the active site in the ethylene polymerization^[4].



Scheme 1. Supporting reaction of Cp_2ZrCl_2 catalyst on the PEVP carrier

Effect of Particle Size of PE Powder

The grafting results affected by the size of PE are listed in Table 2. With decreasing grain size of the PE powder, the grafted 4-vinylpyridine content on the PE powder increased. Accordingly it should be easily noted that the zirconium content of the anchored catalyst is strongly dependent on the grain size of the PE powder, because the smaller PE powder particle could provide much more surface area under the same irradiation conditions. Therefore the smaller particle particles could contact more 4-vinylpyridine monomers. As a result, the more monomer could be grafted on the PE powder, the more Zr catalyst (active sites) could be supported on the PE powder. The ethylene polymerization results also coincided with the sequences, the activities of the Zr supported catalysts increased from 0.97 to $5.67 \times 10^5\text{ g PE/molZr} \cdot \text{h}$. However, all of them were still lower than that of the parent Cp_2ZrCl_2 catalyst. The ethylene polymerization results are listed in Table 3 along with the measurements of the corresponding PEs.

Table 3. The ethylene polymerization results and properties of resulting PEs

Entry no.	Activity ($10^{-5}\text{ gPE/molZr} \cdot \text{h}$)	M_n	M_w	M_w/M_n	T_m ($^{\circ}\text{C}$)	α_c^a (%)
Cat1	0.97	66400	255800	3.85	133.2	51.2
Cat2	1.39	94000	350700	3.73	134.6	47.3
Cat3	2.42	129800	461600	3.56	135.6	53.4
Cat4	5.67	134100	575700	4.29	136.5	51.4
Cp_2ZrCl_2	10.32	65400	158300	2.42	133.8	54.2

Polymerization conditions: $\text{Al/Zr (mol/mol)} = 500$, $T = 25^{\circ}\text{C}$, 50 mL toluene, 30 min, 0.1 MPa

^a Crystallinity: $\alpha_c = \Delta H_f / \Delta H_{f\alpha} \times 100\%$, $\Delta H_{f\alpha} = 269.9\text{ J/g}^{[15]}$

Polymerization Behaviors of PE Supported Cp_2ZrCl_2

The effect of the MAO amount on the PEVP supported catalyst activity and M_w of PE was examined with Cat4, the data are given in Table 4. As shown in Table 4, on increasing the Al/Zr ratio, the activities increased from 0.31 to 11.6×10^5 gPE/molZr $\cdot$ h. With the same Al/Zr ratio, the activities increased along with increasing reaction temperature, and the proper polymerization temperature was between 40 and 60 $^\circ\text{C}$. However, the molecular weight decreased with increasing reaction temperature.

Table 4. Ethylene polymerization promoted by Cat4

Al/M (mol/mol)	T ($^\circ\text{C}$)	Activity (10^{-5} gPE/molZr $\cdot$ h)	M_w ($\times 10^5$)	M_w/M_n	T_m ($^\circ\text{C}$)	α_c (%)
50	20	0.31	3.57	3.23	133.8	58.9
100	20	0.45	4.18	3.65	134.4	54.6
300	20	1.56	4.87	4.76	134.5	49.3
500	20	5.67	5.76	4.29	136.5	51.4
1500	20	11.62	9.52	3.78	134.5	48.2
500	0	1.34	15.40	3.90	132.4	45.2
500	40	6.42	5.74	3.72	133.5	47.8
500	60	10.83	0.88	4.53	133.6	46.8
500	80	5.32	0.49	3.47	134.7	51.2

Polymerization conditions: 50 mL toluene, 30 min, 0.1 MPa

Observation of the particle morphology by SEM confirmed that the morphology of supported Cp_2ZrCl_2 catalyst is maintained by the polyethylene particle (Fig. 3). There is a smooth surface on the pure PEVP particle (Fig. 3a). After treatment with MAO, the surface of the PEVP particle became loose and rough (Fig. 3b), which meant that the MAO had anchored on the surface of PEVP particle through the reaction of pyridine group with MAO. After the Cp_2ZrCl_2 was supported (Fig. 3c), the surface of the particle grew rougher, which showed that the Cp_2ZrCl_2 had been supported on the PE particle through the MAO, according to the literature about Cp_2ZrCl_2 supported on the PS4VPy copolymer^[4]. The morphology of the polyethylene produced (Fig. 3d) is similar to that of the PE powder, which means that the polymer had a good replicable morphology for the PE particle supported catalyst.

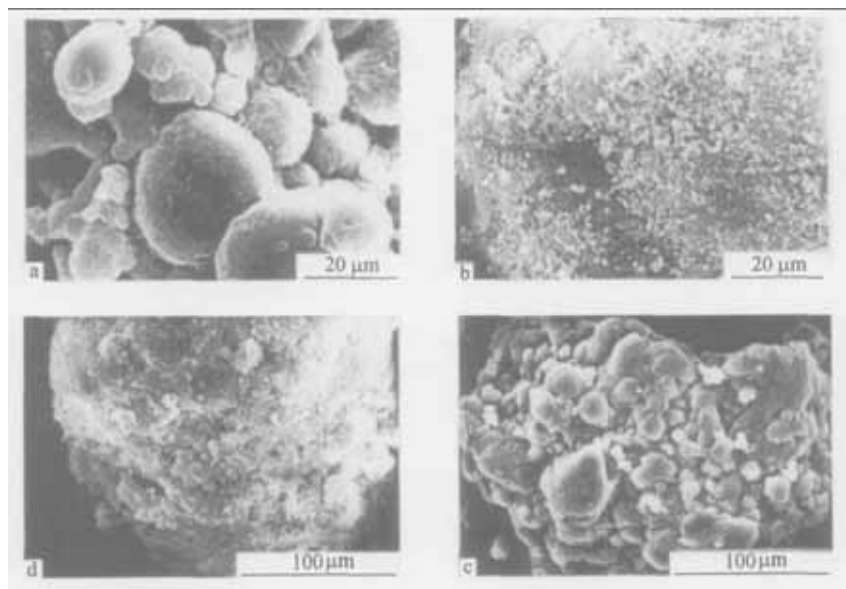


Fig. 3 SEM of PEVP (a), PEVP/MAO (b), PEVP/MAO/ Cp_2ZrCl_2 (c), Polyethylene (d) catalyzed by Cat4 at Al/Zr = 500, 20 $^\circ\text{C}$, 1 h, 50 mL toluene

CONCLUSIONS

Different mesh powders of polyethylene-*graft*-poly(4-vinylpyridine) have been prepared by the irradiation method. After treatment with cocatalyst MAO, the copolymers were used as supports for Cp_2ZrCl_2 catalysts. XPS, FTIR, UV and SEM measurements were used to trace the supporting process; the results showed that the catalytic sites have been linked through MAO on the PEVP carrier. The percentages of grafting of 4-vinylpyridine and supported Cp_2ZrCl_2 depend on the grain size of the polyethylene powder. The smaller the polyethylene powder, the more the 4-vinylpyridine groups and Cp_2ZrCl_2 existed. The PEVP-supported catalyst showed good activities for ethylene polymerization.

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