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ORIGINAL PAPER

Homo- and copolymerizations of ethylene and α-olefins in *n*-hexane catalyzed by Ni(ii)-α-diimine catalyst

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Abstract Ni(II)-α-diimine catalyst [(2,6-i-Pr)$_2$C$_6$H$_3$-DAB(An)]NiBr$_2$ plus methylaluminoxane was successfully used in the homopolymerization of ethylene, 1-hexene, and 1-octene and the copolymerization of ethylene with 1-hexene and 1-octene in *n*-hexane. The polymerization of 1-octene was conducted in a controlled manner with a narrow molecular weight distribution ($M_w/M_n = 1.2$–1.5) and with the weight-average molecular weight increasing linearly with the monomer conversion. The molecular weights, T_g, T_m, branching degree, and density of the obtained (co)polymers were greatly controlled by ethylene pressure and polymerization temperature. Compared with that of ethylene homopolymer, the branching degree of the copolymers prepared by the copolymerization of ethylene with 1-hexene or 1-octene increased, whereas the molecular weight, density, T_m, and catalyst activity decreased. However, compared with those of the homopolymer of 1-hexene or 1-octene, the copolymer density, T_m, and catalyst activity increased, whereas the branching degree declined.

Keywords Ni(II)-α-diimine catalyst · α-Olefins · *n*-Hexane · Coordination polymerization

Introduction

The homo- and copolymerizations of ethylene and α-olefins have been extensively investigated in recent years. Compared with the Ziegler–Natta and metallocene catalysts, late-transition metal catalysts can catalyze the polymerization of olefins to yield polymers with different microstructures. They are also less oxophilic and are

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therefore more tolerant of functionalized monomers. Currently, well-defined catalysts based on complexes of cobalt [1–3], rhodium [4, 5], nickel [6–27], palladium [10, 28, 29], platinum [5], and iron [30–33] have been reported. Specifically, the catalysts based on cationic α-diimine complexes of nickel and palladium, which were reported in 1995 [10–12], can polymerize ethylene and α-olefins to a high molecular mass polymer with the activity comparable to that of early-transition-metal systems. Dramatic differences in the microstructure and properties of the obtained polymers using these nickel- and palladium-based catalysts are observed than in those prepared using early metal Ziegler–Natta and metallocene technology. For example, branching in polyethylene prepared with nickel(II)- or palladium(II)-based catalysts can vary from highly branched to linear; thus, the properties vary from soft elastomers to rigid plastics. The polymer properties are greatly dependent on reaction conditions, ligand structure, and metal [34]. For example, catalysts lacking bulky substituents in the *ortho* aryl positions have been found to oligomerize ethylene selectively to α-olefins [14, 15]. Furthermore, bulky nickel(II) catalysts have been shown to catalyze the living polymerization of α-olefins (e.g., propylene, 1-hexene, etc.) in toluene at −10 °C, thus providing access to diblock and multiblock copolymers [13]. Recently, Sivaram and coworkers [35] studied the homopolymerization of 1-hexene with nickel (α-diimine) catalyst in toluene and found that the obtained poly(1-hexene) contained different types of branches and varying number of ethylene units in the backbone. Santos et al. [36] presented a stochastic model to simulate the chain-walking mechanism during the polymerization of 1-hexene with α-diimine nickel catalysts based on the kinetic mechanism.

Toluene has been used as solvent in the polymerization of olefins catalyzed by the nickel(II)-based-α-diimine catalyst system [10–12, 34–36]. However, its toxicity is much higher than that of *n*-hexane, which is a common solvent in the present industrial polymerization of olefins. To the best of our knowledge, *n*-hexane has never been used as the solvent in the nickel(II)-based-α-diimine catalyst system for the polymerization of olefins. If nickel(II)-based-α-diimine catalyst can catalyze the polymerization of olefins in *n*-hexane, then it will become important for its industrial application.

In this article, the homopolymerization of ethylene, 1-hexene, and 1-octene and the copolymerization of ethylene with 1-hexene and 1-octene catalyzed by methylalumoxane-activated Ni(II)-based-α-diimine complexes $[(2,6\text{-i-Pr})_2C_6H_3\text{-DAB(An)}]NiBr_2$ were investigated in *n*-hexane. The molecular weights of the obtained polymers and the polymerization behavior of 1-octene were characterized by gel permeation chromatography (GPC), and T_g, T_m, degree of branching, and density of the polymers were determined by DSC, ^1H NMR, and FTIR.

Experimental

Materials

THF, *n*-hexane, and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride was distilled under nitrogen from P_2O_5.

1,2-Dimethoxy ethane bromide nickel ((DME)-$NiBr_2$), acenaphthoquinone, 2,6-diisopropylaniline, and a 10% solution of MAO in toluene purchased from Aldrich Chemical Co were used directly. 1-Octene and 1-hexene were purchased from Alfa Aesar Chemical Co, purged with argon, and dried over 4 Å molecular sieves. Polymerization-grade ethylene (99.5%) was purchased from National Specialty Gases and used without further purification. High pressure polymerizations were performed in a mechanically stirred 2000 mL Parr autoclave.

Synthesis of Ar=C(An)–C(An)=NAr (Ar = 2,6-i-PrPh)

A 50 mL flask was charged with 2.659 g (15 mmol) of 2,6-diisopropylaniline and 1.184 g (6.5 mmol) of acenaphthoquinone. Methanol (25 mL) and formic acid (1 mL) were added, and the reaction was carried out under stirring at room temperature overnight. An orange solid was collected via filtration and washed with methanol. After recrystallization from CH_2Cl_2, 3.22 g of diimine was obtained with yield of 83%.

Synthesis of the (Ar=C(An)–C(An)=NAr)$NiBr_2$ (Ar = 2,6-i-PrPh)

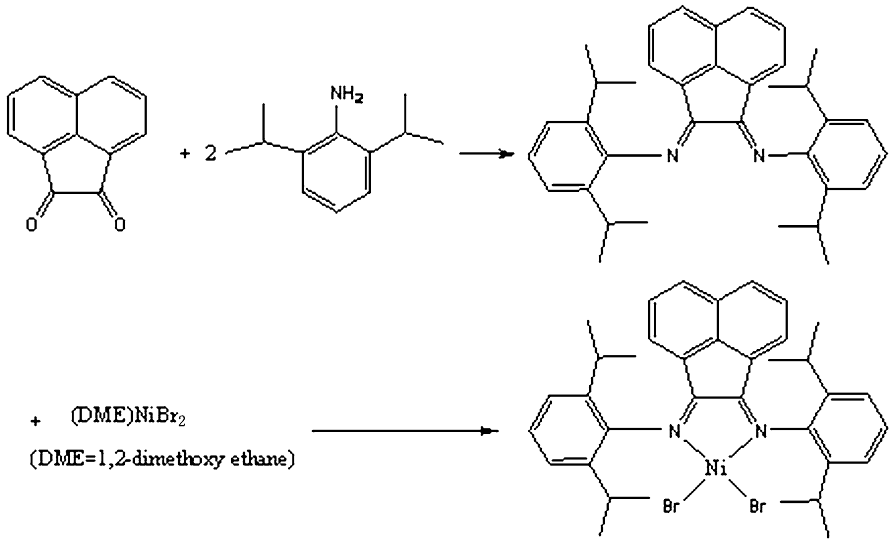
0.187 g (0.4 mmol) of (2,6-i-$Pr)_2C_6H_3$-DAB(An) and 0.111 g (0.36 mmol) of (DME)$NiBr_2$ were combined as solids in flame-dried schlenk flask under an argon atmosphere. 20 mL of methylene chloride was added to the solid mixture, and the mixture was stirred at room temperature for 18 h. The solvent was removed under vacuum, resulting in a red/brown solid which was washed with 2× 10 mL of diethyl ether and 3× 10 mL of hexane and dried under vacuum. The product was isolated as red powder, and 250 mg of complex was obtained with yield 80%. The synthesis route is shown in Scheme 1.

Polymerization of ethylene using (Ar=C(An)–C(An)=NAr)$NiBr_2$ as catalyst

A 2000 mL Parr autoclave was washed with *n*-hexane and replaced three times by ethylene. A 10% MAO solution in toluene (10.00 mL, 17 mmol) was then added to a suspension of [(2,6-i-$Pr)_2C_6H_3$-DAB(An)]$NiBr_2$ (122 mg, 0.17 mmol) in 1000 mL of dry *n*-hexane. The autoclave was sealed and pressurized to the desired ethylene pressure (8–10 atm) under stirring. The mixture was stirred at 35 or 45 °C. The reaction was quenched by venting the autoclave followed by addition of methanol. The precipitated polymers were filtered from solution and dried under vacuum.

Polymerization of 1-hexene using (Ar=C(An)–C(An)=NAr)$NiBr_2$ as catalyst

1-Hexene (10 mL) was added to a suspension of [(2,6-i-$Pr)_2C_6H_3$-DAB(An)]$NiBr_2$ (12 mg, 0.017 mmol) in 90 mL of dry *n*-hexane. 1.00 mL of 10% MAO toluene solution was then added. The mixture was stirred at room temperature for 90 min. Acetone and water were added to quench the polymerization and precipitate the polymer. Solid poly(1-hexene) was recovered by filtration from the flask and



Scheme 1 The synthesis route of the catalyst [(2,6-i-Pr)2C_6H_3-DAB(An)]$NiBr_2$ 83 × 50 mm (600 × 600 DPI)

washed with 6 M HCl, H_2O, and acetone. Solid poly(1-octene) was obtained after drying under vacuum.

Polymerization of 1-octene using (Ar=C(An)–C(An)=NAr)$NiBr_2$ as catalyst

10 mL of 1-octene was added to a suspension of [(2,6-i-Pr)$_2C_6H_3$-DAB(An)]$NiBr_2$ (12 mg, 0.017 mmol) in 90 mL of dry *n*-hexane. 1.00 mL of 10% MAO toluene solution was then added. The mixture was stirred at room temperature for 90 min. Aliquots were withdrawn at 20, 30, 40, and 50 min. Acetone and water were added to quench the polymerization and precipitate the polymer. Solid poly(1-octene) was recovered by filtration from the flask and washed with 6 M HCl, H_2O, and acetone. Solid poly(1-octene) was obtained after drying under vacuum.

Copolymerization of ethylene with 1-hexene and 1-octene using (Ar=C(An)–C(An)=NAr)$NiBr_2$ as catalyst

A 2000 mL Parr autoclave was washed using *n*-hexane and replaced three times with ethylene. A 10% MAO solution in toluene (10.00 mL, 17 mmol) was then added to a suspension of [(2,6-i-Pr)$_2C_6H_3$-DAB(An)]$NiBr_2$ (122 mg, 0.17 mmol) with 50 mL 1-hexene or 1-octene in 1000 mL of dry *n*-hexane. The autoclave was sealed and pressurized to the desired ethylene pressure (10 atm) under stirring. The temperature (35 °C) was maintained by cooling with an ice/water cooled circulator. The polymerization was quenched by venting the autoclave followed by addition of methanol. The precipitated polymers were filtered from solution and dried under vacuum.

Characterization

Monomer conversion was obtained gravimetrically. ^{1}H NMR spectra were recorded on a Bruker AV 600-MHz spectrometer with $CDCl_3$ as solvent at room temperature. The elemental contents were measured by the HP-MOD/106 elemental analysis instrument. The glass transition temperature T_g and melting point T_m were determined by a Netzsch 204F differential scanning calorimetry (DSC). The polymer samples were quenched from the melt to amorphous state, and then heated to the melt again at a rate of 20 °C/min. Weight-average molecular weights and molecular weight distributions of polyethylene and copolymers were determined using a Waters Alliance GPCV 2000 high-temperature GPC equipped with Shodex columns in 1,2,4-trichlorobenzene at 150 °C. A calibration curve was established with polystyrene standards. Weight-average molecular weights and molecular weight distributions of other polymers were measured using a Tosoh HPLC8320 GPC (column: TSK-Gel Super HZM-M × 2) with THF as the eluent (40 °C) at a flow rate of 0.35 mL/min. Narrow polystyrene standards were used to generate the calibration curve. FTIR spectra were recorded at room temperature on a Magna-IR 760 spectrometer. The density was measured according to standard method (GB/T 1033.1-2008).

Results and discussion

Characterization of the Ar=C(An)–C(An)=NAr and (Ar=C(An)–C(An)=NAr) $NiBr_2$ (Ar = 2,6-i-PrPh)

The diimine ligand (2,6-i-Pr)$_2C_6H_3$-DAB(An) and [(2,6-i-Pr)$_2C_6H_3$-DAB(An)]-$NiBr_2$ complex were prepared based on literature procedures [10–12, 34]. ^{1}H NMR of (2,6-i-Pr)2Ph-DAB(An) ($CDCl_3$, ppm): δ 7.86 (d, 2H, An: Hp), δ 7.36 (dd, 2H, An: Hm), δ 6.62 (d, 2H, An: Ho), δ 7.27 (m, 6H, Ar: Hm, Ho and Hp), δ 3.02 (septet, 4H, –$CH(CH_3)_2$), δ 0.97 (s, 24 H, –$CH(CH_3)_2$); Anal. Calcd for $C_{36}H_{40}N_2$: C 86.40%, H 8.00%, N 5.6%. Found: C 85.90%, H 8.00%, N 5.43%.

Anal. Calcd for $C_{36}H_{40}N_2NiBr_2$: C 60.12%, H 5.61%, N 3.89%. Found: C 59.71%, H 5.69%, N 3.96%.

Polymerization of ethylene using (Ar=C(An)–C(An)=NAr)$NiBr_2$ as catalyst

Brookhart and coworkers [34] conducted detailed investigations on the polymerization of ethylene catalyzed by nickel(II)-α-diimine catalysts with different *ortho* substituents in toluene. The Ni(II)-based-α-diimine catalyst [(2,6-i-Pr)$_2C_6H_3$-DAB(An)]$NiBr_2$ activated by MMAO in toluene exhibits the highest catalyst activity (1.57 kg/mol Ni h^{-1} for 1 atm at 35 °C; 67.2×10^3 kg/mol Ni h^{-1} for 130 atm at 35 °C). The effects of ethylene pressure and temperature on polymerizations were also reported. The branching degree in the polymers rapidly decreased (from 106 to 24 and from 122 to 58) with increasing ethylene pressure (from 1 to 130 atm at 35 and 60 °C), but the molecular weights were not markedly affected.

The temperature increase (from 35 to 85 °C at 1 and 130 atm) resulted in more extensive branching (from 106 to 124 and from 24 to 83) and moderate reductions in molecular weights, and catalyst productivity decreased above 60 °C because of catalyst deactivation.

The Ni(II)-based-α-diimine complex $[(2,6\text{-i-Pr})_2C_6H_3\text{-DAB(An)}]NiBr_2$ activated by methylalumoxane was used to catalyze the polymerization of ethylene in *n*-hexane in this study. Until now, *n*-hexane has never been used as the solvent in the nickel(II)-based-α-diimine catalyst system for the polymerization of olefins. Compared with toluene, *n*-hexane has lower toxicity and is a common solvent in the current industrial polymerization of olefins. The GPC traces of polyethylenes obtained at different polymerization temperatures and ethylene pressures are shown in Fig. 1.

In Fig. 1, with the rise in ethylene pressure, the molecular weight of the polymer increases from 446 kg/mol for 8 atm to 547 kg/mol for 10 atm at 35 °C. Moreover, with the rise in polymerization temperature, the catalyst activity and molecular weight of the polymer declines from 3.9×10^3 kg/mol Ni h^{-1} and 446 kg/mol at 35 °C to 3.5×10^3 kg/mol Ni h^{-1} and 327 kg/mol for 8 atm at 45 °C, respectively. The rise in the molecular weight of the polymer suggests that with the increase in ethylene pressure, the increased monomer concentration in the solvent leads to the acceleration of the reaction rate, and with the rise in polymerization temperature, the catalyst activity declines.

The polymer properties are listed in Table 1 (entries 1–3). In Table 1, the polymer density decreases from 0.906 to 0.897 g/cm^3, and T_m declines from 122.3 to 112.5 °C when the temperature rises from 35 to 45 °C at 8 atm. Moreover, the polymer density decreases from 0.911 to 0.906 g/cm^3, and T_m declines from 127.6 to 122.3 °C when the ethylene pressure is reduced from 10 to 8 atm at 35 °C. This finding can be attributed to the rise in the branching degree with the decline in ethylene pressure and the increase in polymerization temperature. For instance, the branching degree of polymer increased from 20.4 to 22.7 when the ethylene pressure decreased from 10 to 8 atm at 35 °C and then increased from 22.7 to 24.3 when the temperature rised from 35 to 45 °C at 8 atm, as shown in Table 1 (entries 1–3).

Comparing the ethylene polymerization in toluene by Brookhart and coworkers [34] with the results in *n*-hexane, ethylene pressure and reaction temperature had

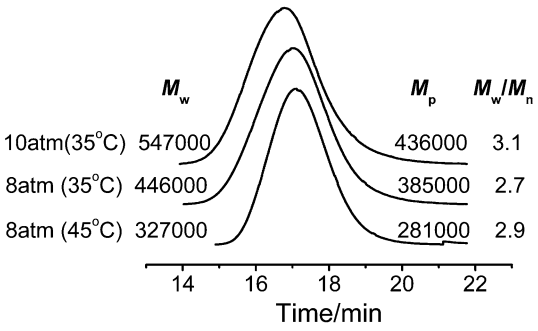


Fig. 1 The GPC traces of polyethylenes obtained at different polymerization temperature and ethylene pressure 80 × 56 mm (600 × 600 DPI)

Table 1 Data for α-olefin polymerization

Entry	Moles of catalyst[a] ($\times 10^6$)	Al:Ni mole ratio	Monomer[b]	Reaction condition		Catalyst efficiency (kg/mol Ni h^{-1}) ($\times 10^{-3}$)	Polymer properties				
				Time (min)	Temperature (°C)		M_w[c] ($\times 10^{-3}$)	M_w/M_n	Thermal Analysis (°C)[d]	Branching degree/1000 °C[e]	Density (g/cm^3)[f]
1	170	100	E(10 atm)	30	35	4.0	547	3.19	127.60(T_m)	20.4	0.9114
2	170	100	E(8 atm)	30	35	3.9	446	2.70	122.26(T_m)	22.7	0.9057
3	170	100	E(8 atm)	30	45	3.5	327	2.91	112.51(T_m)	24.3	0.8970
4	17	100	H(0.6 M)	30	25	0.37	573	1.54	−51.50(T_g)	98	0.7808
5	17	100	O(0.6 M)	30	25	0.42	577	1.48	−60.10(T_g)	102	0.7601
6	170	100	E(10 atm) H(0.3 M)	30	35	1.56	233	2.67	51.06(T_m)	23.2	0.8737
7	170	100	E(10 atm) O(0.3 M)	30	35	1.94	196	2.45	−61.50(T_g) 47.59(T_m)	25.4	0.8649

[a] Ni complex (0. 17 or 0.017 mmol) activated with 100 equiv of MAO

[b] *E* ethylene; *H* 1-hexene; *O* 1-octene

[c] Molecular weight data were determined by GPC with polystyrene standards

[d] T_m and T_g were determined by DSC

[e] Branching degree was determined by ^{1}H NMR and IR spectroscopy (accurate to ca. 2%)

[f] Density was determined by standard method (GB/T 1033.1-2008)

greater influence on the ethylene polymerization in both solvents. With the rise in ethylene pressure, the branching degree and density decreased, whereas T_m and catalyst activity increased, without markedly affecting the molecular weights. With the rise in polymerization temperature, the branching degree and density increased, whereas the molecular weights, T_m, and catalyst activity declined. When *n*-hexane was used as the solvent, the branching degree of the polymers obtained at a lower pressure (10 atm) in *n*-hexane was as low as the level of polymers obtained at a higher pressure (>130 atm) in toluene. The results suggest that because of the reduction of β-H elimination in the process of ethylene polymerization in *n*-hexane, the branching degree of polyethylenes declines, leading to the rise in T_m and density. T_m (ca. 120 °C) of the polymers obtained at a lower pressure (10 atm) in *n*-hexane can increase to the level of polymers obtained only at a higher pressure (>260 atm) in toluene [34]. The density of the polyethylene can rise to 0.9114 g/cm^3, which is in the range of the LLDPE when ethylene pressure is 10 atm at 35 °C. Based on the properties of polyethylene obtained in *n*-hexane, the polymers are qualified for LLDPE products commonly used as film materials and generally produced by the copolymerization of ethylene and long-chain α-olefins (1-hexene, 1-octene, etc.) catalyzed by Ziegler–Natta or Metallocene catalysts. As a result, polyolefins with multi-branched and different physical properties can be obtained easily by tuning the reaction conditions of ethylene homopolymerization catalyzed through the Ni(II)-based-α-diimine complex [(2,6-i-Pr)$_2$C$_6$H$_3$-DAB(An)]NiBr$_2$ activated by methylalumoxane in hexane.

Polymerization of 1-hexene and 1-octene using (Ar=C(An)–C(An)=NAr)NiBr$_2$ as catalyst

The Ni(II)-based-α-diimine complex [(2,6-i-Pr)$_2$C$_6$H$_3$-DAB(An)]NiBr$_2$ activated by methylalumoxane was used to catalyze the homopolymerization of 1-hexene and 1-octene in *n*-hexane at 25 °C. The obtained poly(1-hexene) and poly(1-octene) were all amorphous, and their glass transition temperature T_g shown in Table 1 (entries 4, 5) was −51.5 and −60.1 °C, respectively. In Table 1, their density (<0.800 g/cm^3) is much lower than that of polyethylene. This finding may be due to

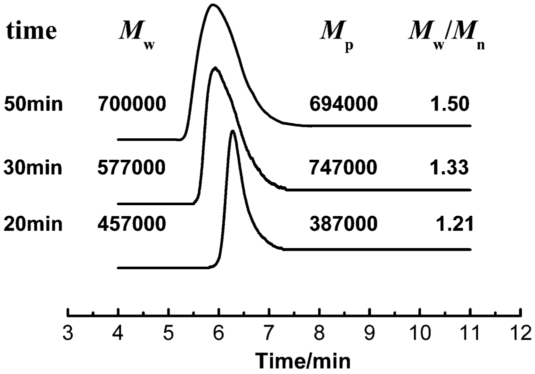


Fig. 2 The GPC traces of poly(1-octene)s obtained at different times in *n*-hexane at 25 °C. 83 × 58 mm (600 × 600 DPI)

the increase in branching degree from 22.7 to about 100.0. The catalyst activity is about 420 kg/mol Ni h^{-1}. The literature [11–14] only reports the living polymerization of α-olefins (propylene, 1-hexene) in toluene at −10 °C catalyzed by Ni(II)-based-α-diimine complex [(2,6-i-Pr)$_2$C$_6$H$_3$-DAB(An)]NiBr$_2$. The polymerization of 1-octene can even carry on in a controlled manner in *n*-hexane even at 25 °C. The GPC traces of poly(1-octene)s obtained at different reaction times are shown in Fig. 2.

Figure 3 shows the M_w and M_w/M_n values monitored as a function of monomer conversion for the polymerization of 1-octene. The molecular weight determined by GPC calibrated using PS standards increases linearly with the monomer conversion over a broad molecular weight range (200–700 kg/mol). The polydispersity indexes are between 1.20 and 1.50, indicating that this polymerization system possesses the characteristic of controlled polymerization.

Copolymerization of ethylene with 1-hexene and 1-octene using (Ar=C(An)–C(An)=NAr)NiBr$_2$ as catalyst

The literature [13] not only reports the living polymerization of α-olefins (propylene, 1-hexene) in toluene at −10 °C using α-diimine Ni(II)-based catalysts but also the synthesis of a variety of unique diblock (polypropylene-*b*-poly(1-hexene)) and triblock poly(1-octadecene)-*b*-polypropylene-*b*-poly(1-octadecene) polymers at −10 or −15 °C through the sequential monomer addition to catalyst [(2,6-i-Pr)$_2$C$_6$H$_3$-DAB(An)]NiBr$_2$/MMAO in toluene. The preparation of α-olefin-based A-B-A triblock copolymers provides a methodology for the synthesis of elastomeric polyolefins. However, the operation procedures for low-temperature reaction conditions and sequential monomer addition are complex and trivial. Moreover, the toxicity of toluene is much higher than that of *n*-hexane.

In our study, the Ni(II)-based-α-diimine complex [(2,6-i-Pr)$_2$C$_6$H$_3$-DAB(An)]-NiBr$_2$ activated by methylalumoxane was also used to catalyze the copolymerization

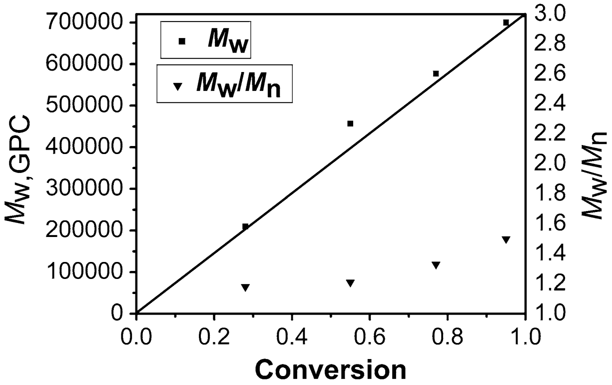


Fig. 3 Dependence of molecular weight and polydispersity on monomer conversion for the polymerization of 1-octene in *n*-hexane 83 × 58 mm (600 × 600 DPI)

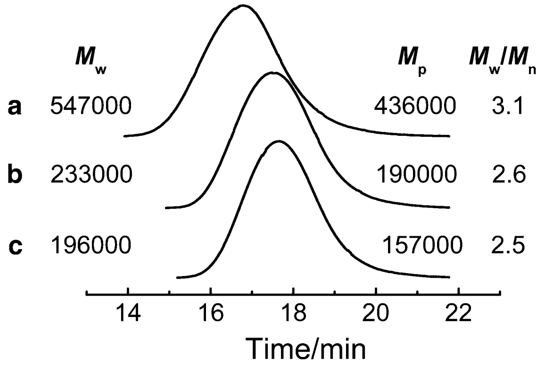


Fig. 4 The GPC traces of polymers produced in hexane at 35 °C: *a* polyethylene; *b* ethylene/1-hexene copolymer; *c* ethylene/1-octene copolymer 83 × 58 mm (600 × 600 DPI)

of ethylene with 1-hexene and 1-octene in *n*-hexane at 35 °C. The GPC traces of polyethylene and copolymers are shown in Fig. 4.

In Fig. 4, the molecular weights of ethylene/1-hexene and ethylene/1-octene copolymers are lower than that of polyethylene obtained under the same reaction conditions. The catalyst activity (1.56×10^3 and 1.94×10^3 kg/mol Ni h^{-1} for ethylene/1-hexene and ethylene/1-octene copolymerization system, respectively) is also lower than that (4.0×10^3 kg/mol Ni h^{-1}) for the homopolymerization of ethylene. The density and T_m of ethylene copolymer with 1-hexene is 0.874 g/cm^3 and 51.1 °C, respectively. The copolymer of ethylene and 1-octene is semicrystalline polymer, and its T_g and T_m is −61.5 and 47.6 °C, respectively; these results are similar to those of triblock poly(1-octadecene)-*b*-polypropylene-*b*-poly(1-octadecene) ($T_g = -52$ °C and $T_m = 69$ °C) reported by Brookhart and coworkers [13]. The density is 0.865 g/cm^3. All these values are presented in Table 1 (entries 6–7). Compared with that of ethylene homopolymer, the branching degree of the copolymers increased. This finding indicates that 1-hexene and 1-octene participated in the copolymerization with ethylene, leading to the rise in branching degree and the decline in copolymer density compared with polyethylene. However, compared with those of the homopolymer of 1-hexene and 1-octene, the copolymer density, T_m, and catalyst activity all increased, whereas the branching degree decreased. This finding further confirms that 1-hexene and 1-octene copolymerized with ethylene efficiently and that the activity of ethylene was higher than 1-hexene and 1-octene, leading to the decline in branching degree and rise in the copolymer density, T_m, and catalyst activity compared with the homopolymer of 1-hexene and 1-octene. These results suggest that through the ordinary copolymerization of ethylene and α-olefin using this catalyst in *n*-hexane at room temperature, the elastomeric copolymers can also be prepared and the operation procedure can be simple.

During (co)polymerization, the long-chain α-olefin insertions occur in a 2,1 or 1,2 manner. The migration of nickel caused not only the formation of branches but also the runs of methylene units in the backbone caused by chain running, producing the microstructures of these polymers unlike those of poly(α-olefins) made by early metal catalysts [35].

Conclusions

(1) The Ni(II)-α-diimine catalyst $[(2,6\text{-i-Pr})_2C_6H_3\text{-DAB(An)}]NiBr_2$ plus methylaluminoxane was successfully used for the homopolymerization of ethylene, 1-hexene, and 1-octene and the copolymerization of ethylene with 1-hexene and 1-octene in *n*-hexane. In the polymerization of 1-octene, the molecular weight increased linearly with the monomer conversion over a broad molecular weight range of 200–700 kg/mol, and the polydispersity index was between 1.20 and 1.50. These findings indicate that this polymerization system possesses the characteristic of controlled polymerization.

(2) By determining the molecular weight, T_g, T_m, branching degree, and density of the obtained polymers, ethylene pressure and polymerization temperature were found to have a greater influence on the molecular weight, T_m, branching degree, and density of polyethylene. Compared with that of ethylene homopolymer, the branching degree of ethylene copolymers prepared by the copolymerization of ethylene with 1-hexene or 1-octene increased, whereas the molecular weight, density, T_m, and catalyst activity declined. However, compared with those of the homopolymer of 1-hexene or 1-octene, density, T_m, and catalyst activity of the copolymers increased, whereas the molecular weight and branching degree decreased.

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