

Vinyl-polymerization of norbornene with novel anilido–imino nickel complexes/methylaluminoxane: Abnormal influence of polymerization temperature on molecular weight of polynorbornenes

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Abstract

Herein reported are investigations of norbornene polymerization by novel anilido–imino nickel complexes $[(Ar^1N=CHC_6H_4NAr^2)NiBr]_2$ ($Ar^1 = Ar^2 = 2,6$ -dimethylphenyl, **1**; $Ar^1 = 2,6$ -dimethylphenyl, $Ar^2 = 2,6$ -diisopropylphenyl, **2**; $Ar^1 = Ar^2 = 2,6$ -diisopropylphenyl, **3**; $Ar^1 = 2,6$ -diisopropylphenyl, $Ar^2 = 2,6$ -dimethylphenyl, **4**) activated with methylaluminoxane (MAO). It was found that at polymerization temperatures below 50 °C, the average molecular weights of the obtained polynorbornenes catalyzed by these four catalytic systems increase with raising temperature, displaying bimodal distribution in GPC curves. The abnormal influence of polymerization temperature could be attributed to the existence of two kinds of catalytic species: heterobimetallic species $LNi(II)(\mu-Me)_2AlMe_2$ (**I**) and monometallic species $LNi(II)Me$ (**II**) ($L =$ anilido–imino ligand) at lower temperature. The former affords a lower molecular weight polymer and the latter higher molecular weight one. With raising polymerization temperature above 50 °C, the species **I** disappears and only species **II** exists in polymerization systems, resulting in a normal relation of molecular weight to polymerization temperature. From a kinetic study of the norbornene polymerization catalyzed by **1**/MAO catalyst at 70 °C, the polymerization rate (R_p) can be expressed by the formulation: $R_p = k[NBE]^{1.93}[Ni]^{0.88}$. Moreover, the mechanism of the norbornene polymerization using the anilido–imino nickel complexes activated with MAO is also presented and discussed. © 2005 Elsevier B.V. All rights reserved.

Keywords: Anilido–imino nickel complexes; Norbornene; Addition polymerization; Polynorbornene

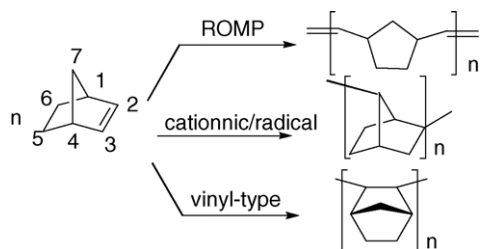
1. Introduction

Norbornene (bicyclo[2,2,1]hept-2-ene) can be polymerized via ring-opening metathesis polymerization (ROMP), cationic or radical polymerization and vinyl-type polymerization, which leads to their corresponding polymers with different structures and properties (Scheme 1) [1]. For vinyl addition polymerization, the bicyclic structural unit remains intact, and only the double bond of the π component is opened. Therefore, vinylic polynorbornene, a special polymer with constrained rings in each unit, possesses interesting and unique properties such as high chemical resistance, good

UV resistance, low dielectric constant, high glass transition temperature, excellent transparency, large refractive index and low birefringence [1e,f]. However, the addition polymerization is much less developed for norbornene than ROMP [1e,f].

Driven by industrial application, the vinyl-polymerization of norbornene inspired the interest of chemists and chemical engineers [2]. Conventional Ziegler–Natta catalysts, such as the $TiCl_4-AlR_3$ [1a], $TiCl_3-AlMe_3$ [1c] and $TiCl_4-LiAlH_4$ [3] systems, can cause ROMP or addition polymerization, depending on the ratio of the cocatalyst Al component to Ti. It is well known that α -olefins and cyclic olefins can be efficiently polymerized with metallocene/methylaluminoxane catalytic systems [4]. Most of the obtained polynorbornenes are insoluble in common hydrocarbons due to high crys-

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Scheme 1. Three polymerization mechanisms of norbornene.

tallinity and decompose before they melt [5], though the half-titanocene complexes have recently been reported to produce soluble polynorbornenes [6]. In 1981, the complex $[\text{Pd}(\text{CH}_3\text{CN})_4][\text{BF}_4]_2$ was first employed for the polymerization of norbornene by Sen and Lai [7]. Subsequently, various late transition metal complexes of nickel, cobalt and palladium have been used as catalysts for norbornene vinyl-polymerization [8]. The obtained polymers have high molecular weights with low polydispersities and are soluble in chlorohydrocarbons.

In order to fully exploit the potential of this interesting class of polymers, designing new catalyst for vinyl-polymerization and copolymerization of norbornene is still a great challenge. We have concentrated our attention on the vinylic addition homopolymerization and the copolymerization of norbornene with other monomers due to their high glass transition temperatures (T_g) [6a,8g–i,9]. Previously, in a comparison of the steric effect of β -diketiminato ligand with more easily modified features of the salicylaldiminate ligand, we have reported the synthesis and molecular structure of anilido–imino nickel complexes, and found that the nickel complexes showed high activities for norbornene polymerization. Additionally, anilido–imino nickel complexes exist in the form of dinuclear and bromine-bridged structure with tetrahedral geometries about nickel in the solid state. However, there is an equilibrium that shifts between the monomer and dimer depending on solvent, concentration and temperature [9].

In this paper, as a followup to our preliminary results, we report the detailed investigation of the norbornene polymerization behavior using anilido–imino nickel complexes activated with MAO. Influences of temperature, reaction time, catalyst concentration and monomer concentration on norbornene polymerization were investigated. Moreover, mechanistic consideration for norbornene polymerization using anilido–imino nickel complexes/MAO systems are also proposed.

2. Experimental

2.1. Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried

and purified nitrogen using standard Schlenk and vacuum-line techniques. Toluene was dried over sodium metal and distilled under nitrogen. Anilido–imino nickel complexes were synthesized according to the previous reported methods [9]. Norbornene (Acros) was purified by distillation over potassium and used as a solution (4.26 mol/L) in toluene. Methylaluminoxane was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0–60 °C with $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ as a water source. The initial $[\text{H}_2\text{O}]/[\text{TMA}]$ molar ratio was 1.3. Other commercially available reagents were purchased and used without purification.

2.2. Polymerization

In a typical procedure, the appropriate MAO solid was introduced into a round-bottom glass flask, and then a toluene solution of norbornene (4.26 mol/L) was added via a syringe. Toluene and nickel complexes solution (10^{-3} M) were syringed into the well-stirred solution in order, and the total reaction volume kept 20 mL. The reaction was continuously stirred for an appropriate period at polymerization temperature. Except for 0 °C, which was maintained with an ice-water bath, the other reaction temperatures were controlled with an external oil bath. Polymerizations were terminated by adding 200 mL of the acidic ethanol (ethanol–HCl, 95:5). The resulting precipitated polymers were collected and treated by filtration, washing with ethanol several times and drying in vacuum at 60 °C to a constant weight.

2.3. Characterization

Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution (MWD) of the polymers were performed on a Waters 150C instrument using standard polystyrene as the reference and with chlorobenzene as the eluent at 40 °C. The polymer samples were processed into KBr thin films for IR measurements. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet NEXUS–670 FTIR spectrometer. ^1H NMR spectra were measured on an INOVA 500 MHz at room temperature in *o*-dichlorobenzene- d_4 solution for polymers (using TMS as internal standard). ^{13}C NMR spectra of the polymers in *o*-dichlorobenzene- d_4 were recorded on an INVOA 500 MHz spectrometer operating at 120 °C. The chemical shift value (127.3 ppm) of *o*-dichlorobenzene was used as an internal standard. Differential scanning calorimetry (DSC) analysis was conducted with a Perkin-Elmer DCS-7 system. The DSC curves were recorded at a heating rate of 10 °C/min. The cooling rate was 10 °C/min. TGA data were collected with a TG-290C thermal analysis system instrument under a nitrogen atmosphere up to 600 °C at heating rate of 10 °C/min. Wide-angle X-ray diffraction (WAXD) curves of the polymer powders were obtained using a D/Max-III A powder X-ray diffractometer.

3. Results and discussion

The anilido–imine ligands and the corresponding nickel complexes **1–4** $[(Ar^1N=CHC_6H_4NAr^2)NiBr]_2$ ($Ar^1 = Ar^2 = 2,6$ -dimethylphenyl, **1**; $Ar^1 = 2,6$ -dimethylphenyl, $Ar^2 = 2,6$ -diisopropylphenyl, **2**; $Ar^1 = Ar^2 = 2,6$ -diisopropylphenyl, **3**; $Ar^1 = 2,6$ -diisopropylphenyl, $Ar^2 = 2,6$ -dimethylphenyl, **4**) were prepared according to our previously reported methods [9]. Anilido–imino nickel complexes can catalyze norbornene polymerization activated with MAO over a wide range of polymerization temperature. As shown in Table 1, the reaction temperature strongly affected the catalytic activities. When polymerization temperature was kept 0 °C, activities and yields for norbornene polymerization were low. With an increase in the reaction temperature, the catalytic activities for norbornene polymerizations increased obviously. All complexes showed the highest activity for norbornene polymerization at 70 °C. Table 1 also shows that activity of complex **3** with two 2,6-diisopropyl *N*-aryl groups most significantly increased among four complexes when temperature was raised from 0 to 70 °C, which results from large barrier energy for insertion in the polymerization reaction caused by big steric hindrance.

The polymerization temperature strongly affected molecular weights and MWD of the polymers. To our surprise, low average molecular weight and broad MWD were observed at lower polymerization temperature for four catalytic systems, and average molecular weight of the obtained polymers increased and MWD was narrowed with the increase in the temperature, which is quite different from those of well-behaved single-site catalysts [7,8].

GPC curves of the obtained polynorbornene samples with complex **2**/MAO at various temperatures are typically shown in Fig. 1A. The polymers display a broad MWD of 9.58 at 0 °C and 5.46 at 27 °C with a bimodal distribution (Fig. 1). This result suggests that the polymers are comprised of two kinds of polynorbornene with different average molecular weight produced by different catalytic species.

Recent NMR studies have provided important information on the structures of ‘cation-like’ species formed upon activation of group **4** metallocenes with MAO in toluene [10]. For the catalytic system Cp_2MMe_2/MAO ($M = Ti, Zr$), four different types of species were identified: $Cp_2MeM-Me \rightarrow Al \equiv MAO$ (**M-I**) and $[Cp_2MMe(\mu-Me)-Cp_2MMe]^+[Me-MAO]^-$ (**M-II**) at low Al/M ratios (<100/1), $[Cp_2M(\mu-Me)_2-AlMe_2]^+[Me-MAO]^-$ (**M-III**) and $Cp_2MMe^+ \leftarrow Me^- - Al \equiv MAO$ (**M-IV**) at high Al/M ratios. Ethylene polymerization mechanism catalyzed by bis(imino)pyridine iron(II)-based catalysts has been reported in literature [11]. Bryliakov et al. showed that neutral species $LFeMe(\mu-R)AlMe_2$ ($R = Me, Cl$) were formed in the bis(imino)pyridine iron/ $AlMe_3$ systems, whereas ion pairs $[LFeMe(\mu-R)AlMe_2]^+[Me-MAO]^-$ ($R = Me, Cl$) ($L =$ bis(imino)pyridine ligand) were formed in the bis(imino)pyridine iron/MAO systems [11b].

Treatment of nickel complex **2** with MAO results in an immediate color change from green to yellow, indicating that the new species are formed in the **2**/MAO system. According to previous investigations on active species and our experimental results, we can reasonably assume that two species $LNi(II)(\mu-Me)_2AlMe_2$ (**I**) and $LNi(II)Me$ (**II**) ($L =$ anilido–imino ligand) are formed in the **1–4**/MAO

Table 1
Influence of reaction temperature on norbornene polymerization with anilido–imino nickel complexes **1–4**/MAO^a

Run	Complexes	Temperature (°C)	Yield (%)	Activity ^b	M_w^c	MWD
1	1	0	13.5	1.08	7.48	9.36
2	1	27	28.8	2.30	9.69	5.67
3	1	50	32.6	2.61	12.89	2.21
4	1	70	39.5	3.16	12.08	2.25
5	1	90	35.3	2.82	11.71	2.75
6	2	0	11.0	0.88	6.42	9.58
7	2	27	27.7	2.22	12.66	5.46
8	2	50	38.0	3.04	15.11	2.17
9	2	70	48.5	3.88	13.93	2.19
10	2	90	38.3	3.06	11.28	2.58
11	3	0	4.0	0.32	11.48	9.06
12	3	27	12.3	0.98	12.30	4.25
13	3	50	28.2	2.26	14.08	2.00
14	3	70	57.5	4.60	13.91	2.07
15	3	90	46.8	3.74	13.32	2.35
16	4	0	9.8	0.78	9.63	8.60
17	4	27	36.2	2.90	11.16	4.84
18	4	50	50.5	4.04	14.47	2.35
19	4	70	55.9	4.47	13.73	2.49
20	4	90	50.8	4.06	7.43	2.56

^a Polymerization conditions—reaction time: $t = 30$ min, catalyst concentration: $[Ni] = 5 \times 10^{-5}$ mol/L, monomer concentration: $[NBE] = 2.13$ mol/L, solvent: 20 mL toluene, Al/Ni = 3000.

^b In units of 10^{-6} g PNBE/(mol Ni h).

^c In units of 10^{-5} g/mol.

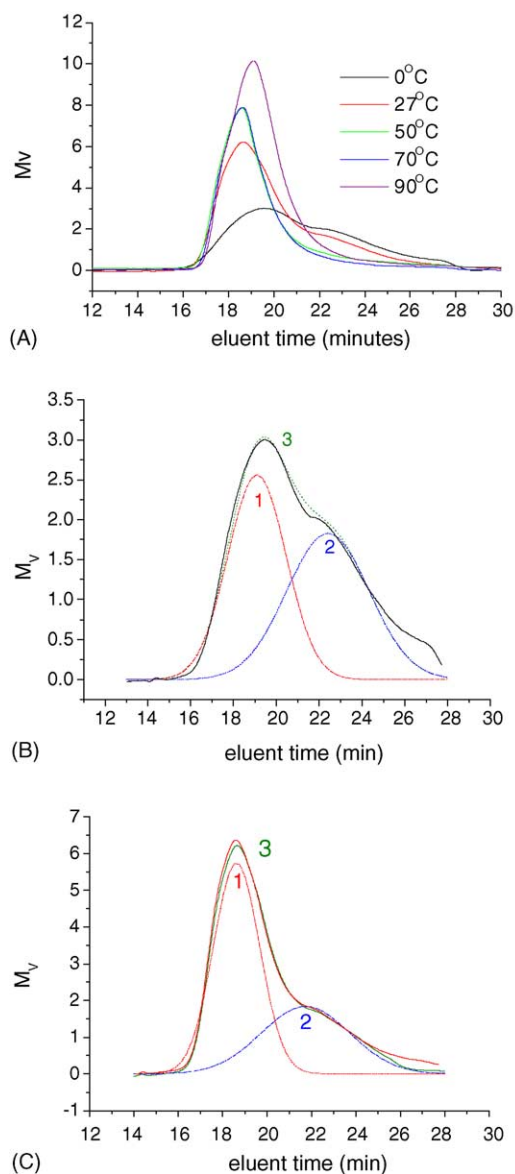


Fig. 1. GPC curves of the polynorbornenes obtained by complex **2**/MAO at various temperatures (A). The spectral components of the pattern (curves 1 and 2) were obtained by deconvolution of the observed spectrum (curve 3) according to Gaussian-Fit at 0 °C (B) and 27 °C (C).

system in toluene (Scheme 2), and that there is an equilibrium ($\mathbf{I} = \mathbf{II} + 1/2\text{Al}_2\text{Me}_6$) shifts between two kinds of species because the solid MAO used in our experiments always contained a small amount of AlMe_3 [11b]. To confirm these assumptions, we attempt to undertake a ^1H NMR spectroscopic study of intermediates formed upon activation anilido-imino nickel complex **2** with MAO at various temperatures (–15 to 30 °C). Unluckily, we fail because they are paramagnetic.

The bimodal MWD of polymers could be attributed to the existence of two catalytic active species **I** and **II** at low polymerization temperature (Scheme 2). The Ni/Al heterobimetallics **I** is stable below 50 °C, but only monometallic **II** can exist at higher temperature; analogous results of the met-

allocenium/MAO system have been reported by Bochmann and Lancaster [10a]. Therefore, at lower polymerization temperatures, two kinds of active species catalyze norbornene polymerization simultaneously, which could cause markedly different polymerization results from those obtained at high temperatures. Because the metal center is close to AlMe_3 , the chain transfer reaction takes place more easily on the propagating chain linked with the species **I** than that linked with the species **II**. Thus, the polynorbornenes produced by the active species **II** (Fig. 1B and C, curve 1) exhibit higher average molecular weight than those produced by the active species **I** (Fig. 1B and C, curve 2).

Owing to the shift in equilibrium between two active species **I** and **II**, the obtained polymers have broad dispersion and show bimodal elution peaks at low temperature, and the elution peak corresponding to the lower molecular weight component part produced by species **I** decreases with an increase in polymerization temperature and disappears above 50 °C. As a result, the total average molecular weights of the obtained polymers increase with an increase in polymerization temperature. When polymerization temperature increased to above 50 °C, due to existence of single active species **II**, the polymerization systems show normal behavior of single-site catalysts: MWD is close to 2 and the average molecular weights of the obtained polymers decrease with an increase in polymerization temperature.

To further investigate other reaction parameters affecting vinyl-polymerization of norbornene, the complex **1** was used in various conditions. The polymerization temperature was 70 °C, at which high polymerization activity was achieved and behavior characteristic of single-site catalyst was observed. Fig. 2 shows the influence of polymerization time on the polymer yields. The polymer yields increased with reaction time, and the polymerization rate gradually slowed down with the monomer consumed. No induction period was observed in the polymerization process. This observation suggests that the active species can be formed

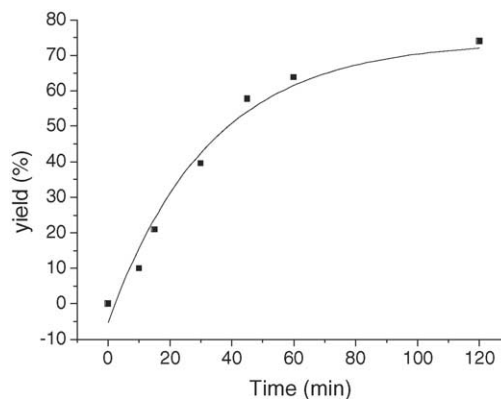
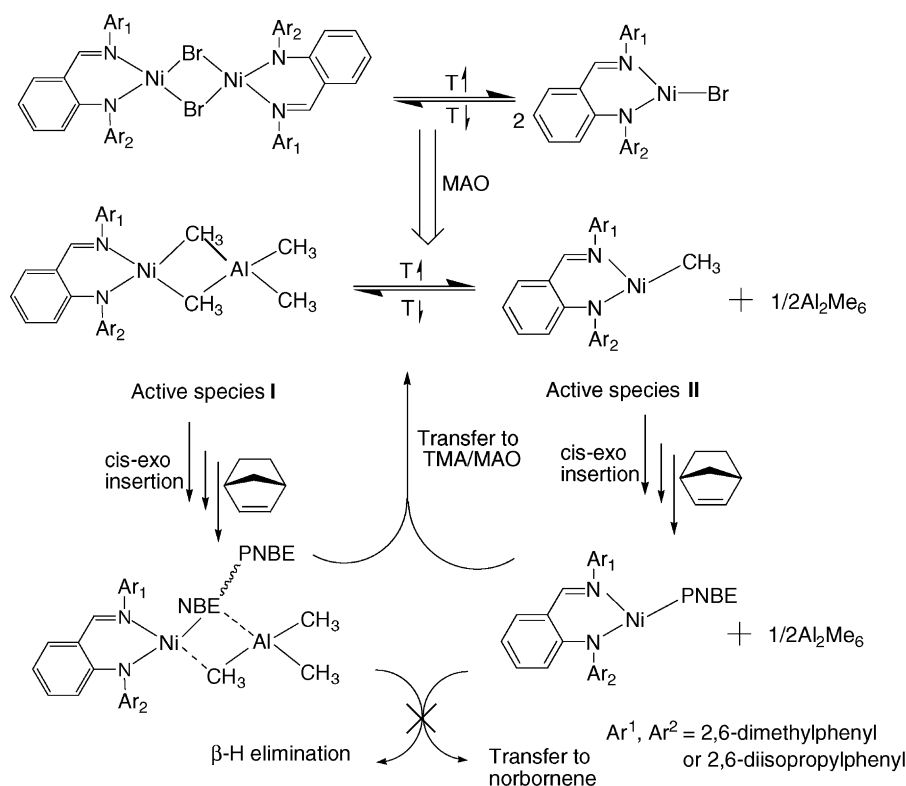


Fig. 2. Influence of reaction time on polymerization yield with **1**/MAO. Polymerization conditions—reaction temperature: $T = 70$ °C, catalyst concentration: $[\text{Ni}] = 5 \times 10^{-5}$ mol/L, monomer concentration: $[\text{NBE}] = 2.13$ mol/L, solvent: 20 mL toluene, $\text{Al/Ni} = 3000$.



Scheme 2. Proposed coordination mechanism for norbornene polymerization catalyzed by anilido-imino nickel complexes activated with MAO.

rapidly at the initial stage of the reaction, then being stabilized at 70 °C.

Increasing the monomer concentration with other reaction conditions fixed resulted in dramatic increase in polymerization rate (Runs 21–24 and 4 in Table 2). The influence of catalyst concentration on norbornene polymerization was also studied at a fixed Al/Ni ratio of 3000. The results (Runs 4 and 25–28 in Table 2) show that the yields increased with increasing catalyst concentration. Monomer concentration had greater influence on polymerization activity than catalyst concentration. Under the polymerization conditions of low catalyst concentration ($\approx 10^{-5}$ mol/L), low monomer concentration (< 3 mol/L) and high temperature, and neglecting

diffusion effect, the kinetics equation for polymerization of norbornene can be simply expressed as

$$R_p = k[\text{NBE}]^m \times [\text{Ni}]^n \quad (1)$$

where k is the overall polymerization rate constant and m and n are the kinetic order.

As shown in Fig. 3, a good linear relationship exists between denary logarithm of rate of propagation ($\log R_p$) and denary logarithm of monomer concentration ($\log[\text{NBE}]$). The kinetic order of the monomer concentration can be estimated from the slope to be $m = 1.93$. As depicted in Fig. 4, R_p increased with increasing catalyst concentration, and from the slope of the line the kinetic order of the catalyst concen-

Table 2

Norbornene polymerization using 1/MAO system at various monomer concentrations and catalyst concentrations^a

Run	Norbornene concentration ^b	Catalyst concentration ^c	Yield (%)	Activity ^d
21	1.06	5	20.3	0.81
22	1.70	5	34.1	2.18
4	2.13	5	39.5	3.16
23	2.55	5	46.6	4.47
24	3.19	5	57.8	6.94
25	2.13	2	18.0	3.60
26	2.13	4	34.8	3.48
27	2.13	6	46.8	3.12
28	2.13	8	61.6	3.08

^a Polymerization conditions—reaction time: $t = 30$ min, reaction temperature: $T = 70$ °C, Al/Ni = 3000, total solvent volume: 20 mL toluene.

^b In units of mol/L.

^c In units of 10^5 mol/L.

^d In units of 10^{-6} g PNBE/(mol Ni h).

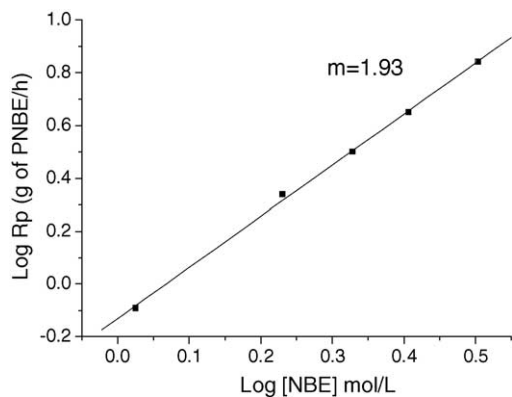


Fig. 3. The $\log R_p$ – \log [NBE] plots of complex **1**/MAO catalyst.

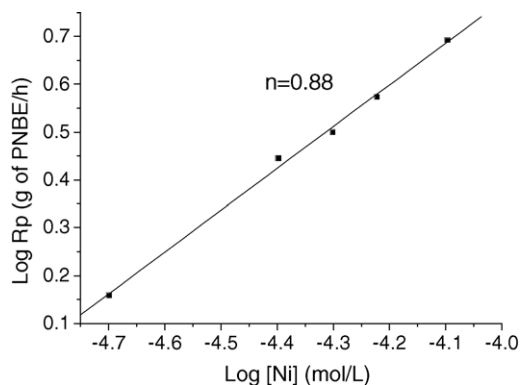


Fig. 4. The $\log R_p$ – \log [Ni] plots of complex **1**/MAO catalyst.

tration can be estimated to be $n = 0.88$. Thus, the rate equation for the norbornene polymerization with the **1**/MAO at 70 °C can be expressed as:

$$R_p = k[\text{NBE}]^{1.93} \times [\text{Ni}]^{0.88} \quad (2)$$

where k is the overall polymerization rate constant.

Eq. (2) shows that the polymerization rate order relative to monomer concentration is close to 2, which indicates that two norbornene monomers are involved at the chain propagation step. This result can be explained according to the trigger mechanism proposed by Ystenes [12]. The coordination site is always occupied by a norbornene monomer, and the complexed norbornene monomer will be inserted if and only if a new monomer is ready to complex. Besides, two norbornene monomers are associated with the active specie in the transition state. Therefore, polymerization kinetic order related to the monomer concentration is secondary.

4. Polymer characterization

All of the obtained polymers were soluble in chlorobenzene, *o*-dichlorobenzene and cyclohexane at room temperature, and showed similar IR and ^1H NMR spectra. The IR spectra revealed no traces of double bond, which often appear at 1620–1680, 966 and 735 cm^{-1} , and ^1H NMR spec-

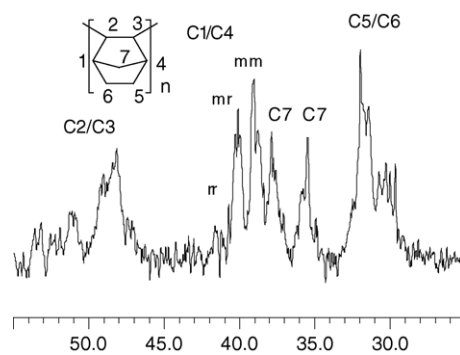


Fig. 5. ^{13}C NMR spectrum of polynorbornene prepared by **1**/MAO (Run 4).

tra (0.86–2.38 ppm) also proved no traces of any double bond, ensuring the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization [13].

^{13}C NMR spectrum also further confirmed that the obtained polymers are vinyl-type polynorbornene [6,14]. Fig. 5 shows the ^{13}C NMR spectrum of polymer obtained with **1**/MAO at 70 °C. Several signals were observed from 28 to 55 ppm. The absence of any signal at 20–24 ppm strongly indicates that the polynorbornene was *exo* enchainment [15]. Each signal of the saturated carbon was split into several peaks, which comes from the different stereoisomers of norbornene unit in the polymer chain. The resonances of methenes and methines appear at 29.7–32.0 ppm for C5 and C6, 35.5–37.9 ppm for C7, 38.8–41.8 ppm for C1 and C4 and 48.1–54.0 ppm for C2 and C3. The distribution of the stereotriad sequences of the polynorbornene is determined from the C1 and C4 regions (mm at 38.8 ppm, mr at 40.1 ppm and rr at 41.8 ppm) to be [mm]=58%, [rr]=6.6% and [mr]=35.4%. A calculation result of $[\text{mr}]/(2[\text{mm}] + [\text{mr}]) + [\text{mr}]/(2[\text{rr}] + [\text{mr}]) = 0.96$, close to the criterion of Bernoullian statistics which is satisfied with 1, indicates that the stereochemistry of the chain propagation follows a chain-end control model favoring slightly mesomeric enchainment.

TGA curves of the obtained polymer showed that all of the polymer samples were stable up to 450 °C. Attempts to measure glass transition temperature (T_g) of polynorbornene from DSC curve was unsuccessful [16]. The wide-angle X-ray diffraction analysis of the obtained polynorbornene catalyzed by **1**/MAO showed two major broad peaks ($2\theta = 9$ –11° and 17–19°), which indicates that the obtained polymers were non-crystalline and had low stereoregularity [17,18].

5. Mechanistic consideration

Some authors have already pointed out that the polymerization with nickel-based catalysts may proceed by a coordination mechanism [19]. In fact, NMR and IR spectra of the obtained polynorbornene show that no ROMP occurs in the polymerization processes but via 2,3-addition. The molecular weights of the obtained polynorbornenes

are high from 10^5 to 10^6 g/mol. This means that the polymerization is not a typical cationic or radical polymerization, which usually results in low molecular weights (molecular weight < 1000) and low yield because of rearrangements and transfer reactions [20]. Though Myagmarsuren et al. have prepared 2,7-addition polynorbornene of high molecular weights ($M_w > 300,000$ g/mol) catalyzed by $\text{Pd}(\text{acac})_2/\text{BF}_3\text{OEt}_2$, there are difference in NMR spectra and glass transition temperature between 2,7-addition polynorbornene and 2,3-addition polynorbornene [21]. Therefore, we can safely draw a conclusion that the norbornene polymerizations catalyzed by the anilido–imino nickel complexes/MAO system proceed through a vinyl-addition coordination mechanism.

A possible coordination mechanism for norbornene polymerization is proposed for the anilido–imino nickel complexes/MAO system. At the initiation step, anilido–imino nickel complexes activated with MAO produce two active species **I** and **II**. According to the results of kinetic study described above, the chain propagation can be explained by the trigger mechanism [12]. The norbornene monomer always occupies coordination site, and the complexed norbornene monomer will insert Ni–carbon by *cis–exo* insertion if and only if a new monomer is ready to complex. Repetition of the complexation–coordination–insertion steps will lead to polymer chain growth. For the vinyl addition polymerization of norbornene, the chain termination via β -hydrogen elimination is prohibited because the β -hydrogen of the propagation chain end is at the *endo* position of the norbornene unit. The chain transfer to monomer would be also prohibited because of the sterically hindered propagation chain end and norbornene monomer. Considering the fact that the polymerization successfully proceeded in the absolute dried system, chains mainly transfer to AlMe_3 , which is in accord with previous experimental results [9]. Since the active species **I** is coordinated with AlMe_3 , the propagating chains more easily shift from Ni centre to Al compound than those linked with AlMe_3 -free species **II**, resulting in producing two parts of polynorbornenes with different molecular weights at low polymerization temperatures.

6. Conclusions

Abnormal influence of temperature on norbornene polymerization with novel anilido–imino nickel complexes/MAO is observed. With an increase in the reaction temperature, the catalytic activities for norbornene polymerizations increase obviously. However, broad and bimodal MWD is observed below 50°C for the four catalyst systems, and average molecular weight of polymers increases and MWD is narrowed with the increase in the temperature, which results from the equilibrium shift between two active species in solution. From a kinetic study of the polymerization of norbornene with complex **1**/MAO, the polymerization rate (R_p) can be expressed as

follows: $R_p = k[\text{NBE}]^{1.93}[\text{Ni}]^{0.88}$, which can be explained by the trigger mechanism. The IR and NMR spectra proved the occurrence of vinyl-type polymerization rather than ROMP.

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