

POLYMERIZATION OF 1-OCTENE AND DETERMINATION OF MARK-HOUWINK CONSTANTS OF POLY(1-OCTENE)^{*}

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Abstract The polymerization of 1-octene initiated by methylalumoxane (MAO)-activated Ni(II)-based- α -diimine complexes [(2,6-*i*-Pr)₂C₆H₃-DAB(An)]NiBr₂ was investigated. Using this catalyst, poly(1-octene)s with molecular weight between 100×10^3 and 400×10^3 and polydispersity (M_w/M_n) between 1.3 and 1.5 were synthesized successfully by varying reaction time at room temperature. The poly(1-octene)s were amorphous polymers and could be well soluble in tetrahydrofuran (THF). After fractional precipitation, poly(1-octene)s with narrow molecular weight distributions ($M_w/M_n \leq 1.12$) were obtained. Their weight-average molecular weights were measured by gel permeation chromatography (GPC) in conjunction with online model BI-MwA multiangle laser light scattering (MALLS), and their intrinsic viscosities were measured by Maron's single-point method. The k and α values in Mark-Houwink equation $[\eta] = KM^\alpha$ in THF at 40°C were 0.089 mL/g and 0.61 respectively.

Keywords: Nickel(α -diimine) catalyst; Poly(1-octene); Mark-Houwink constants.

INTRODUCTION

In recent years, the polymerization of α -olefins has been extensively investigated, especially the long-chain α -olefins. Guevara *et al.*^[1] studied the homopolymerization of long chain α -olefin (1-octadecene) and its copolymerization with ethylene using metallocene catalysts *rac*-Et(Ind)₂ZrCl₂ and *rac*-Me₂Si(Ind)₂ZrCl₂. Quijada *et al.*^[2] further studied the homopolymerization of 1-octadecene and its copolymerization with ethylene using Ph₂C(Flu)(CP) ZrCl₂ as catalyst. Brull *et al.*^[3] synthesized poly- α -olefins ranging from poly(1-pentene) to poly(1-octadecene) with narrow polydispersities catalyzed by (CH₃)₂Si(2-methylbenze indenyl)₂ZrCl₂ and methylaluminoxane. Skupinski *et al.*^[4] carried out the homopolymerization of ethylene, propylene, 1-butene, 1-pentene, 1-hexene and their copolymerization with ethylene using cyclopentadienyl-titanium complexes containing-OC₆H₄X ligands (X = Cl, Me). Brookhart *et al.*^[5, 6] synthesized a series of Pd(II)- and Ni(II)-based-diimine catalysts and used them to catalyze the homopolymerization of ethylene and α -olefins (propylene, 1-hexene and 1-octadecene). Santos *et al.*^[7] 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.

The long chain α -olefin polymers have been widely used as lubricating oils^[8], oil-soluble drag reduction agent^[9–11] and solubilizer^[12]. Among long chain α -olefin polymers, poly(1-octene) is a very effective drag

^{*} This work was supported by the program for new century excellent talents in Chinese universities and Beijing Municipal Education Commission.

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Received August 28, 2010; Revised November 3, 2010; Accepted November 5, 2010

doi: 10.1007/s10118-011-1069-z

reduction agent. Its drag reduction rate is more than 40%^[13]. Therefore, the study on poly(1-octene) is of great use. Scientists^[14–16] have conducted extensive study on its preparation and the relationship of its structure and properties. The polymerization of 1-octene has been catalyzed by Ziegler-Natta catalysts^[17–20], metallocene catalysts^[21–24] and the late transition metal catalysts^[25]. For example, Kaur *et al.*^[20] synthesized poly(1-octene) using high performance MgCl₂-supported TiCl₄ in combination with triethyl aluminum as cocatalyst in *n*-hexane. Kotzabasakis *et al.*^[24] synthesized the poly(1-octene) using Cs-symmetry hafnium metallocene[(*p*-Et₃Si)C₆H₄]₂C(2,7-di-*tert*-BuFlu)(C₅H₄)Hf(CH₃)₂ and tetrakis(pentafluorophenyl) borate dimethylanilinium salt ([B(C₆F₅)₄]-[Me₂NHPh]⁺) in toluene at 0°C. Subramanyam *et al.*^[25] studied the homopolymerization of 1-hexene and 1-octene with nickel(α -diimine) catalyst and found that different types of branch structures were formed in the backbone. However, to the best of our knowledge, the polymerization of 1-octene catalyzed by late transition metal catalysts has seldom been reported so far. Generally, polyolefins are difficult to be dissolved in common solvents at room temperature. Their molecular weights and molecular weight distributions are often measured using higher temperature GPC in trichlorobenzene or benzene halides. Although poly(1-octene) can be dissolved in cyclohexane and bromobenzene at room temperature^[26], and their *k* and α values in Mark-Houwink equation have been measured, their real molecular weights can not be measured by common GPC in mostly used solvent THF. We found that poly(1-octene) could be well soluble in THF. If *k* and α value in THF could be obtained, molecular weights and molecular weight distributions of poly(1-octene) will be determined conveniently by GPC with THF as mobile phase.

In this paper, the polymerization of 1-octene initiated by methylalumoxane-activated Ni(II)-based- α -diimine complexes [(2,6-*i*-Pr)₂C₆H₃-DAB(An)]NiBr₂ was investigated. This catalyst allowed us to prepare poly(1-octene) with molecular weight between 100 × 10³ and 400 × 10³ and polydispersity (*M_w*/*M_n*) between 1.3 and 1.5 by varying reaction time at room temperature. Furthermore, using fractional precipitation technique, poly(1-octene)s with different molecular weights and narrow molecular weight distribution (*M_w*/*M_n* ≤ 1.12) were obtained. Their weight-average molecular weights were measured by GPC in conjunction with online model BI-MwA MALLS, and their intrinsic viscosities were measured by Maron's single-point method. The *k* and α values in Mark-Houwink equation [η] = *KM^α* were then calculated.

EXPERIMENTAL

Materials

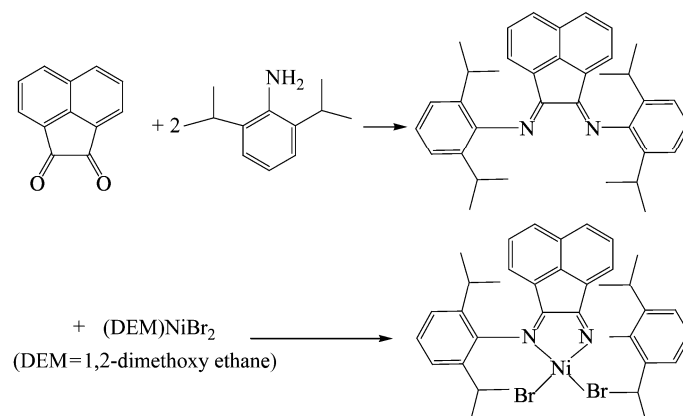
Toluene, hexane, THF and diethyl ether were distilled under nitrogen from sodium benzophenone ketyl. Methylene chloride was distilled under nitrogen from P₂O₅. 1-Octene was purchased from Alfa Aesar Chemical Co, purged with argon and dried over 0.4 nm molecular sieves. 1,2-Dimethoxy ethane bromide nickel ((DME)-NiBr₂), acenaphthoquinone, 2,6-diisopropylaniline and a 10% solution of MAO in toluene purchased from Aldrich Chemical Co were used directly.

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 CH₂Cl₂, 3.22 g of diimine were obtained with yield 83%. It should be pointed out that acenaphthoquinone was not completely soluble in our reaction conditions.

Synthesis of the (Ar=C(An)-C(An)=NAr)NiBr₂ (Ar = 2,6-*i*-PrPh)

0.187 g (0.4 mmol) of (2,6-*i*-Pr)₂C₆H₃-DAB(An) and 0.111 g (0.36 mmol) of (DME)NiBr₂ 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 reaction was stirred at room temperature for 18 h. The solvent was removed under vacuum resulting in a red/brown solid which was then 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 were obtained with yield 80%. The synthesis route of the catalyst was shown in Scheme 1.



Scheme 1 The synthesis route of the catalyst [(2,6-*i*-Pr)₂C₆H₃-DAB(An)]NiBr₂

Polymerization of 1-Octene Using (Ar=C(An)-C(An)=NAr)NiBr₂ as Catalyst

1-Octene (10 mL) was added to a suspension of [(2,6-*i*-Pr)₂C₆H₃-DAB(An)]NiBr₂ (12 mg, 0.017 mmol) in 40 mL of dry toluene. The temperature was controlled at room temperature and 2.00 mL of a 10% MAO solution in toluene was added. After stirring the reaction for 2 h, diluted hydrochloric acid and excess of methanol were added to quench the polymerization and precipitate the polymer. Solid poly(1-octene) was recovered from vacuum overnight to yield 2 g polymer.

Purification and Fractionation of Poly(1-octene)

The poly(1-octene)s obtained from our study were somewhat discolored. In order to get clear polymer fractions, the poly(1-octene)s were redissolved in tetrahydrofuran, followed centrifugation and reprecipitation using methanol as precipitant was undertaken. The resulting clear polymer was separated by fractional precipitation performed by the standard technique of solvent-nonsolvent pair (tetrahydrofuran-methanol) precipitation at room temperature in very dilute solution into seven fractions.

Characterization

Monomer conversion was obtained gravimetrically. ¹H-NMR spectra were recorded on a Bruker AV 600-MHz spectrometer purchased from Brook-Heaven Corporation of America with CDCl₃ as solvent at room temperature. The elemental contents of the compounds were measured by an HP-MOD/106 elemental analysis instrument. The glass transition temperature *T*_g of poly(1-octene) was determined by a 204F differential scanning calorimeter (DSC) purchased from Netzsch Company, Germany, the polymer samples were quenched from the melt to amorphous state and then heated to the melt again at a rate of 20 K/min. The specific refractive index increment (*dn/dc* value) of poly(1-octene) was measured using a model BI-DNDC differential refractometer at 620 nm and 40°C in THF. Weight-average molecular weights and molecular weight distributions of poly(1-octene) which was obtained by fractional precipitation were determined by GPC in conjunction with online model BI-MwA multiangle laser light scattering (MALLS). The instrument was purchased from Brook-Heaven Corporation. The THF was used as the mobile phase at 1 mL/min driven *via* a 515 HPLC pump at 40°C, the columns were shodex-KF-806M × 2 and the laser was a 35 mW solid-state laser at 620 nm and a value of 0.07979 mL/g was used for *dn/dc* value of poly(1-octene). All solutions were filtered through 0.2 μm filters before analysis. Intrinsic viscosities were measured using Ubbelohde viscometer with capillary diameter of 0.47 mm and ball volume 3 mL. Solutions with relative viscosities between 1.2 and 1.4 were used. The temperature control was maintained to ±0.01°C using a thermostated water bath. Solvents and solutions were filtered through 0.2 μm pore size teflon membrane filters directly into the viscometers. Measurements were made in THF at 40°C.

RESULTS AND DISCUSSION

Characterization of $Ar=C(An)-C(An)=NAr$ 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)] $NiBr_2$ complexes were prepared based on literature procedures^[5, 6, 27]. The ^1H -NMR of the $(2,6-i-Pr)_2Ph$ -DAB(An) ($CDCl_3$, δ): 7.86 (d, 2H, An: Hp), 7.36 (dd, 2H, An: Hm), 6.62 (d, 2H, An: Ho), 7.27 (m, 6H, Ar: Hm, Ho and Hp), 3.02 (septet, 4H, $-CH(CH_3)_2$), 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 1-Octene Using $(Ar=C(An)-C(An)=NAr)NiBr_2$ as Catalyst

The Ni(II)-based- α -diimine complexes $[(2,6-i-Pr)_2C_6H_3$ -DAB(An)] $NiBr_2$ activated by methylalumoxane were used to catalyze the polymerization of 1-octene at room temperature. The GPC traces of poly(1-octene)s obtained at different reaction times are shown in Fig. 1.

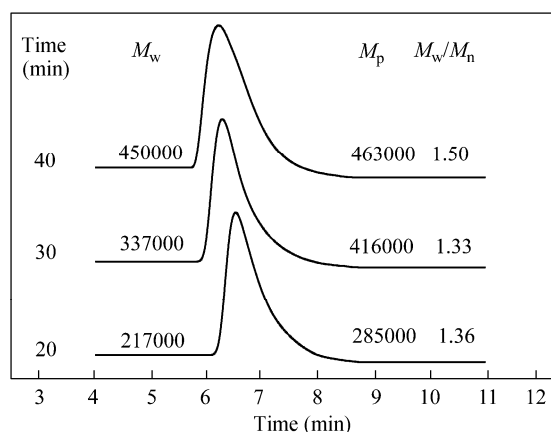


Fig. 1 The GPC traces of poly(1-octene)s obtained at different times in toluene

Figure 2 are the M_w and M_w/M_n values monitored as a function of conversion for the polymerization of 1-octene. The molecular weight determined by GPC calibrated using PS standards increased linearly with conversion over a broad molecular weight range (200×10^3 to 450×10^3), and the polydispersity indexes were between 1.30 and 1.50. It can be seen that the polymerization possessed characteristics of controlled polymerization. The catalytic efficiency of catalyst was up to 180 kg/(mol Ni h). The obtained poly(1-octene) was amorphous and its glass transition temperature T_g determined by DSC was $-54^\circ C$ as shown in Fig. 3.

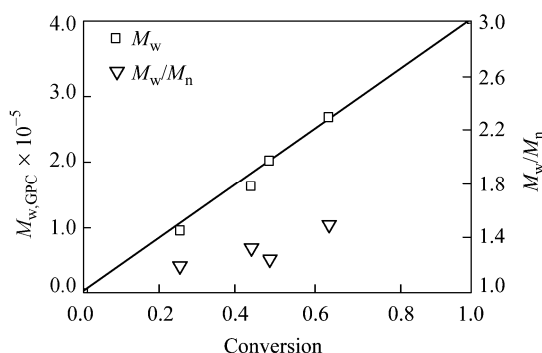


Fig. 2 Dependence of molecular weight and polydispersity on conversion in coordination polymerization of 1-octene in toluene

Figure 4 was the ^1H -NMR spectrum of poly(1-octene). The signal in the region of $\delta = 1.0\text{--}1.4$ was the overlapping peaks of methylene and methine groups. The signals at $\delta = 0.75$, 0.83 and 0.88 were attributed to methyl branches of poly(1-octene).

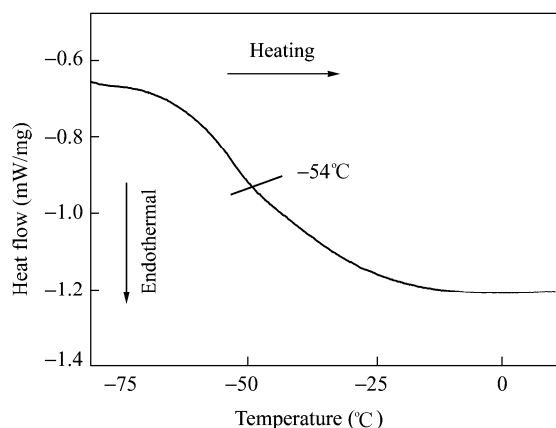


Fig. 3 DSC thermogram of poly(1-octene)

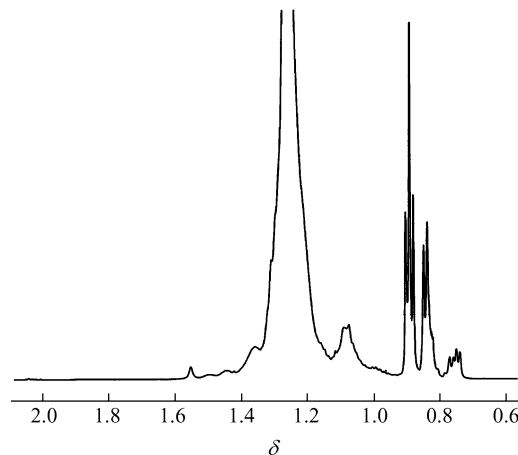


Fig. 4 ^1H -NMR spectrum of poly(1-octene) synthesized using $[(2,6\text{-}i\text{-Pr})_2\text{C}_6\text{H}_3\text{-DAB(An)}]\text{NiBr}_2/\text{MAO}$ in toluene

The degree of branching was estimated from ^1H -NMR integration of the methyl, methylene and methine groups according to the Eq. (1). It was found that there were 98 branching points per one thousand carbon atoms.

$$\text{Degree of branching} = \frac{S_{\text{CH}_3} / 3}{S_{\text{CH}_3} / 3 + S_{\text{CH}} + S_{\text{CH}_2} / 2} \times 1000 \quad (1)$$

where S_{CH_3} , S_{CH_2} and S_{CH} are the integrated area of methyl, methylene and methine groups, respectively.

Determination of dn/dc of the Poly(1-octene) in THF

In order to calibrate the instrument to get the calibration constant of the instrument, seven different concentrations of KCl aqueous solution (1, 2, 3, 4, 5, 6 and 7 mg/mL) were prepared respectively. The calibration constant was calculated according to the Eq. (2).

$$\Delta n = K \cdot \Delta V_g \cdot n_0 \quad (2)$$

where Δn is the literature value for the difference in refractive index between the KCl aqueous solution and pure water at the concentration. ΔV_g is the difference in voltage which formed in order to calculate the instrument's calibration constant K . n_0 is the refractive index of the pure water. It was $(2.665 \times 10^{-4} \pm 1.6 \times 10^{-6}) \text{ V}^{-1}$ with the error to be 0.6%, which was less than 1%. The calibration constant was $(2.665 \times 10^{-4} \pm 1.6 \times 10^{-6}) \text{ V}^{-1}$ with the error to be 0.6%, which was less than 1%.

Poly(1-octene) solutions in THF with five different concentrations (1.2, 1.4, 1.6, 1.8 and 2.0 mg/mL) were prepared respectively to calculate the dn/dc value of poly(1-octene) in THF. The left-hand graph in Fig. 5 is the plot of V_g versus polymer concentration. At each polymer concentration the difference in voltage ΔV_g is determined. Given the THF's refractive index ($n = 1.396$) and the calibration constant ($k = 2.665 \times 10^{-4}$), Δn is then calculated from ΔV_g according to Eq. (2). The right-hand graph in Fig. 5 is the plot of Δn versus polymer concentration. The slope of this line is the dn/dc value which is $(7.979 \times 10^{-2} \pm 1.6 \times 10^{-4}) \text{ mL/g}$.

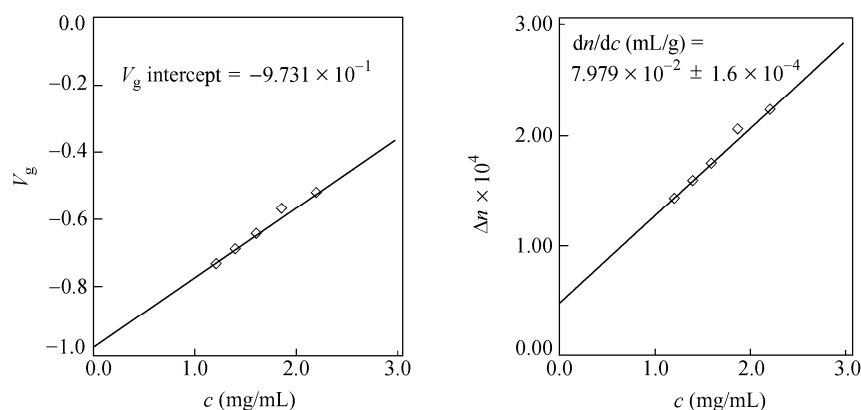


Fig. 5 The curves for determining the dn/dc value of poly(1-octene) in THF at 40°C

Determination of Weight Average Molecular Weight and Molecular Weight Distribution of Poly(1-octene)s by GPC in Conjunction with Online MALLS

The real weight-average molecular weights of poly(1-octene)s were determined by GPC in conjunction with online model BI-MwA MALLS. Figure 6 shows their GPC curves. It can be seen that the poly(1-octene) samples with molecular weight between 120×10^3 and 750×10^3 and polydispersities (M_w/M_n) between 1.04 and 1.12 were obtained by fractional precipitation using THF as the solvent and methanol as the precipitant. The molecular weight distributions were narrow and the curves content with Gaussian distributions.

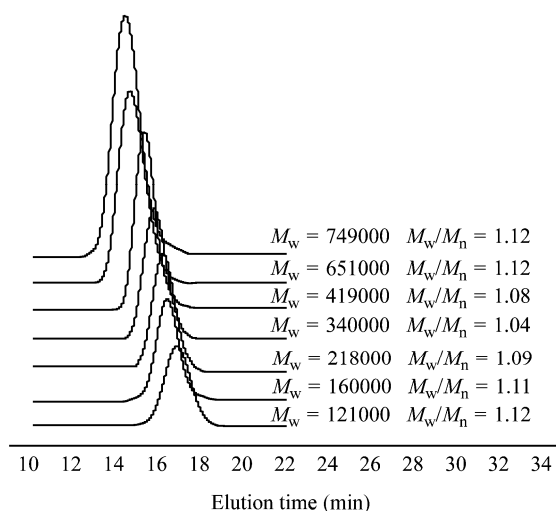


Fig. 6 The GPC traces of poly(1-octene)s obtained by fractional precipitation

Measurement of the Intrinsic Viscosities of the Poly(1-octene)s

The intrinsic viscosity of polymer solutions could be determined by dilution method. But this method must measure the viscosity of polymer solutions with five different concentrations. The operation is complex and time consuming. Especially when the amount of polymer sample is very little, it is difficult to obtain polymer solution by dilute method. Although some people had proposed to determine the intrinsic viscosity of polymer solutions by measuring the viscosity at only two different concentrations, it was still based on the procedure of dilute extrapolation. Therefore, the intrinsic viscosity of polymer solution is often determined by single-point method, which is simple and effective. The most commonly used equation in single-point method is shown in Eq. (3).

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2}/c \quad (3)$$

However, the essential prerequisite for using the above Eq. (3) is that the sum of K' value in Huggins Eq. (4) plus β value in Kramer Eq. (5) should be 0.5^[28]. For linear and flexible polymer chains in good solvents, the value of $K' + \beta$ is generally 0.5.

$$\eta_{sp}/c = [\eta] + K'[\eta]^2 c \quad (4)$$

$$\ln \eta_r/c = [\eta] - \beta[\eta]^2 c \quad (5)$$

A poly(1-octene) sample with weight-average molecular weight 750×10^3 was chosen to confirm whether $K' + \beta$ is equal to 0.5 or not using dilution extrapolation. The results are summarized in Fig. 7.

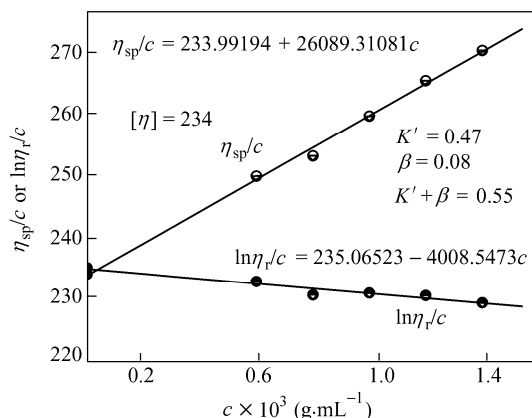


Fig. 7 Plot of η_{sp}/c and $\ln \eta_r/c$ for a sample of poly(1-octene) in THF at 40°C

It can be seen that the value of K' was 0.47 and that the value of β was 0.08. The sum of K' plus β was 0.55, which was somewhat deviated from 0.5. If Eq. (3) was used to calculate the intrinsic viscosity in single-point method, a considerable error will not be neglected. The above result also further confirm that the poly(1-octene)s synthesized in this study was branched polymers. For the case that $K' + \beta$ was not equal to 0.5, Maron^[29] proposed another method to calculate intrinsic viscosity according to Eq. (6), where $\gamma = K'/\beta$. It is worth noting that the Eq. (6) is not only applicable to the polymers with linear and flexible chain but also for branching or rigid chain polymers.

$$[\eta] = [\eta_{sp} + \gamma \ln \eta_r/c]/(1 + \gamma)c \quad (6)$$

The intrinsic viscosity of seven poly(1-octene) samples with different weight-average molecular weights and narrow molecular weight distributions was measured. The results are summarized in Table 1.

Table 1. The weight average molecular weights of poly(1-octene)s and their corresponding intrinsic viscosities

Samples	1#	2#	3#	4#	5#	6#	7#
M_w	121000	160000	218000	340000	419000	651000	749000
$[\eta]$ (mL·g ⁻¹)	108.6	128.8	165.1	205.1	228.0	312.9	338.9

Calculation of k and α Value of Poly(1-octene)

The relationship of the intrinsic viscosity of poly(1-octene)s with their weight average molecular weight could be expressed by Mark-Houwink Eq. (7). The logarithmic equation of Mark-Houwink equation is shown in Eq. (8).

$$[\eta] = kM^\alpha \quad (7)$$

$$\lg[\eta] = \lg k + \alpha \lg M \quad (8)$$

A plot of $\lg[\eta]$ versus $\lg M_w$ is shown in Fig. 8. The linear correlation coefficient R is 0.99732. The k value of the poly(1-octene) solution was 0.089 mL/g calculated from the intercept of the longitudinal coordinate and the α value of the poly(1-octene) was 0.61 calculated from the slope of this line.

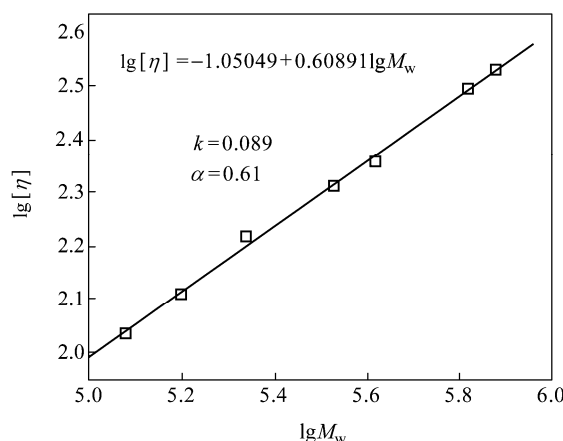


Fig. 8 Plot of $\lg[\eta]$ versus $\lg M_w$ of the poly(1-octene)s in THF at 40°C

CONCLUSIONS

The polymerization of 1-octene initiated by methylalumoxane-activated Ni(II)-based- α -diimine complex $[(2,6-i\text{-Pr})_2\text{C}_6\text{H}_3\text{-DAB(An)NiBr}_2]$ could proceed in a living fashion. The molecular weight increased with reaction time, and the polydispersity index was between 1.30 and 1.50. The dn/dc value of poly(1-octene) measured in THF at 40°C was 0.07979 mL/g. The k and α value of poly(1-octene) in Mark-Houwink equation $[\eta] = KM^\alpha$ in THF at 40°C was 0.089 mL/g and 0.61 respectively.

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