

# Polymerization of Styrene Using Novel Bispyrazolyimine Dinickel (II)/Methylaluminoxane Catalytic Systems

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**ABSTRACT:** The polymerization of styrene with a series of bispyrazolyimine dinickel (II) complexes of bis-2-(C<sub>3</sub>HN<sub>2</sub>(R<sub>1</sub>)<sub>2</sub>-3,5)(C(R<sub>2</sub>) = N(C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>-2,6)Ni<sub>2</sub>Br<sub>4</sub> (complex 1: R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = Ph; complex 2: R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = 2,4,6-trimethylphenyl; complex 3: R<sub>1</sub> = R<sub>2</sub> = Ph; complex 4: R<sub>1</sub> = Ph, R<sub>2</sub> = 2,4,6-trimethylphenyl) in the presence of methylaluminoxane (MAO) was studied. The influences of polymerization parameters such as polymerization temperature, Al/Ni molar ratio, reaction time, and catalyst concentration on catalytic activity and molecular weight of the polystyrene were investigated in detail. The influence of the bulkiness of the substituents on polymerization activity was also studied. All of the four catalytic systems exhibited high activity (up to 10.50 × 10<sup>5</sup> gPS/(mol Ni h)) for styrene polymerization

and provide polystyrene with moderate to low molecular weights ( $M_w = 4.76 \times 10^4$ – $0.71 \times 10^4$  g/mol) and narrower molecular weight distributions about 2. The obtained polystyrene was characterized by means of FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR techniques. The results indicated that the polystyrene was atactic polymer. The analysis of the end groups of polystyrene indicated that styrene polymerization with bispyrazolyimine dinickel complexes/MAO catalytic systems proceeded through a coordination mechanism. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 545–550, 2011

**Key words:** bispyrazolyimine dinickel (II); complexes; methylaluminoxane; styrene polymerization; coordination mechanism

## INTRODUCTION

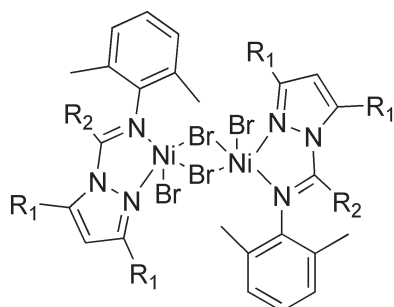
During the past decades, the utilization of soluble transition metal complexes for styrene polymerization has received considerable attention.<sup>1</sup> Styrene is one of only a few monomers capable of being polymerized through all the known polymerization mechanisms, i.e., radical, anionic, cationic, and coordinated mechanisms,<sup>2–4</sup> and each has led to polystyrenes with different stereoregularities. Ziegler-Natta catalysts based on titanium tetrachloride and aluminum alkyls yielded isotactic polystyrene,<sup>5–7</sup> however, titanium complexes/methylaluminoxane (MAO) catalytic systems obtained syndiotactic polystyrene.<sup>8–13</sup> Recently, various systems based on nickel complexes have been explored for styrene polymerization. For example, cationic  $\eta^3$ -allylnickel complexes alone<sup>14,15</sup> or modified by phosphine and phosphate ligands<sup>14,16,17</sup> as well as cationic  $\eta^3$ -benzyl nickel complexes<sup>18</sup> were active homogeneous

catalysts for the low molecular weight polymerization of styrene by simple cationic mechanism. Neutral allylnickel complexes alone<sup>19–22</sup> or with the activation of electron-poor additives can produce nonstereospecific polystyrene, and a coordination mechanism was proposed.<sup>20,23</sup> Neutral  $\sigma$ -acetylide nickel (II) complexes as high active initiators in chloroform solution exhibited catalytic activity in the polymerization of styrene and atactic polymers with high molecular weight were obtained, however, a radical mechanism was proposed.<sup>24</sup> The latest contribution showed that styrene polymerization with  $\alpha$ -diimine nickel catalyst led to atactic polymer.<sup>25</sup> The catalytic behavior of the anilido-imino nickel complexes/MAO systems for styrene polymerization was investigated.<sup>26</sup> End group analysis of the polymer confirmed a coordination mechanism, and atactic polystyrene was obtained. Moreover, styrene polymerization using  $\beta$ -diketiminato nickel (II) complexes with activation of MAO was reported and the resulting polystyrene also was atactic polymer.<sup>27</sup>

Previously, we have reported the synthesis, molecular structure of dinickel (II) complexes bearing two pyrazolyimine ligands bis-2-(C<sub>3</sub>HN<sub>2</sub>(R<sub>1</sub>)<sub>2</sub>-3,5)(C(R<sub>2</sub>) = N(C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)<sub>2</sub>-2,6)Ni<sub>2</sub>Br<sub>4</sub> (complex 1: R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = Ph; complex 2: R<sub>1</sub> = CH<sub>3</sub>, R<sub>2</sub> = 2,4,6-trimethylphenyl; complex 3: R<sub>1</sub> = R<sub>2</sub> = Ph; complex 4: R<sub>1</sub> =

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- Complex 1  $R_1=CH_3$ ,  $R_2=Ph$   
 Complex 2  $R_1=CH_3$ ,  $R_2=2,4,6\text{-Trimethylphenyl}$   
 Complex 3  $R_1=Ph$ ,  $R_2=Ph$   
 Complex 4  $R_1=Ph$ ,  $R_2=2,4,6\text{-Trimethylphenyl}$

**Scheme 1** The structures of four bispyrazolylimine dinickel (II) complexes.

Ph,  $R_2 = 2,4,6\text{-trimethylphenyl}$ ) (Scheme 1) and their catalytic behavior toward norbornene with the activation of MAO.<sup>28</sup> The purpose of this work is to further investigate catalytic activity in styrene polymerization using these four dinickel complexes with activation of MAO. Influence of steric hindrance of the complexes and polymerization conditions, such as reaction temperature, Al/Ni molar ratio, polymerization time, and catalyst concentration on catalytic activity were investigated in detail. Moreover, the polymerization mechanism for styrene polymerization was proposed with the analysis of end groups of polystyrene.

## EXPERIMENTAL

### General procedures

All manipulation involving air- and moisture-sensitive compounds were performed under a dried and purified atmosphere of nitrogen using standard glove box and Schlenk techniques. Toluene was dried over metallic sodium for 24 h and distilled under nitrogen before use. Styrene was purchased from Guangzhou Chemical Co. (Guangzhou, China) and dried over  $CaH_2$ , and then freshly distilled under vacuum before use. The other reagents were purchased and used as received. Methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0–60°C with  $H_2O$  from  $Al_2(SO_4)_3 \cdot 18H_2O$ . The pyrazolylimine ligands and corresponding dinickel complexes were prepared according to our previous methods.<sup>28</sup>

### Polymerization

In a typical procedure, the appropriate MAO solid was added into a 50 mL flask, and then freshly distilled toluene was added via syringe. Styrene and precursor catalyst solution in toluene (2 mM) was

injected into the well-stirred solution in order, and the total reaction volume was remained at 20 mL. The polymerization was carried out for the desired time and then quenched with concentrated HCl in ethanol (HCl/ethanol, 5 : 95, v/v). The resulting precipitated polymer was collected, filtered, and washed with ethanol for several times, and then dried in vacuum at 50°C to a constant weight.

### Characterization

Gel permeation chromatography (GPC) analyses of molecular weight and molecular weight distribution of the polymers were performed on a Waters Breeze instrument using THF as eluent at 40°C and standard polystyrene as reference. FTIR spectra were recorded as KBr pellets on a Perkin–Elmer 1600 spectrometer.  $^1H\text{-NMR}$  and  $^{13}C\text{-NMR}$  spectra were recorded on a Varian Mercury-Plus 300 NMR spectrometer at room temperature using  $CDCl_3$  as solvent and TMS as internal standard.

## RESULTS AND DISCUSSION

### Polymerization of styrene

The bispyrazolylimine dinickel (II) complexes 1–4 showed good catalytic activities for styrene polymerization using methylaluminoxane (MAO) as cocatalyst over a wide range of polymerization temperature. The molecular weights of all polystyrenes (PS) were moderate to low between  $10^4$  g/mol and  $10^3$  g/mol ( $M_w = 4.76 \times 10^4\text{--}0.71 \times 10^4$  g/mol), and the molecular weight distribution (MWD) was around 2.0 as shown in Tables I and II. Moreover, according to the polymerization results, the yield, catalytic activity, molecular weight, and the molecular weight distribution depended significantly on the polymerization parameters, such as polymerization temperature and Al/Ni molar ratio.

Polymerization temperature had a remarkable effect on catalytic activity and molecular weight of the obtained polymers. As shown in Table I, these catalytic systems exhibited high activity over a wide temperature range of 20 to 80°C. The catalytic activities of four complexes increase first and then decrease with polymerization temperature increasing. As for the catalytic activity, the optimum reaction temperature for complexes 1 and 2 is 40°C; for complexes 3 and 4 is 60°C. Increasing temperature is helpful to enhance the yield and activity but the activity decreases with temperature further increase probably because of thermal instability of the nickel complexes at higher temperature. However, the molecular weight decreased significantly with the increasing of temperature all the while. In general, the rate of chain transfer is more sensitive to

TABLE I  
Influences of Polymerization Temperature on Styrene Polymerization with  
Complexes 1–4/MAO Catalytic Systems<sup>a</sup>

Complex	Entry	Tp (°C)	Activity <sup>b</sup>	Yield (%)	$M_w^c$	$M_w/M_n$
1	1	20	2.27	20.0	3.45	2.26
1	2	40	9.68	85.2	2.85	2.44
1	3	60	8.92	78.5	1.24	2.38
1	4	80	8.50	74.8	0.71	2.63
2	5	20	2.14	18.8	3.77	2.33
2	6	40	9.85	86.7	2.62	2.69
2	7	60	8.56	75.3	1.79	2.30
2	8	80	7.62	67.1	1.54	2.42
3	9	20	2.62	23.1	4.04	2.02
3	10	40	7.20	63.4	2.98	2.54
3	11	60	7.90	69.5	1.63	2.48
3	12	80	7.46	65.6	1.26	2.45
4	13	20	1.25	11.0	4.76	2.05
4	14	40	6.70	59.0	3.05	2.65
4	15	60	7.18	63.2	2.21	2.35
4	16	80	6.85	60.3	1.58	2.58

<sup>a</sup> Polymerization conditions: precursor catalyst concentration:  $[\text{Ni}] = 2.0 \times 10^{-4}$  mol/L; styrene addition: 5 mL; Al/Ni = 600; reaction time: 1 h; solvent: toluene; total volume: 20 mL.

<sup>b</sup> In units of  $10^5$  gPS/(mol Ni h).

<sup>c</sup> In units of  $10^4$  g/mol.

temperature relative to that of chain growing, and at higher temperature, chain transfer is in predominated state. So, the molecular weight of polymer will fall as the polymerization temperature increasing.

Comparing the activities of these four complexes at the same conditions, it can be found that the steric hindrance of the activities of nickel complexes affect their catalytic activities obviously. The presence of bulky pyrazolyl-aryl groups reduced the catalytic activity; for example, at 40°C, complexes 3 and 4 with 3,5-diphenyl-pyrazolyl group have lower activities for styrene polymerization (complex 3,  $7.20 \times 10^5$  gPS/(mol Ni h); complex 4,  $6.70 \times 10^5$  gPS/(mol Ni h)), whereas complexes 1 and 2 with 3,5-dimethyl-pyrazolyl group have relatively higher activities (complex 1,  $9.68 \times 10^5$  gPS/(mol Ni h); complex 2,  $9.85 \times 10^5$  gPS/(mol Ni h)).

Al/Ni molar ratio played an important role in affecting the catalytic activities. As shown in Table II, the four catalytic systems showed similar tendency. The polymer yield and the catalyst activity increased with the increasing of MAO amount until the Al/Ni molar ratio is up to 900 for complexes 1–4/MAO catalytic systems, and then decreased, respectively, with further enlarging MAO ratio. The highest catalytic activity up to  $10.50 \times 10^5$  gPS/(mol Ni h) could be observed in complex 1/MAO catalytic system (Entry 3 in Table II). In addition, the Al/Ni molar ratio also affected the molecular weight of the polymers, because MAO, a cocatalyst, was used to activate bispyrazolylimine dinickel complexes on the one hand, however, it may be a trans-

fer agent for these catalytic systems on the other hand.

According to our previous work,<sup>28</sup> though bispyrazolylimine dinickel complexes are five coordinate dinuclear species in the solid state confirmed by X-ray single-crystal analyses, there is an equilibrium between the five-coordinate dimer and four-coordinate monomer in solution, based on UV–Vis spectrophotometry, which support the monomer/dimer equilibrium in solution. As shown in Tables I and II, the molecular weight distributions of obtained polystyrenes were between 2.02 and 2.83, implied that under the effect of MAO, the two bromine bridges in each dinickel complex were both ruptured, forming single active species to polymerize styrene between 20 and 80°C.

Figure 1 shows the influence of polymerization time on the polymer yields using complex 1/MAO at 40°C and complex 3/MAO at 60°C. Obviously, with prolonging reaction time, the polymer yields increased progressively, and the polymerization rate slowed down gradually with the monomer consuming. This result suggested that the active species can be produced rapidly at the original stage of the polymerization, and then being stabilized at 40°C for complex 1/MAO and 60°C for complex 3/MAO.

The effect of catalyst concentration on the polymer yields was also investigated with complex 1/MAO at 40°C and complex 3/MAO at 60°C and the results were shown in Figure 2. The results suggest that the both two catalytic systems exhibited low catalytic activities when the concentration of  $[\text{Ni}]$  was low

TABLE II  
Influences of Al/Ni Molar Ratio on Styrene Polymerization with  
Complexes 1-4/MAO Catalytic Systems<sup>a</sup>

Complex	Entry	Al/Ni	Activity <sup>b</sup>	Yield (%)	$M_w^c$	$M_w/M_n$
1	1	300	4.72	41.5	3.05	2.28
1	2	600	9.68	85.2	2.85	2.44
1	3	900	10.50	92.4	2.68	2.54
1	4	1200	9.20	81.0	2.21	2.75
2	5	300	4.18	36.8	2.88	2.17
2	6	600	9.85	86.7	2.62	2.69
2	7	900	10.42	91.7	2.40	2.39
2	8	1200	8.95	78.8	2.55	2.51
3	9	300	4.09	36.0	1.59	2.08
3	10	600	7.90	69.5	1.63	2.48
3	11	900	8.46	74.4	2.08	2.36
3	12	1200	7.17	63.1	2.37	2.83
4	13	300	3.12	27.5	2.26	2.20
4	14	600	7.18	63.2	2.21	2.35
4	15	900	8.35	73.5	1.74	2.56
4	16	1200	7.42	65.3	2.04	2.48

<sup>a</sup> Polymerization conditions: precursor catalyst concentration:  $[\text{Ni}] = 2.0 \times 10^{-4}$  mol/L; styrene addition: 5 mL; polymerization temperature: complexes 1 and 2, 40°C; complexes 3 and 4, 60°C; reaction time: 1 h; solvent: toluene; total volume: 20 mL.

<sup>b</sup> In units of  $10^5$  gPS/(mol Ni h).

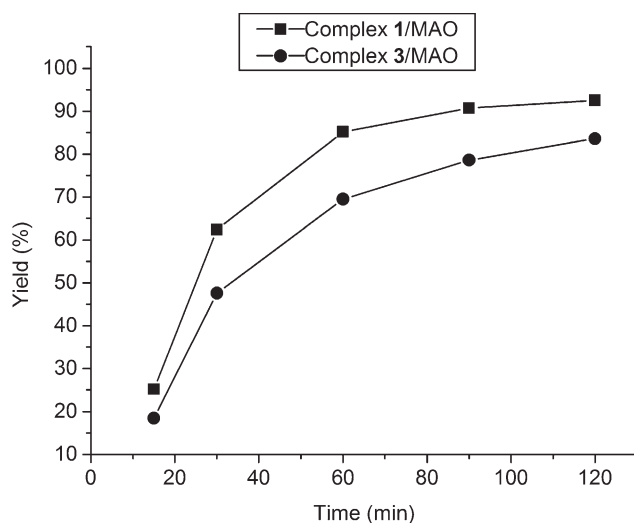
<sup>c</sup> In units of  $10^4$  g/mol.

( $[\text{Ni}] = 1.0 \times 10^{-4}$  mol/L); with concentration of  $[\text{Ni}]$  enhanced ( $[\text{Ni}] = 2.0 \times 10^{-4}$  mol/L), the amount of effectively active species was increased, and then polymerization rate was speeded up so that polymer yield and catalytic activity were accelerated sharply. However, if the concentration of  $[\text{Ni}]$  was enhanced more as  $3.0 \times 10^{-4}$  mol/L and  $4.0 \times 10^{-4}$  mol/L, polymer yield was increased slightly, whereas catalytic activity decreased because mono-

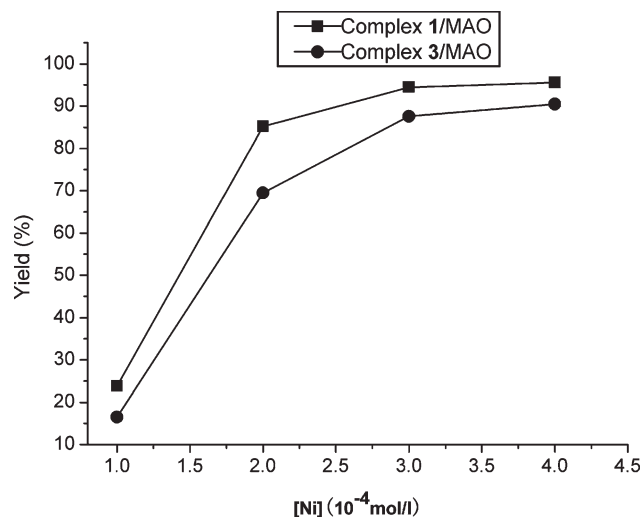
mer's diffusion to active species was hindered owing to the high viscosity of polymerization system.

#### Microstructure analysis of polystyrene and reaction mechanism of styrene polymerization

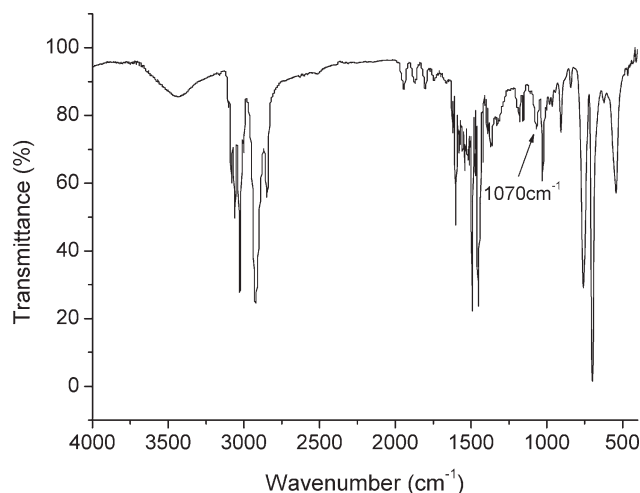
All of the obtained polymers were completely soluble in many organic solvents, such as chloroform, 2-butanone, acetone, and THF, indicating that atactic polystyrene with low stereoregularity was obtained.



**Figure 1** Influence of the reaction time on the styrene polymerization with complex 1/MAO and complex 3/MAO catalytic systems. Polymerization conditions: precursor catalyst concentration:  $[\text{Ni}] = 2.0 \times 10^{-4}$  mol/L; styrene addition: 5 mL; polymerization temperature: complex 1, 40°C; complex 3, 60°C; Al/Ni = 600; solvent: toluene; total volume: 20 mL.



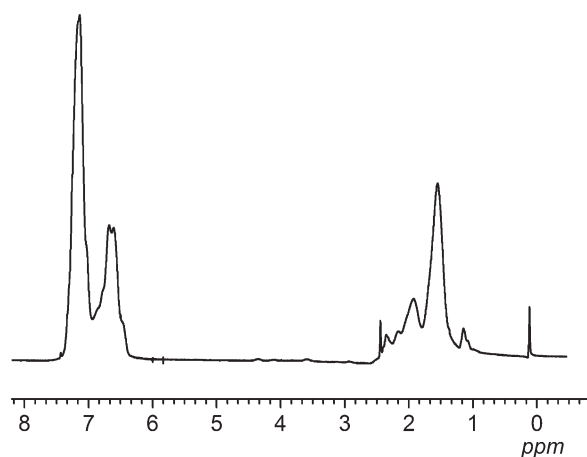
**Figure 2** Influence of the catalyst concentration on the styrene polymerization with complex 1/MAO and complex 3/MAO catalytic systems. Polymerization conditions: styrene addition: 5 mL; polymerization temperature: complex 1, 40°C; complex 3, 60°C; Al/Ni = 600; reaction time: 1 h; solvent: toluene; total volume: 20 mL.



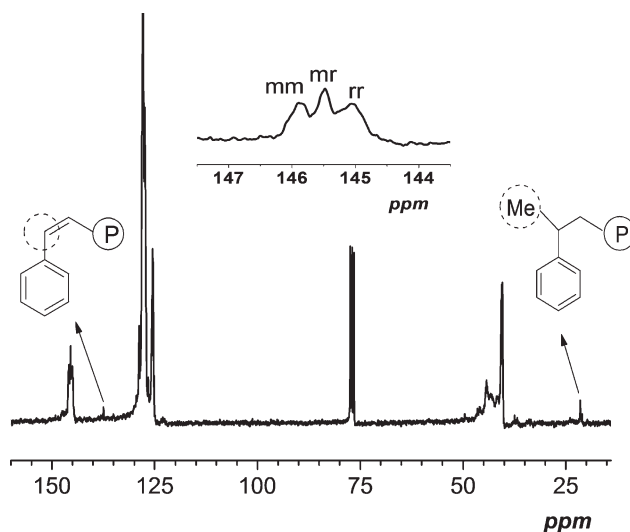
**Figure 3** FTIR spectrum of polystyrene obtained by complex 1/MAO catalytic system (Entry 2 in Table I).

The microstructure of a representative polystyrene sample obtained from Entry 2 in Table I was characterized by IR,  $^1\text{H-NMR}$ , and  $^{13}\text{C-NMR}$ . IR spectrum (Fig. 3) revealed that there are no obvious absorption bands appearing at 1217.6 and 1220  $\text{cm}^{-1}$ , which are assigned to the characteristic signal of sPS.<sup>29,30</sup> However, the presence of absorption at 1070  $\text{cm}^{-1}$  in the IR spectrum supports that atactic polystyrene was observed.

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra shown in Figures 4 and 5, respectively, also further confirmed that the resulting polystyrene was atactic polymer. As displayed in Figure 3, three groups of hydrogen proton signals were found. Chemical shifts at 6.45–7.20 ppm are aromatic hydrogen signals, those at 1.75–2.15 ppm are methine hydrogen signals, and those at 1.00–1.69 ppm are methylene hydrogen signals in polystyrene referring to the literature.<sup>31</sup>  $^{13}\text{C-NMR}$  spectrum of the polystyrene was analyzed for aro-



**Figure 4**  $^1\text{H-NMR}$  spectrum of polystyrene in  $\text{CDCl}_3$  obtained by complex 1/MAO catalytic system (Entry 2 in Table I).



**Figure 5**  $^{13}\text{C-NMR}$  spectrum of polystyrene in  $\text{CDCl}_3$  obtained by complex 1/MAO catalytic system (Entry 2 in Table I).

matic C-1 in the terms of triads (Fig. 4). Three main peaks at 146.0 ppm, 145.6 ppm, and 145.2 ppm were assigned to isotactic triad (mm), heterotactic triad (mr), and syndiotactic triad (rr), respectively.<sup>32–34</sup> The stereo-triad distributions of mm, mr and rr, calculated from the triad resonance integral, are [mm] = 28.5%, [mr] = 34.2%, and [rr] = 37.3%.

The polymer end-groups were analyzed by  $^{13}\text{C-NMR}$  to confirm the reaction mechanism (Fig. 4). It can be found that the  $^{13}\text{C-NMR}$  spectrum of polystyrene obtained by complex 1/MAO was very similar to that obtained by  $\beta$ -anilido-imino nickel (II) complexes in comparison with literature reported by Gao et al.,<sup>26</sup> in which at aromatic regions of  $^{13}\text{C-NMR}$  spectrum, a weak signal observed at 137.7 ppm (Fig. 4; 137.5 ppm) has been assigned to the carbon of double bond of chain end, resulting from  $\beta$ -H elimination engendering the vinylene end group ( $-\text{CH}=\text{CHPh}$ ), and at aliphatic regions, the signal at 21.5 ppm has been assigned to methyl carbon deriving from styrene secondary insertion to styrene primary insertion into the Ni–H bond. This result confirms that the active species of polymerization is Ni–H. Gao et al.<sup>26</sup> proposed a coordination mechanism. So, we can also suggest that the styrene polymerization with bispyrazolyimine dinickel complexes/MAO catalytic systems proceeded with a coordination mechanism.

## CONCLUSIONS

The four bispyrazolyimine dinickel (II) complexes exhibited good activity for styrene polymerization in the presence of methylaluminumoxane (MAO). The catalytic activity, molecular weight, and molecular weight distribution could be controlled over a wide

range by variation of the polymerization parameters. The presence of bulky prazolyl-aryl groups reduced the catalytic activity; complexes **1** and **2** with 3,5-dimethyl-pyrazolyl group have relatively higher activities than complexes **3** and **4** with 3,5-diphenyl-pyrazolyl group for styrene polymerization. Under appropriate polymerization conditions, the catalytic activity could be up to  $10.50 \times 10^5$  gPS/(mol Ni h) (complex **1**: polymerization temperature = 40°C, Al/Ni molar ratio = 900), and the molecular weights of all polystyrenes were between  $0.71 \times 10^4$  g/mol and  $4.76 \times 10^4$  g/mol. Also, the molecular weight distribution of obtained polystyrenes was between 2.02 and 2.83, implied styrene was polymerized by single active species. The results of FTIR, <sup>1</sup>H-NMR, and <sup>13</sup>C-NMR indicated that obtained polymer was atactic polystyrene. The analysis of the end groups of polystyrene indicated that styrene polymerization with bispyrazolylimine dinickel complexes/MAO catalytic systems proceeded through a coordination mechanism.

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