

Copolymers of Ethylene and Vinyl Amino Acidic Ester with High Molecular Weight Prepared by Non-metallocene Catalysts

Jing $Wang^1 \cdot Feng Nan^1 \cdot Jiangping Guo^1 \cdot Jian Wang^2 \cdot Xianghui Shi^1 \cdot Haibing Huang^1 \cdot Qigu Huang^1 \cdot Wantai Yang^1$

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Abstract Non-metallocene catalysts containing [N, Si, N, P]-type ligands based on diphenyl phosphorus-phenylamine and their derivatives were synthesized and characterized by H(¹³C) NMR, ESI–MS and micro analysis. They were able to catalyze copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester after activated by methylaluminoxane (MAO). Effects of transition metal atoms (Ti, Zr and Hf), ligand structures and polymerization conditions were investigated. The structures and properties of the obtained polymers were characterized by FT-IR, ¹³C NMR, GPC and DSC. The results indicated that the obtained copolymers had high weight average molecular weight of 2.70×10^5 g/mol and high comonomer incorporation rate of 23.07 wt% within the copolymer chain. The melting temperature of the copolymer was up to 138.6 °C higher than that of the polyethylene.

Qigu Huang huangqg@mail.buct.edu.cn

- ¹ State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, The College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing 100029, China
- ² Liaoyang Petrochemical Corporation, China National Petroleum Corporation, Liaoyang 111003, China

Graphical Abstract



Keywords Non-metallocene catalysts · N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester · Copolymer

1 Introduction

Polyolefins, such as polyethylene and polypropylene, are the most widely used polymers in a broad range of commercial applications. In recent decades, considerable attention has been paid to synthesis of new polyolefins with high performance or functionality. Ziegler–Natta catalysts can catalyze the polymerization of olefins efficiently. However, coordination copolymerization of ethylene with polar comonomers can not be realized by using Ziegler– Natta catalyst system because the active site is easy to be poisoned by electron-donating atoms from the polar comonomers, such as N, O, S, P, etc [1–7]. Metallocene catalysts can catalyze polymerization of limited polar monomers, but the catalytic activity decreases dramatically [8]. So far, copolymers of ethylene with polar monomers mainly have been prepared by conventional radical process, which needs harsh technology with high pressure and high temperature [9]. Non-metallocene catalysts can catalyze copolymerization of olefins with polar comonomers containing N, O, S and other heteroatoms because this kind of catalyst possesses broad "tolerance" to the electrondonating atoms, so design of non-metallocene catalysts has attracted much attention. Marks [10] adopted CGCTiMe₂/ $Ph_3CB^+(C_6F_5)_4^-$ to catalyze the copolymerization of ethylene with 5-hexenylsilane, functional group was introduced to the copolymer. The results showed that 5-hexenylsilane readily underwent insertion into the polymer chain as well as effects intramolecular chain termination. Palladium complexes with bulky substituted α -diimine ligands can catalyze the copolymerization of ethylene and α -olefins with methyl acrylate to give high-molar-mass polymers [11]. Mecking et al. [12] prepared copolymer of ethylene with acrylamide by employing palladium complexes as catalyst precursor. They also demonstrated that copolymerization of ethylene with acrylic acid was successful by using neutral palladium (II) phosphine-sulfonato catalysts. [13] Titanium complexes bearing phenoxy-phosphine or thiphenoxy-phosphine ligands promoted copolymerization of ethylene with methyl 10-undecenoate efficiently. [14] In 2007, Nozaki et al. [15] synthesized linear copolymers of ethylene with acrylonitrile by isolated phosphine-sulfonate methyl palladium complex. It was observed that acrylonitrile units were inserted into not only at the terminating end of the copolymer chain but also in the backbone. In the following years, Nozaki et al. prepared copolymers of ethylene with various polar monomers such as allyl monomers [16], vinyl acetate [17] etc. by palladium/ phosphine-sulfonate catalyst. Furthermore, they utilized palladium/alkylphosphine-sulfonate catalyst to synthesize copolymers of ethylene with polar monomers featured with higher weight average molecular weight of $1.77 \times$ 10^5 g/mol by tuning the substitunent groups of phosphorus atom consisting of the ligand [18].

Before the report, the copolymers of ethylene with polar monomers have low weight average molecular weight about 1.0×10^4 g/mol. Guan et al. [19] and Ye et al. [20] adopted Pd-diimine catalysts to catalyze the copolymerization of ethylene and acrylic monomers, comonomer insertion rate was 2.0 and 3.6 mol%, respectively. Nevertheless, the catalytic activities were relatively low, about 1.6×10^2 g/(molPd.h) and 9.2×10^2 g/(molPd.h), respectively. Pugh et al. [21] investigated that [P, O]-type palladium complexes catalyzed copolymerization of ethylene with acrylic ester and the comonomer incorporation rate was up to 10 mol% in the copolymer. In our previous work, non-metallocene catalysts with [N, N, O] [22], [N, N, N] [23] and [N, N, O, O] [24, 25] ligands were synthesized and carried out for polymerization of ethylene and copolymerization of ethylene with α -olefins or polar monomer such as acrylonitrile. In generally, dimer, trimer, or oligomer of amino acid can be synthesized by condensation polymerization. Many polymerization techniques, such as ringopening metathesis polymerization (ROMP), acyclic diene metathesis (ADMET) and atom transfer radical polymerizations (ATRP) are not efficient for copolymerization of ethylene with polar monomers. Kim et al. [26] recently reported that polyethylene drug delivery nanocapsules consisting of polyethylene and poly(ethylene glycol)₁₀₆*b*-poly(propylene glycol)₇₀-*b*-poly(ethylene glycol)106 copolymer was obtained by self-assembled to capsule paclitaxel. Polyamino esters are a promising alternative for clinical applications used as polymeric vectors for gene delivery, as they are generally safer than viral counterparts. [27] The copolymers with bioactive groups have been taken much attraction due to their outstanding potential applications in pharmacological and biological fields used as inviral vectors [28, 29].

Herein, we reported that the copolymers of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester prepared by non-metallocene catalysts with [N, Si, N, P]type ligands based on diphenyl phosphorus-phenylamine and their derivatives. The copolymers with pendent bioactive groups should have new properties due to hydrophilic side chain being compatibilic with tissues and hydrophobic backbone being compatibilic with many hydrophobic drugs.

2 Experimental

2.1 General Remarks

Aniline (99.8 %), N-acetyl-L-tyrosine ethyl ester (99 %) and 6-bromo-1-hexene (97 %) were purchased from J&K in Beijing, China. 2,4,6-trimethylaniline (99 %), dichlorodimethylsilane (99.8 %),diphenyldichlorosilane (97 %), 2,4,6-trifluoroaniline (97 %), methylmagnesium chloride (CH₃MgCl) with 22 wt% in THF and MAO with 10 wt% in toluene were purchased from Acros Organics Agent in Shanghai, China. Chlorodiphenylphosphine (99 %)was purchased from Strem Chemicals in Beijing, China. Toluene, n-hexane, acetone and diethyl ether were from Beijing Chemicals Company in Beijing, China. Toluene and n-hexane were further purified by refluxing over sodium under normal pressure for 48 h prior to use. Acetone and diethyl ether were dried over activated Davison 5 Å molecular sieves prior to use.

2.2 Characterization

¹H NMR spectra were recorded on a Varian INOVA 600 MHz spectrometer in deuterated chloroform (CDCl₃) solution at 25 °C and tetramethylsilane (TMS) was used as reference. Elemental analyses were performed on a Perkin Elmer 2400 microanalyzer, using combustion method with quantitative oxygen with thermal conductivity detector. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 5DXC FT-IR spectrograph. The spectra were obtained at 40 cm⁻¹ resolution, and average data were obtained from at least 32 scans in the standard wavenumber range from 500 to 4000 cm⁻¹. Mass spectrum was recorded by Esquire-LC mass spectroscopy, acetone as dissolvent. ¹³C NMR spectra were obtained on a Varian INOVA 500 MHz (125 MHz for ¹³C NMR) instrument. The conditions used for quantitative ¹³C NMR were a copolymer content up to 15 wt% in solution, using ortho-dichlorobezene (d_4) as the solvent at 125 °C, tetramethylsilane (TMS) as internal reference. The molecular weight and molecular weight distribution (MWD) were measured with a PL-GPC 200 instrument, using standard polyethylene (PE) as reference and 1,2,4-trichlorobenzene as solvent at 150 °C. DSC thermograms were recorded with a PA5000-DSC instrument at a rate of 10 K min⁻¹.

2.3 Polymerization Procedure

All polymerization manipulations were carried out in a flamed 300 mL Schlenk-type glassware on a dual-manifold Schlenk line. Freshly distilled toluene (80 mL), the desired amount of catalysts (Cat.1-Cat.9) and MAO were introduced into the glassware. The mixture was stirred for 15 min for preactivation. A desired amount of N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester dissolved in toluene was treated by an equivalent of AlEt₃ for the desired time before it was injected into the Schlenk flask. Pressure of ethylene in feed was 0.2 MPa and the reactor was rapidly heated to the desired temperature. The polymerization maintained for 10 min. The reaction was terminated with 10 wt% HCl in alcohol. The obtained product was filtered, washed, dried to constant weight in a vacuum oven at 80 °C, then weighted and the catalytic activity was calculated.

2.4 Synthesis of N-acetyl-O-(hex-5-enyl)-L-tyrosine Ethyl Ester

N-acetyl-L-tyrosine ethyl ester (5 g, 18.6 mmol) in acetone (80 mL), K_2CO_3 (3.7 g, 26.8 mmol) and 6-bromo-1-hexene (2.5 mL, 18.6 mmol) were added to Schlenk-type glassware in order. The mixture was stirred at reflux for 2 days. Then the solvent was removed in vacuo, and the remaining viscous oil was dissolved in a mixture of aqueous 5 % NaOH/Et₂O (200 mL). The organic layer was collected, dried with MgSO₄ and concentrated. The resultant viscous oil was washed with 200 mL of hexane, 50 mL at a time, and purified by vacuum. Yellow liquid was obtained with yield of 31 %. ¹H NMR(600 MHz, CDCl₃): δ 6.99 (d, 2H, benzene), δ 6.81 (d, 2H, benzene), δ 5.90 (m,1H, CH=CH₂), δ 5.83 (d, 1H, NH-CH), δ 4.97-5.00 (d, 2H, -CH₂-CH=CH₂), δ 4.82 (q, 1H, CH-NH), δ 4.18 (q, 2H, CH₂-CH₃), δ 3.93 (t, 2H, CH₂-O), δ 3.06 (d, 2H, CH₂=CH), δ 2.12 (m, 2H, CH₂-CH), δ 1.99 (s, 3H, CH₃-C), δ 1.8 (m, 2H, CH₂-CH₂), δ 1.6 (m, 2H, CH₂-CH₂), δ 1.3 (t, 3H, CH₃-CH₂); FT-IR (cm⁻¹, KBr): 3365 (N-H), 1722 (C=O), 1657 (C-N), 1513 (N-H). Anal. Calc.(%) for C₁₉H₂₇NO₄ (333.42 g/mol): C, 68.47; H, 8.11; N, 4.20. Found: C, 68.56; H, 8.03; N, 4.25. ESI-MS m/z calculated for $[M+H]^+$. $C_{19}H_{28}NO_4$: 334.42 found 334.31.

2.5 Synthesis of Catalyst Precursors

Aniline (1.5 mL, 16.2 mmol) was treated with an equiv. of CH₃MgCl for 3 h in toluene (80 mL), then chlorodiphenylphosphine (3 mL, 16.2 mmol) was injected with a syringe. The mixture was stirred for 5 h at room temperature. Subsequently, the solvent was removed in vacuo and the residual was dissolved by hexane (50 mL). The solution was concentrated and put in a refrigerator at -10 °C. White crystal with a yield of 70.2 % was obtained. 2, 4, 6-trifluoroaniline was treated with an equiv. of CH₃MgCl for 3 h in toluene, then dichlorodimethylsilane (2 mL, 16.2 mmol) was injected. The mixture was stirred for 5 h at room temperature. Subsequently, the solvent was removed in vacuo and the residual was dissolved by hexane. The solvent was removed in vacuo. Light yellow liquid with a yield of 83.0 % was obtained. Diphenylphosphone-aniline (3.15 g, 11.4 mmol) was treated with an equiv. of CH₃MgCl for 3 h in toluene, then (2.72 g, 11.4 mmol) chlorodimethyisilane-(2, 4, 6-trifluoroaniline) was added. The mixture was stirred for 5 h at room temperature. Subsequently, the solvent was removed in vacuo and the residual was dissolved in hexane. The solution was concentrated and put in a refrigerator at -10 °C. White crystal (Ligand 1 (L1)) was obtained (1.03 g, 18.8 %; Scheme 1). L1 ($C_{26}H_{24}N_2SiPF_3$, Fw = 480): ¹H NMR (DMSO-d₆), δ 0.14 (s, 6H, methyl), δ 4.0 (s, 1H, N-H), δ 6.20 (s, 2H, benzene), δ 6.46-7.01 (m, 5H, benzene); δ 7.22–7.46 (m, 10H, benzene). Element analysis calculated (%): C, 64.98; H, 5.00; N, 5.83; found: C, 65.06; H, 4.98; N, 5.80. FT-IR (cm⁻¹, KBr): 3274 (N-H). ESI-MS m/z calculated for $[M+H]^+$. $C_{26}H_{25}N_2SiPF_3$: 481.02 found 481.12 Scheme 1).



 $R = F, CH_3, H; M = Ti, Zr, Hf$

Scheme 1 Synthesis of the non-metallocene catalysts

The ligand **2** (L**2**) derived from 2, 4, 6-trimethylaniline and the ligand **3** (L**3**) from aniline. L**2** ($C_{29}H_{33}N_2SiP$, Fw = 468): ¹H NMR (DMSO-d₆), δ 0.15 (s, 6H, methyl), δ 2.36 (s, 9H, methyl on benzene), δ 4.3 (s, 1H, N–H), δ 6.36 (s, 2H, benzene), δ 6.43–7.12 (m, 5H, benzene); δ 7.12-7.43 (m, 10H, benzene). Element analysis calculated (%): C, 64.98; H, 5.00; N, 5.83; found: C, 65.07; H, 4.92; N, 5.88. FT-IR (cm⁻¹, KBr): 3289 (N–H). ESI–MS m/z calculated for [M + H]⁺. C₂₉H₃₄N₂SiP: 469.56 found 469.42.

L3 (C₂₆H₂₇N₂SiP, Fw = 426): ¹H NMR (DMSO-d₆), δ 0.14 (s, 6H, methyl), δ 4.2 (s, 1H, N–H), δ 6.42-7.00 (m, 10H, benzene); δ 7.28–7.61 (m, 10H, benzene). Element analysis calculated (%): C, 64.98; H, 5.00; N, 5.83; found: C, 65.01; H, 4.98; N, 5.85. FT-IR (cm⁻¹, KBr): 3305

(N–H). ESI–MS m/z calculated for $[M + Na]^+$. C₂₆H₂₇ N₂SiPNa: 449.32 found 449.25.

L1 Ti complex (Cat.1) was prepared by the treatment of L1 (0.48 g, 1.0 mmol) with TiCl₄ (0.11 mL, 1.0 mmol) adding by syringe into toluene 50 mL at 0 °C. The reaction was lasted for 6 h at 40 °C. The mixture was filtered. After washing for four times and then drying, a light brown powder (Cat.1) was obtained (0.63 g, 85.1 %; Scheme 1) and further characterized. Cat.1 was confirmed by ¹H (¹³C, ²⁹Si, ³¹P, ¹⁹F) NMR, MS and elemental microanalysis. Cat.1 (C₂₆H₂₃N₂SiPF₃TiCl₃, Fw = 634): ¹H NMR (DMSO-d₆): δ 0.16 (s, 6H, methyl), δ 6.23 (s, 2H, benzene), δ 6.46-7.04 (m, 5H, benzene), δ 7.22-7.42 (m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 98.9 (Ar–C), δ 113.6 (C–N), δ 115.1 (Ar–C),



Scheme 2 Copolymerization of ethylene and N-acetyl-O-(hex-5enyl)-L-tyrosine ethyl ester

δ 118.6 (Ar–C), δ 129.5 (Ar–C), δ 130.1 (Ar–C), δ 149.1 (C-F), δ 153.8 (C–F). ¹⁹F NMR (DMSO-d₆): δ –122.20, –129.01. ³¹P NMR (DMSO-d₆): δ 42.86. ²⁹Si NMR (DMSO-d₆): δ –10.20. Element analysis calculated (%): C 49.21, H 3.63, N 4.42; found C 49.19, H 3.61, N 4.45. ESI–MS m/z calculated for [M+H]⁺.C₂₆H₂₄N₂SiPF₃TiCl₃: 635.82 found 635.77.

Cat.**2-9** were synthesized and confirmed according to the method mentioned above. L**1** Zr complex (Cat.**2**) (C₂₆H₂₃ N₂SiPF₃ZrCl₃, Fw = 677): ¹H NMR (DMSO-d₆): δ 0.15 (s, 6H, methyl), δ 6.21 (s, 2H, benzene), δ 6.46-7.02 (m, 5H, benzene), δ 7.22–7.38 (m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 98.7 (Ar–C), δ 113.5 (C–N), δ 115.2 (Ar–C), δ 118.7 (Ar–C), δ 129.5 (Ar–C), δ 130.0 (Ar–C), δ 149.2 (C–F), δ 153.6 (C–F). ¹⁹F NMR (DMSO-d₆): δ –122.32, –129.43. ³¹P NMR (DMSO-d₆): δ 43.03. ²⁹Si NMR (DMSO-d₆): δ –10.32. Element analysis calculated (%): C 48.83, H 3.60, N 4.38; found C 48.81, H 3.64, N 3.57. ESI–MS m/z calculated for [M+H]⁺. C₂₆H₂₃N₂SiPF₃ZrCl₃: 678.39 found 678.31.

L1 Hf complex (Cat.3) ($C_{26}H_{23}N_2SiPF_3ZrCl_3$, Fw = 677): ¹H NMR (DMSO-d₆): δ 0.15 (s, 6H, methyl), δ 6.25 (s, 2H, benzene), δ 6.46–7.03 (m, 5H, benzene), δ 7.22–7.41 (m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 98.8 (Ar–C), δ 113.2 (C– N), δ 115.0 (Ar–C), δ 118.9 (Ar–C), δ 129.2 (Ar–C), δ 130.3 (Ar–C), δ 149.3 (C–F), δ 153.7 (C–F). ¹⁹F NMR (DMSO-d₆): δ –122.24, –129.32. ³¹P NMR (DMSO-d₆): δ 42.98. ²⁹Si NMR (DMSO-d₆): δ –10.41. Element analysis calculated (%): C 50.24, H 3.70, N 4.51; found C 50.27, H 3.72, N 4.48. ESI–MS m/z calculated for $[M+Na]^+$. C₂₆₋H₂₃N₂SiPF₃HfCl₃Na: 787.64 found 787.59.

L2 Ti complex (Cat.4) ($C_{29}H_{32}N_2SiPTiCl_3$, Fw = 622): ¹H NMR (DMSO-d₆): δ 0.15 (s, 6H, methyl), δ 2.36(s, 9H, methyl on benzene), δ 6.38 (s, 1H, benzene), δ 6.46–7.02 (m,7H, benzene), δ 7.22–7.41(m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 12.8 (C(CH₃)), δ 21.6 (C(CH₃)), δ 25.8 (C(CH₃)), δ 115.1 (Ar– C), δ 118.5 (Ar–C), δ 121.5 (C(CH₃)), δ 125.8 (C(CH₃))), δ 127.8 (Ar–C), δ 129.5 (Ar–C), δ 130.1 (Ar–C), δ 141.8 (C– N), δ 146.6 (C–N). ¹⁹P NMR (DMSO-d₆): δ 49.98. ²⁹Si NMR (DMSO-d₆): δ -9.82. Element analysis calculated (%): C 55.35, H 4.94, N 4.61; found C 55.39, H 4.91, N 4.63. ESI–MS m/z calculated for [M+Na]⁺. C₂₉H₃₂N₂ SiPTiCl₃Na: 645.43 found 645.38.

L2 Zr complex (Cat.5) (C₂₉H₃₂N₂SiPZrCl₃, Fw = 665): ¹H NMR (DMSO-d₆): δ 0.15 (s, 6H, methyl), δ 2.35 (s, 9H, methyl on benzene), δ 6.38 (s, 1H, benzene), δ 6.43-7.02 (m, 7H, benzene), δ 7.22–7.37(m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 12.7 (C(CH₃)), δ 21.3 (C(CH₃)), δ 25.9 (C(CH₃)), δ 115.2 (Ar–C), δ 118.7 (Ar–C), δ 121.6 (C(CH₃)), δ 125.3 (C(CH₃)), δ 127.6 (Ar–C), δ 129.3 (Ar–C), δ 129.9 (Ar–C), δ 141.6 (C–N), δ 146.3 (C–N). ¹⁹P NMR (DMSO-d₆): δ 49.45. ²⁹Si NMR (DMSO-d₆): δ -9.67. Element analysis calculated (%): C 54.90, H 4.90, N 4.58; found C 54.87, H 4.89, N 4.61. ESI–MS m/z calculated for [M+H]⁺. C₂₉ H₃₂N₂SiPZrCl₃: 666.57 found 666.58.

L2 Hf complex (Cat.6) ($C_{29}H_{32}N_2SiPHfCl_3$, Fw = 752): ¹H NMR (DMSO-d₆): δ 0.14 (s, 6H, methyl), δ 2.35 (s, 9H, methyl on benzene), δ 6.38 (s, 1H, benzene), δ 6.46-7.02 (m, 7H, benzene), δ 7.22–7.37 (m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 12.9 (C(CH₃)), δ 21.5 (C(CH₃)), δ 25.7 (C(CH₃)), δ 114.8 (Ar–C), δ 118.6 (Ar–C), δ 121.7 (C(CH₃)), δ 125.6 (C(CH₃)), δ 127.5 (Ar–C), δ 129.6 (Ar–C), δ 130.3 (Ar–C), δ 141.7 (C–N), δ 146.9 (C–N). ¹⁹P NMR (DMSO-d₆): δ 49.72. ²⁹Si NMR (DMSO-d₆): δ -9.51. Element analysis calculated (%): C 56.57, H 5.05, N 4.71; found C 56.56, H 5.03, N 4.75. ESI– MS m/z calculated for [M+H]⁺. C₂₉H₃₃N₂SiPHfCl₃: 753.25 found 753.21.

L3 Ti complex (Cat.7) ($C_{26}H_{26}N_2SiPTiCl_3$, Fw = 580): ¹H NMR (DMSO-d₆): δ 0.15 (s, 6H, methyl), δ 6.41–7.02 (m, 10H, benzene), δ 7.22–7.53(m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 112.4 (Ar– C), δ 115.1 (Ar–C), δ 117.2 (Ar–C), δ 118.1 (Ar–C), δ 129.7 (Ar–C), δ 130.0 (Ar–C), δ 143.3 (C–N), δ 146.5 (C–N). ¹⁹P NMR (DMSO-d₆): δ 49.40. ²⁹Si NMR (DMSO-d₆): δ –9.55. Element analysis calculated (%): C 53.89, H 4.49, N 4.84; found C 53.87, H 4.51, N 4.82. ESI–MS m/z calculated for [M+H]⁺. C₂₆H₂₇N₂SiPTiCl₃:581.31 found 581.34. L3 Zr complex (Cat.8) ($C_{26}H_{26}N_2SiPZrCl_3$, Fw = 623): ¹H NMR (DMSO-d₆): δ 0.14 (s, 6H, methyl), δ 6.43–7.05 (m, 10H, benzene), δ 7.22–7.53(m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 112.1 (Ar–C), δ 115.3 (Ar–C), δ 117.1 (Ar–C), δ 118.3 (Ar–C), δ 129.6 (Ar–C), δ 130.0 (Ar–C), δ 143.4 (C–N), δ 146.6 (C–N). ¹⁹P NMR (DMSO-d₆): δ 49.36. ²⁹Si NMR (DMSO-d₆): δ –9.61. Element analysis calculated (%): C 53.33, H 4.44, N 4.79; found C 53.34, H 4.45, N 4.81. ESI– MS m/z calculated for [M+Na]⁺. C₂₆H₂₆N₂SiPZrCl₃Na: 646.69 found 646.65.

L3 Hf complex (Cat.9) ($C_{26}H_{26}N_2SiPHfCl_3$, Fw = 710): ¹H NMR (DMSO-d₆): δ 0.13 (s, 6H, methyl), δ 6.41-7.05 (m, 10H, benzene), δ 7.22–7.52 (m, 10H, benzene). ¹³C NMR (DMSO-d₆): δ 1.1 (Si(CH₃)₂), δ 1.2 (Si(CH₃)₂), δ 112.1 (Ar–C), δ 115.2 (Ar–C), δ 117.2 (Ar– C), δ 118.4 (Ar–C), δ 129.6 (Ar–C), δ 130.2 (Ar–C), δ 143.6 (C–N), δ 146.8 (C–N). ¹⁹P NMR (DMSO-d₆): δ 49.39. ²⁹Si NMR (DMSO-d₆): δ –9.63. Element analysis calculated (%): C 55.03, H 4.59, N 4.94; found C 55.04, H 4.63, N 4.92. ESI–MS m/z calculated for [M+H]⁺. C₂₆ H₂₇N₂SiPHfCl₃: 711.62 found 711.58.

From the ¹³C NMR results mentioned above, the complexes from the same ligand (L1, L2 or L3) complexed with different transition metals (Ti, Zr and Hf) showed almost identical chemical shifts, which indicated that the transition metals did coordinate with the heteroatoms, not with the carbon atoms of these ligands. A lot of work was done for single crystal, unfortunately, there was no one good enough for X-ray analysis.

3 Results and Discussion

The obtained [N, Si, N, P] non-metallolene catalysts (Cat.**1–9**) were utilized for ethylene (co)polymerization, MAO used as cocatalyst (Scheme 2). The effects of centre metal atoms (Ti, Zr and Hf) and the structure of catalyst ligands on ethylene (co-) polymerization were investigated, and the data were compiled in Table 1.

From Table 1, the results indicated that these catalysts were favorable for both homopolymerization of ethylene and copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester with high catalytic activity. The highest catalytic activity for homopolymerization of ethylene was up to 1.66×10^6 gPE (mol Zr)⁻¹.h⁻¹ and that of copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester was up to 6.24×10^4 gP (mol Zr)⁻¹.h⁻¹ catalyzed by Cat. **2**. The catalyst with zirconium as center metal showed the higher catalytic activity for ethylene (co)polymerization. However, the polymer obtained by catalyst with hafnium as metal center had the highest weight average molecular weight. Cat.**4**, Cat.**5** and

Cat.6 with L2: Cat.7. Cat.8 and Cat.9 with L3 showed the similar polymerization behavior for homopolymerization of ethylene and copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester. We can also notice that the structure of the ligands and the center metal atoms of these catalysts influenced the ethylene (co) polymerization behavior. Cat.1 to Cat.3 were used for both homopolymerization of ethylene and copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester. The MWs were ranged from 8.65×10^5 to 6.42×10^5 g/mol for polyethylene, from 2.56×10^5 to 1.41×10^5 g/mol for copolymer of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester. The MWDs were slightly broadened from 1.75 to 1.86 for polyethylene and from 2.76 to 2.87 for the copolymers. This result implied that the chain transfer for the copolymerization took place in some extent, compared to the homopolymerization of ethylene.

It was obvious that Cat.1 to Cat.3 with L1 exhibited the highest catalytic activity (Runs 1 to 6 in Table 1), compared with other catalysts with the same transition metals. This depended on the electric and steric effect of ligands. Compared with L1, L2 with methyl on benzene ring had large steric block. Methyl on *para*-position of L2 had strong electron donating effect that led to high electron density around the active center. It hindered the coming monomer from approaching to metal atom.

As shown in Table 1, the catalyst with fluorine atom on para-position of aniline showed higher activity than that with methyl group, it was due to that fluorine atom on paraposition of aniline would decrease the electron cloud density of metal center, attracting ethylene move to the active center. The catalysts include a large five-membered ring, making sure the stability of the active centers.

The effects of polymerization conditions on copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester catalyzed by Cat.2 were investigated: temperature, Al/Zr ratio in mol, comonomer concentration and catalysts concentration. The results were listed in Table 2.

From Table 2, we can notice that Cat.2 featured rather high tolerance to the reaction conditions and exhibited highest catalytic activity of 6.56×10^4 g P (mol⁻¹ Zr⁻¹ h⁻¹) (run 20 in Table 2) at 50 °C for the copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester. With an increase of reaction temperature from 25 to 70 °C, the MW of the obtained copolymers decreased gradually and MWDs became broader slightly. It is possible that the weight–average MW of the obtained copolymers is determined by Kp/Ktr ratio. With the increasing of the polymerization temperature, Ktr increases faster than Kp. Therefore, rate of chain transfer to monomers and MAO enhances much more than propagation

Run	Catalysts	$A^{a} (\times 10^{-4})$	N-cont ^b (wt%)	$M_{\rm w}^{\rm c}(\times 10^{-5})$	$M_{\rm w}/M_{\rm n}^{\rm c}$	T_m^d (°C)
1	Cat.1 (Ti, L1)	145	_	6.42	1.81	134.5
2 ^e		2.35	9.25	1.41	2.87	135.8
3	Cat.2 (Zr, L1)	166	_	8.23	1.75	134.2
4 ^e		6.24	22.42	1.65	2.76	137.2
5	Cat.3 (Hf, L1)	133	_	8.65	1.86	134.5
6 ^e		4.13	13.00	2.70	2.85	138.1
7	Cat.4 (Ti, L2)	107	_	7.21	1.79	134.5
8 ^e		2.03	5.75	1.32	2.89	135.3
9	Cat.5 (Zr, L2)	119	_	7.63	1.93	134.2
10 ^e		5.53	17.56	1.43	3.06	136.3
11	Cat.6 (Hf, L2)	101	_	8.17	1.78	134.4
12 ^e		3.86	9.45	2.56	3.08	137.7
13	Cat.7 (Ti, L3)	94.4	_	7.38	2.47	134.8
14 ^e		1.52	3.79	1.27	2.76	135.1
15	Cat.8 (Zr, L3)	125	_	7.52	1.81	134.7
16 ^e		3.78	13.36	1.48	2.96	134.8
17	Cat.9 (Hf, L3)	107	-	7.92	1.93	134.6
18 ^e		2.13	1.06	2.54	3.03	137.9

Reaction conditions: pressure of ethylene, 0.2×10^6 Pa; catalyst concentration, 2.0×10^{-4} mol L⁻¹; Al/M in mol, 600; reaction temperature, 60 °C; solvent, toluene, 80 mL; polymerization time, 10 min

^a Catalytic activity, gPE/(molM.h)

^b Incorporation content of N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester, determined by ¹³C NMR

^c Determined by GPC

^d Determined by DSC

^e Comonomer: 10 g/L

 Table 2
 Effects of polymerization conditions on copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester catalyzed by Cat.2

Run	$T^{a}\left(^{\circ }C\right)$	C ^b (×10 ⁴)	Comon ^c (g/L)	Al/Zr ^d	$A^{e} (\times 10^{-4})$	$M_{w}^{\rm f}(\times 10^{-5})$	$M_w/M_n^{\rm f}$	$T_m^g \ (^\circ C)$	N-Cont ^h (wt%)
19	25	2.0	10	600	4.63	3.79	2.78	137.9	19.61
20	50	2.0	10	600	6.56	2.67	2.82	138.6	22.40
21	70	2.0	10	600	4.93	2.11	3.13	138.4	21.57
22	50	1.0	10	600	3.84	2.76	3.01	135.8	9.94
23	50	5.0	10	600	4.96	2.16	3.25	137.5	14.54
24	50	2.0	5	600	6.52	2.66	2.83	137.2	13.63
25	50	2.0	20	600	5.23	2.33	3.07	138.7	23.07
26	50	2.0	10	300	2.32	1.76	2.98	137.8	18.64
27	50	2.0	10	1000	3.03	0.93	3.57	138.0	20.64
28	50	3.0	10	600	6.07	2.58	3.09	138.1	20.17
29	50	4.0	10	600	5.54	2.32	3.18	137.8	18.39

Reaction conditions: pressure of ethylene, 0.2×10^6 Pa; dissolvent, toluene, 100 mL; polymerization time, 10 min

^a Reaction temperature

Table 1 Effects of the metalatoms and the structure ofcatalyst ligands on ethylene (co-

) polymerization

^b Catalyst concentration

^c Comonomer, N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester in feed

^d Al/Zr in mol

^e Activity of catalysts, g PE(mol⁻¹ Zr⁻¹ h⁻¹)

f Results of GPC

^g Results of DSC

^h Incorporation content of 1-octene, results of ¹³C NMR

reaction. [25] The incorporation rate of N-acetyl-O-(hex-5enyl)-L-tyrosine ethyl ester was changed slightly at different temperature.

As shown in Table 2, when catalyst concentration was 2.0×10^{-4} g/L, catalytic activity exhibited the highest value of 6.56×10^4 g PE(mol⁻¹ Zr⁻¹ h⁻¹). With catalyst concentration increased from 1.0×10^{-4} to 2.0×10^{-4} g/L, catalytic activity increasing from 3.84×10^4 g PE (mol⁻¹ Zr⁻¹ h⁻¹) to 6.56×10^4 g PE (mol⁻¹ Zr⁻¹ h⁻¹). However, when catalyst concentration increased from 2.0×10^{-4} to 5.0×10^{-4} g/L, catalytic activity decreased. Because the active centers of the catalysts were devitalized by impurity easily, when catalyst concentration was 1.0×10^{-4} g/L, the number of activity species was less. But too high catalyst concentration leads to fast polymer chain aggregation within the same polymerization



Fig. 1 High temperature liquid 13 C NMR spectra of ethylene/N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester copolymer from run 20 in Table 2

time, it is more difficult for the monomers approaching to the active centers. Therefore, polymer chain can be snarled easily, resulting in the chain propagation rate decreasing. Furthermore, catalyst concentration influenced the incorporation rate of N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester slightly.

The concentration of N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester in feed influenced the incorporation content of N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester. For example, when the concentration of N-acetyl-O-(hex-5-envl)-L-tyrosine ethyl ester was 5 g/L in the reaction system, the insertion content of the comonomer was 13.63 wt%; while the concentration increased to 10 g/L, the insertion content of the comonomer increased to 22.40 wt%. However, keeping on increasing the concentration to 20 g/L, the insertion content of the comonomer slightly raised to 23.07 wt% (runs 24, 20 and 25 in Table 2). The results indicated that there was a limit to amount of the comonomer in feed. When it's enough for the polymerization, the extra comonomer would not work anymore. The MWDs of copolymers was about 3.0, indicating that the polymerization behavior followed singlemetal mechanism.

The catalytic activity was influenced by Al/Zr molar ratio strongly. When Al/Zr molar ratio in mol was 600, catalytic activity of the copolymerization of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester reached the maximum value of 6.56×10^4 gP/(molZr.h). As Al/Zr molar ratio ranged from 300 to 600, catalytic activity increased from 2.32×10^4 to 6.56×10^4 gP/(molZr.h) (runs 26, and 20 in Table 2). However, catalytic activity decreased with further increasing Al/Zr molar ratio. It is possible that both the reaction system purifying and the chain transfer reaction to MAO consume amount of MAO. However, Trimethylaluminum in MAO can reduce oxidation state of Ti(IV) to Ti(III), but only Ti(IV) is favorable for α -olefin polymerization. In addition, MAO influenced MWs and MWDs of copolymers. Part of active species was transferred to β -H with less MAO, which led to lower activity, lower MWs, and broader MWDs. However, much MAO made chain transfer to MAO easy, resulting in lower MWs and broader MWDs (run 27 in Table 2). Hence, the active center can be stable and chain transfer to B-H and MAO be controlled only when the proper amount of MAO is introduced. The incorporation rate of N-acetyl-O-(hex-5envl)-L-tyrosine ethyl ester was influenced by Al/Zr molar ratio slightly, implying that Al/Zr molar ratio did not the main factor of influencing comonomer incorporation.

The high temperature liquid ¹³C NMR spectra of ethylene/N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester copolymer promoted by Cat.2 was presented in Fig. 1a. One broad signal at $\delta = 23.6-35.5$ ppm represented methylene. The signals at $\delta = 172.32$ and 169.46 ppm were attributed to the carbon atoms (C_a and C_b) from the amino group and the ester group, respectively. The signals at $\delta = 155.61$, 131.83 and 60.06 ppm were attributed to the carbon atoms (Ce, Cd and Cc), however, the signal at $\delta = 131.83$ ppm was overlaped with the signals of the solvent, ortho-dichlorobezene (d_4) . It indicated that the comonomer had been inserted into the polyethylene chain. There are two main patterns of chain transfer in the copolymerization process catalyzed by non-metallocene catalyst [25]: The first is that β -H transfers to active center and monomer; the second is that the growing chain transfers to MAO. The former produces the polymer with unsaturated end group, while the latter obtains the polymer with saturated end group. Chain termination reaction of olefin polymerization catalyzed by non-metallocene catalyst can also get polymer with saturated end group. From Fig. 1b, we can see that there was no signal that represented the unsaturated carbon-carbon double bond, but a signal at δ 14–15 ppm assigned to methyl was observed. This implied that the obtained copolymer of ethylene with N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester, catalyzed by the catalyst system of Cat.2/MAO, was featured methyl group at the chain end. The result confirmed that the chain transfer to MAO was the dominant pattern.

Different carbon atoms between 10 and 40 ppm were assigned in Table 3. According to the area integral of each carbon atom, Randall [30] method was used to calculate the content of different sequence structure, and then calculated the comonomer insertion rate as well as reactivity ratio and average sequence length of the two monomers. The results were shown in Table 4. The calculation results showed that the comonomer insertion rate was 22.40 wt% within the copolymer chain catalyzed by Cat.2. The

Table 3 ¹³C NMR data of

reactivity rates of ethylene and N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester were 152.99 and 0.045, respectively. The average sequence lengths for ethylene units and the comonomer units were 34.52 and 1.03, respectively. Moreover, no continuous fragment of N-acetyl-O-(hex-5enyl)-L-tyrosine ethyl ester was found within the copolymer chain ([NNN] = 0). So we can infer that N-acetyl-O-(hex-5-envl)-L-tyrosine ethyl ester was single dispersed into the polyethylene chain, which can provide the copolymer a good potential application value.

The FT-IR plots of the obtained copolymers were performed (Fig. 2). Signals at 2918, 2849, 1470 and 718 cm⁻¹ are characteristic signals to linear polyethylene. The signal at 718 cm⁻¹ represents the long chain units $[(CH_2)_n, n > 4]$ of methylene. The signals at 2918, 2849 and 1470 cm⁻¹ are C-H stretching vibration absorption and bending vibration absorption peaks. There was an evident band at 1738 cm⁻¹ (Fig. 4d) which was C=O vibration absorption of the saturated ester from the branched group. Compared

Table 4 The content of different sequences on copolymer and reactivity ratio of monomer

[ENE]	[ENN]	[ENN] [NNN]		[NEN]	[EE	N]	[EEE]	
4.524	0.002	0		0.053	0.32	6	95.095	
Sample		Mole fractions		Reactivity ratio		The average sequence length		
		[E]	[N]	r _E	r _N	n _E	n _N	
Run 4 in Table 2		0.9763	0.0237	152.99	0.045	34.52	1.03	

E polyethylene, N poly(N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester)

Table 3 ¹³ C NMR data of carbon atoms on the copolymer	Peak no.	Carbon type	Monomer sequence	Chemical shift	
of ethylene and N-acetyl-O-				Calculated	Found
ester	1	СН	ENE	38.13	37.95
	2	$\alpha\delta^+$ +CH ₂ (6)	NNEE+NNE	34.90	35.35
	3	αγ	ENEN	35.00	35.17
	4	$\alpha\delta^+$ +CH ₂ (6)	ENEE+ENE	34.54	34.63
	5	CH ₂ (3)	ENE + NNE + NNN	32.31	31.64
	6	$\gamma\delta^+$	NEEE	30.47	30.45
	7	$\delta^+\delta^+$	(EEE)n	29.98	29.44
	8	CH ₂ (3)	ENE	29.51	29.17
	9	CH ₂ (5)	ENE+NNE+NNN	27.28	27.24
	10	$\beta\delta^+$	ENEE	27.29	27.18
	11	$\beta\delta^+$	ENEE	26.89	27.16
	12	CH ₂ (2)	ENE+NNE+NNN	23.36	22.97
	13	CH ₃	ENE+NNE+NNN	14.12	14.03

E polyethylene, *N* Poly(N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester)



Fig. 2 FT-IR spectrums of ethylene homopolymer (A, run 1 in Table 1) and ethylene/N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester copolymer (B, run 20; C, run 22; D, run 24 in Table 2)

to C=O vibration absorption of N-acetyl-O-(hex-5-enyl)-Ltyrosine ethyl ester at 1760 cm⁻¹ [31], the bands of C=O of the copolymer B moved toward red area and its vibration absorption wave number became 1738 cm⁻¹, which contributed to the forming of hydrogen bonds among inter- and intra- of the copolymer chains [32]. Band at 1259 cm⁻¹ corresponded to C-O vibration absorption. Stretching vibration absorption and bending vibration absorption of C-O on ester group were shown at 1094 and 1023 cm⁻¹. Band at 1655 cm⁻¹ corresponded to C=O vibration absorption of amide group. Band at 802 cm⁻¹ represented the vibration absorption of substituted benzene. The results indicated that the comonomer N-acetyl-O-(hex-5-enyl)-Ltyrosine ethyl ester had incorporated into the copolymer chains.

As shown in Fig. 3, the melting points of polymers (A, B, C, D) increase in order from 134.5 to 138.6 °C, with the increase of comonomer insertion rate. It can be contributed to the hydrogen bonding interaction between the branch chains. Melting enthalpy of polyethylene (A) was 198.6 J/g and crystallinity was 69.1 % which was calculated from area integration. However, the melting enthalpy of the copolymers (B, C, D) was 159.2, 153.7 and 148.8 J/g, respectively. Using the same method, we figured out that the crystallinity of the copolymers (B, C, D) were 55.4, 53.5 and 51.8 %, respectively. Reducing crystallinity was ascribed to the insertion of N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester, which destroyed the regularity of polymer chain. The higher comonomer insertion rate was, the lower crystallinity became.



Fig. 3 DSC spectrums (the second heating) of ethylene homopolymer (A, run 1 in Table 1) and ethylene/N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester copolymers (B, run 22; C, run 24; D, run 20 in Table 2)



Fig. 4 GPC curves of ethylene homopolymer (A, run 1 in Table 1) and ethylene/N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester copolymers (B, run 22; C, run 20; D, run 24 in Table 2)

The GPC curves of ethylene homopolymer and copolymers (Fig. 4) were monomodal and symmetric in shape, meaning that these copolymers were not a mixture of PE homopolymer and small amount of oligomers containing comonomer. GPC results exhibited that MWs of ethylene homopolymer (Fig. 4a) and copolymers (Fig. 4bd) were 6.42×10^5 , 2.76×10^5 , 2.66×10^5 2.67×10^5 g/mol, respectively. MWs of the copolymers were lower than that of the homopolymer, however, MWDs of the copolymers were broader, which indicated that the chain transfer took place during the copolymerization when N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester was added into the polymerization system. MWD of the copolyethylene was about 3, implying that the copolymerization behavior followed the single mechanism.

4 Conclusions

The copolymers of ethylene and N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester were synthesized by [N. Si, N. P]type non-metallocene catalysts, MAO used as cocatalyst. Cat.2 showed the highest catalytic activity of 6.56×10^4 g/ (molZr.h) for the copolymerization under the optimal reaction conditions: polymerization temperature of 50 °C, Al/Zr molar ratio of 600, catalyst concentration of 2.0×10^{-4} mol/L, the amount of comonomer in feed of 10 g/L, polymerization time of 10 min and toluene as dissolvent. The highest comonomer incorporation rate was 22.40 wt% determined by ¹³C NMR. The melting points of the copolymers increased with the increasing insertion rate of N-acetyl-O-(hex-5-enyl)-L-tyrosine ethyl ester as a result of the hydrogen bonding interaction between the branch chains. GPC results exhibited that MWs of the copolymers were at the range of $9.3 \times 10^4 - 3.79 \times 10^5$ g/mol. However, MWs of the copolymers were lower than those of the homopolymers, and MWDs of the copolymers were broader. This indicated that the chain transfer took place during the copolymerization when N-acetyl-O-(hex-5enyl)-L-tyrosine ethyl ester was added into the polymerization system. These catalysts were also favorable for the homopolymerization of ethylene. The highest catalytic activity was up to 1.66×10^6 g PE (mol Zr)⁻¹ h⁻¹ by Cat.2 for ethylene polymerization. MWs of the polyethylene were high up to 8.65×10^5 g/mol. MWDs of the copolyethylene were about 3, implying that the copolymerization behavior followed the single mechanism.

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References

- 1. Ziegler K, Holzlmmp E, Breil H, Martin H (1955) Angew Chem In Ed 67:541–547
- 2. Ziegler K (1964) Angew Chem In Ed 76(13):545-553
- 3. Sinn H, Kaminsky W (1980) Adv Organomet Chem 18:99-143
- 4. Bialk M, Czaja K (2000) Polymer 41:7899-7904

- Kong Y, Yi JJ, Dou XL, Liu WJ, Huang QG, Gao KJ, Yang WT (2010) Polymer 51:3859–3866
- 6. Luo HK, Tang RG, Gao KJ (2002) J Catal 210:328-339
- Huang QG, Sheng YP, Yang WT (2007) J Appl Polym Sci 103:501–505
- Scheirs J, Kaminsky W (2000) Metallocene-Based Polyolefins, vol 2. Wiley, Chichester
- 9. Ittel SD, Johnson LK, Brookhart M (2000) Chem Rev 100:1169–1204
- 10. Smruti BA, Tobin JM (2006) J Am Chem Soc 128:4506-4507
- Mecking S, Johnson LK, Wang L, Brookhart M (1998) J Am Chem Soc 120(5):888–899
- 12. Friedberger T, Wucher P, Mecking S (2012) J Am Chem Soc 134:1010–1018
- 13. Runzi T, Frohlich D, Mecking S (2010) J Am Chem Soc 132:16623–16630
- He LP, Hong M, Li BX, Liu JY, Li YS (2010) Polymer 51:4336–4339
- 15. Kochi T, Noda S, Yoshimura K, Nozaki K (2007) J Am Chem Soc 129:8948–8949
- Ito S, Kanazawa M, Munakata K, Kuroda J, Okumura Y, Nozaki K (2011) J Am Chem Soc 133:1232–1235
- Ito S, Munakata K, Nakamura A, Nozaki K (2009) J Am Chem Soc 131:14606–14607
- Ota Y, Ito S, Kuroda J, Okumura Y, Nozaki K (2014) J Am Chem Soc 136:11898–11901
- Popeney CS, Camacho DH, Guan ZB (2007) J Am Chem Soc 129:10062–10063
- 20. Wang JL, Zhang KJ, Ye ZB (2008) Macromolecules 41:2290–2293
- Drent E, Dijk RV, Ginkel RV, Oort BV, Pugh RI (2002) Chem Commun 744–745
- Ma LF, Sheng YP, Huang QG, Zhao YF, Deng KX, Li JL, Yang WT (2008) J Polym Sci Part A Polym Chem 46:33–37
- Ma LF, Wang HL, Yi JJ, Huang QG, Gao KJ, Yang WT (2010) J Polym Sci Part A Polym Chem 48:417–424
- Zhang XL, Liu Z, Yi JJ, Huang HB, Dou XL, Zhen HP, Huang QG, Gao KJ, Zhang MG, Yang WT (2013) Polym Int 62(3):419–426
- Zhang XL, Liu Z, Yi JJ, Li FJ, Huang HB, Liu W, Zhen HP, Huang QG, Gao KJ, Yang WT (2012) J Polym Sci Part A Polym Chem 50(10):2068–2074
- Hasani-Sadrabadi MM, Karimkhani V, Jacob KI, Renaud P, Stadler FJ (2014) Adv Mater 26:3118–3123
- Bishop CJ, Ketola TM, Tzeng SY, Sunshine JC, Urtti A, Lemmetyinen H, Laukkanen EV, Yliperttula M, Green JJ (2013) J Am Chem Soc 135:6951–6957
- Patri AK, Majoros IJ, Baker JR (2002) Curr Opin Chem Biol 6:466–471
- 29. Grodzinski J (1999) J React Funct Polym 39(2):99-138
- 30. Hsieh ET, Randall JC (1982) Macromolecules 15:1402-1406
- 31. Fan XY (2003) Life Sci Res 7:83-87
- Senak L, Ju Z, Noy N, Callender R, Manor D (1997) Biospectroscopy 3:131–142