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Styrene polymerization with nickel complexes/methylaluminoxane catalytic system

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Polymerization of styrene using β-diketiminate nickel (II) bromide complexes $CH\{C(R)NAr\}_2NiBr$ ($R = CH_3$, $Ar = 2,6\text{-}^iPr_2C_6H_3$, 1; $R = CH_3$, $Ar = 2,6\text{-}Me_2C_6H_3$, 2; $R = CF_3$, $Ar = 2,6\text{-}^iPr_2C_6H_3$, 3; $R = CF_3$, $Ar = 2,6\text{-}Me_2C_6H_3$, 4) in the presence of methylaluminoxane was studied. Compound 3 is the most active styrene polymerization catalyst of all the nickel complexes tested. The activity of these catalysts increases with increases in steric bulk of the substituents on the aryl rings. The electronic nature of the ligand backbone also affects the activity. Weight-average molecular weight of the prepared polystyrene ranges from 21 000 to 72 000, with polydispersity indexes of 1.95–2.78. The microstructure of the obtained products is atactic polystyrenes from NMR analyses. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: nickel complex; styrene; polymerization; atactic polystyrene

Introduction

Recent progress in transition metal catalysts has led to the development of a wide range of polyolefins. Styrene (St) is one of the few monomers able to polymerize through all the known polymerization mechanisms, i.e. radical, cationic, anionic and coordinated mechanisms,[1–3] and each has led to polystyrenes with different stereoregularities. Heterogeneous titanium catalysts reported by Natta and coworkers could catalyze polymerization of isotactic-specific polystyrene.[4,5] Homogeneous titanium catalysts have led to the synthesis of syndiotactic polystyrene.[6–10] Arai *et al.* reported preparation of isotactic polystyrene using some *ansa*-zirconocene complexes.[11,12] Among catalytic systems for the coordinated polymerization of olefins, based on transition metals like titanium,[4–6] vanadium,[13] neodymium,[14] and nickel,[15–19] the latter present some interesting features. The lower oxophilicity relative to early transition metals make them likely targets to catalyze polymerization of a great variety of olefins. Most importantly, the activity of the catalytic system can be easily tuned by varying the nickel ligand; variation of the reaction parameter was shown to influence the activity as well as the final molecular weight. The nickel complexes bearing α-diimine ligands[15] and salicyaldiminato ligands[16] were reported to exhibit high activity for ethylene polymerization. Previously, many nickel complexes in combination with MAO have been used as catalysts for styrene polymerization. The cationic η^3-allylnickel complexes were active catalysts for styrene polymerization.[20,21] Isotactic polystyrenes with low molecular weight were obtained. The solvents and ancillary ligands of the nickel complex markedly affect catalytic activity. Styrene polymerization with $Ni(acac)_2$ and $NiCl_2$ was performed,[17–19] and a coordination mechanism was proposed. The stereoregularity of polystyrene is strongly dependent on the content of free trimethylaluminium in MAO.[19,22] Neutral σ-acetylide nickel complexes were good initiators for styrene polymerization, and syndio-rich atactic polymers with high molecular weight were obtained.[23] Recently, styrene polymerization with α-diimine nickel catalyst led to atactic polymer with an enhanced isotactic content.[24] The bis(β-ketoamino) nickel complexes were active catalyst precursors for styrene polymerization in the presence of MAO.[25,26] A coordination was proposed, and atactic polystyrene was obtained. The catalytic behavior of the anilido-imino nickel/MAO catalytic system for styrene polymerization was investigated.[27] End group analysis of the polymer confirmed a coordination mechanism, and iso-rich atactic polystyrene was obtained.

Previously, we have reported the synthesis and structure of β-diketiminate nickel complexes [$CH\{C(R)NAr\}_2NiBr$] (Scheme 1), and their catalytic activity toward ethylene and norbornene polymerization in the presence of MAO.[28–31] The versatile catalytic capability of the β-diketiminate nickel complexes makes them candidates for styrene polymerization catalysts. In this paper, results of styrene polymerization with a β-diketiminate nickel/MAO catalytic system are presented. The effects of the steric and electronic properties of the ligand, as well as the reaction conditions, on styrene polymerization were investigated.

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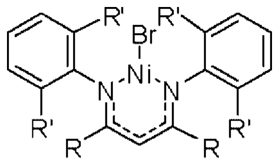

R = CH_3, R' = ^iPr **1**
R = CH_3, R' = Me **2**
R = CF_3, R' = ^iPr **3**
R = CF_3, R' = Me **4**

Scheme 1. Nickel complexes investigated.

Experimental

Materials

All manipulations involving air- and moisture-sensitive compounds were performed under dry, deoxygenated nitrogen atmosphere using standard high vacuum or Schlenk techniques. Toluene was used freshly distilled under nitrogen from sodium/benzophenone. Styrene (Shanghai Reagent Factory) was dried over calcium hydride, and distilled under vacuum prior to use. Solid methylaluminoxane (MAO) was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at 0–60 °C with $Al_2(SO_4)_3{\cdot}18H_2O$ as the water source. The initial $[H_2O]$:[TMA] molar ratio was 1.3. The β-diketiminate ligands and corresponding nickel complexes were prepared according to our previous method.[28–30] Other commercially available reagents were purchased and used without purification.

Polymerization

Styrene polymerization was carried out in a 50 ml glass vessel. In a typical procedure, the appropriate solid MAO was added to the flask, toluene and styrene were added via syringe and 1 ml nickel complex (3.0 µmol) of toluene solution was syringed into the well-stirred solution. The total reaction volume was kept at 20 ml. The reaction system was continuously stirred for an appropriate period at the polymerization temperature. The reaction was quenched by adding 5% HCl–ethanol solution. The polymer was filtered, washed with ethanol several times, and dried at 60 °C under vacuum to a constant weight.

Characterization

Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters Breeze system with tetrahydrofuran (THF) as the eluent at 40 °C using standard polystyrene as the reference. ^1H NMR and ^{13}C NMR spectra were recorded on a Mercury-plus 300 MHz NMR at room temperature in $CDCl_3$ solution. The infrared (IR) spectra were recorded on a Nicolet/Nexus 670 FT-IR spectrometer in the region of 400–4000 cm^{-1} using KBr disks. Differential scanning calorimetry (DSC) was obtained on a Perkin–Elmer DSC-7 instrument under a nitrogen atmosphere with a heating/cooling rate of 10 °C/min.

Table 1. Polymerization of styrene with nickel complexes **1–4**/MAO[a]

Run	Complex	T_p (°C)	Al : Ni	Yield (%)	Activity[b]	M_w[c]	M_w/M_n
1	**1**	30	800	51.8	5.84	62.3	2.20
2	**1**	70	800	61.5	6.92	43.4	2.54
3	**2**	30	800	25.2	2.83	58.3	2.21
4	**2**	70	800	41.7	4.69	31.9	2.65
5	**3**	30	200	11.2	1.26	72.1	1.95
6	**3**	30	800	54.6	6.15	66.5	2.15
7	**3**	50	800	61.4	6.91	60.5	2.41
8	**3**	70	200	15.3	1.72	56.7	2.52
9	**3**	70	400	38.5	4.33	55.2	2.53
10	**3**	70	800	72.4	8.13	53.4	2.55
11	**3**	70	1200	73.2	8.24	46.7	2.62
12	**3**	90	800	67.3	7.57	21.3	2.78
13	**4**	70	800	58.6	6.68	35.6	2.56
14[d]	**3**	70	800	74.0	4.16	53.8	2.26
15[e]	**3**	70	/	Trace	/	/	/

[a] Polymerization conditions: solvent, toluene; total volume, 20 ml; [Ni] = 2×10^{-4} mol l^{-1}; styrene, 5 ml; reaction time, 1 h. [b] 10^5 g PS mol^{-1} Ni h^{-1}. [c] 10^3 g mol^{-1}. [d] Reaction time, 2 h. [e] [Ni] = 0 mol l^{-1}, [Al] = 0.16 mol l^{-1}.

Results and Discussion

Polymerization of Styrene

Different polymerization runs were carried out by using the nickel **1–4**/MAO catalytic systems. The results are listed in Table 1.

Under the same polymerization conditions, the highest activity of 8.24×10^5 g PS mol^{-1} Ni h^{-1} was obtained using the **3**/MAO system at 70 °C (run 11 in Table 1). The highest activity of 8.69×10^5 g PS (polystyrene) mol^{-1} Ni h^{-1} was observed at 70 °C with the anilido-imino nickel/MAO catalytic system.[27] However, the bis(β-ketoamino) nickel exhibited the highest activity of 1.5×10^6 g PS mol^{-1} Ni h^{-1} at 40 °C.[26] It appears that the nickel complexes with [N,O] coordinating ligand are more favorable to monomers with steric hindrance around the double bond than the nickel complexes with [N,N] coordinating ligand, showing that the steric hindrance around the double bond plays an important role in determining the reactivity.

It is clear from the data that the influence of steric bulk of the substituents at the aryl rings on the activity of styrene polymerization is significant. Complex **1** with bulky *N*-aryl (Ar = 2,6-$^iPr_2C_6H_3$) exhibits about double the activity of **2** (Ar = 2,6-$Me_2C_6H_3$). The activity of complex **3** is also much high than that of **4**. These results suggest that the highest styrene polymerization activity is obtained from catalysts with bulkier *ortho*-aryl substituents in these catalytic systems. This is in good agreement with the results for ethylene and norbornene polymerization with the same catalytic systems,[29,30] indicating that the active center is stabilized using a ligand with bulky steric hindrance with these catalytic systems. In addition, the steric hindrance of the *ortho*-aryl substituents influences the molecular weight of the obtained polymer. Compared with the molecular weight of polystyrenes produced by four nickel/MAO systems under the same reaction condition, i.e. polymerization at 70 °C with Al : Ni ratio 800, higher molecular weight of polystyrenes were produced using bulkier nickel complexes. This result is consistent with substituent effect reported in ethylene and norbornene polymerization with these catalytic systems.[29,30]

On the other hand, the electronic structures of the ligands also influence the activity for styrene polymerization. For example, at 70 °C, the fluorinated backbone complexes **3** and **4** exhibited high activities for styrene polymerization (8.13×10^5 g PS mol^{-1} Ni h^{-1} for **3** and 6.68×10^5 g PS mol^{-1} Ni h^{-1} for **4**), while the nonfluorinated backbone analogs **1** and **2** showed lower activities (6.92×10^5 g PS mol^{-1} Ni h^{-1} for **1** and 4.69×10^5 g PS mol^{-1} Ni h^{-1} for **2**) under the same polymerization condition. The higher activities of **3** and **4** than nonfluorinated analogues can be attributed to stronger electronic deficiencies of the active centers, consequently, favoring the coordination of the monomer on the active centers.[32] While the nature of the backbone substituents of the complexes influences the conversion of monomer to polymer, it does not seem to dramatically affect the molecular weight M_w or distribution (M_w/M_n) of the obtained polystyrenes (Table 1).

The Al : Ni ratio played an important role in affecting the catalytic activities. As shown in Table 1, variation of the Al : Ni ratio in the range 200–1200 (runs 8–11) showed a considerable effect of the amount of MAO on activity using **3**/MAO. When the Al : Ni ratio was 200, very low activity was obtained, suggesting that the precatalyst was not fully activated by MAO. With an increase in Al : Ni ratio, the catalytic activities increased. Significant increases in activity to 8.13×10^5 g PS mol^{-1} Ni h^{-1} were observed by increasing the Al : Ni ratio to 800, and then leveling off at about constant values. Nevertheless, the Al : Ni ratio did not markedly influence the molecular weight of the obtained polystyrene.

The polymerization temperature (T_p) drastically affected catalytic behavior. With an increase in the reaction temperature, the catalytic activities increased, and then decreased for **3**/MAO (runs 6, 7, 10 and 12 in Table 1). The highest activity was obtained at 70 °C. Another increase in temperature to 90 °C caused a decrease in the activity for the instability or decomposition of the active species. In addition, the molecular weights of polymer were affected by the polymerization temperature. Molecular weights of the obtained polystyrene decreased with increasing temperature, and molecular weight distributions (M_w/M_n) broadened accordingly (Table 1). This may be caused by fast chain transfer and termination at high temperature.[26] Similar results were obtained for styrene polymerization with the **1, 2** and **4**/MAO systems. However, the molecular weight distributions of the polystyrene were rather narrow in all experiments with these catalytic systems; no bimodal distribution was detected even at 90 °C for **3**/MAO, indicating that a single active species was involved all through polymerizations.

Microstructure and thermal analyses of polystyrene

The microstructure of polystyrene obtained by the β-diketiminate nickel/MAO catalytic systems was characterized by IR and NMR. All polystyrene obtained from these catalytic systems gave similar spectroscopic characteristics. Figure 1 shows IR spectra (1700–700 cm^{-1}) of polystyrene obtained by **3**/MAO. Tadokoro *et al*. concluded that the characteristic signals of isotactic polystyrene appeared at 1364, 1314, 1297 and 1185 cm^{-1}.[33] The characteristic signal of syndiotactic polystyrene was observed at 1217.6 and 1220 cm^{-1}.[6,10] It is clear from the spectrum that the absorption of polymer obtained from the β-diketiminate nickel/MAO catalytic systems is different from the literature. Additionally, the absorption signal at 1070 cm^{-1} was reported to be the characteristic signal of atactic polystyrene.[6,10]

Figures 2 and 3 show ^{1}HNMR and ^{13}C NMR spectra of polystyrene obtained by **3**/MAO in $CDCl_3$ solution. In the ^{1}HNMR spectrum of polystyrene, three groups of hydrogen proton signals were observed. Chemical shifts ar 6.46–7.20 ppm are aromatic hydrogen signals, those at 1.75–2.16 ppm are methine hydrogen signals, and those at 1.00–1.69 ppm are methylene hydrogen signals in polystyrene. These were assigned by peak integral in the ^{1}H NMR spectra and referring to the literature.[26] It is worth mentioning that the proton signal of methine was observed to split into many peaks; they can be used as a characteristic resonance for differentiating the stereoregularity of polymer microstructure.[34] Figure 3 shows the ^{13}C NMR spectra of polystyrene obtained by **3**/MAO at room temperature. Six typical signals which are assigned to C1–C6 of polystyrene were observed. According to the literature, broad signals between 145 and 147 ppm are the aromatic carbon C1s of atactic polystyrene.[6,35] The C1 carbon signals in isotactic and syndiotactic polystyrene were observed at 146.2 and 145.6 ppm as sharp peaks, respectively.[6,35] The results indicate that atactic polystyrene was prepared using these catalytic system. The aromatic C1 spectrum was analyzed in term of triads. Three main peaks at 146.0, 145.5 and 145.1 ppm were assigned to isotactic triad (mm), heterotactic triad (mr) and syndiotactic triad (rr), respectively.[36–38] The stereo-triad distributions of mm,

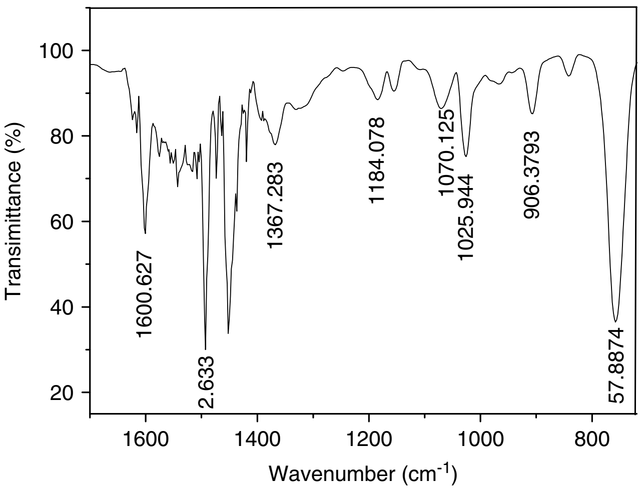

Figure 1. IR spectrum of polystyrene obtained by **3**/MAO catalytic system at 70 °C.

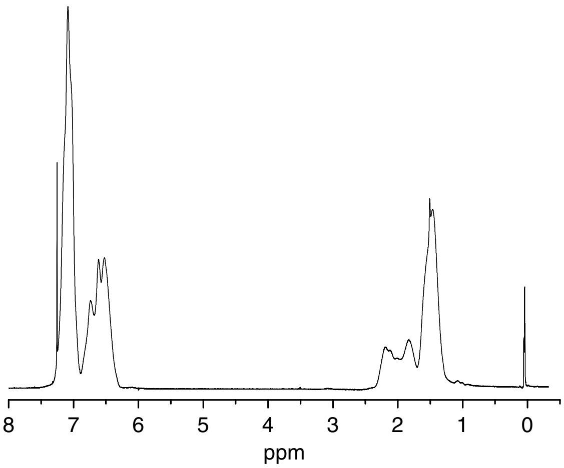

Figure 2. ^{1}H NMR spectrum of polystyrene obtained by **3**/MAO catalytic system at 70 °C.

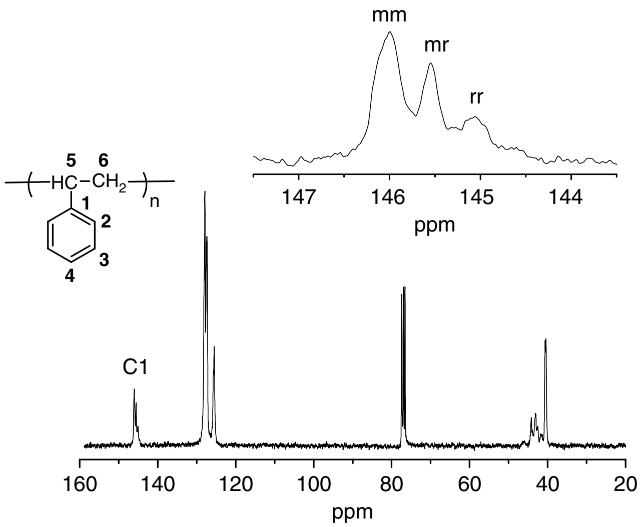

Figure 3. ^{13}C NMR spectrum of polystyrene obtained by **3**/MAO catalytic system at 70 °C.

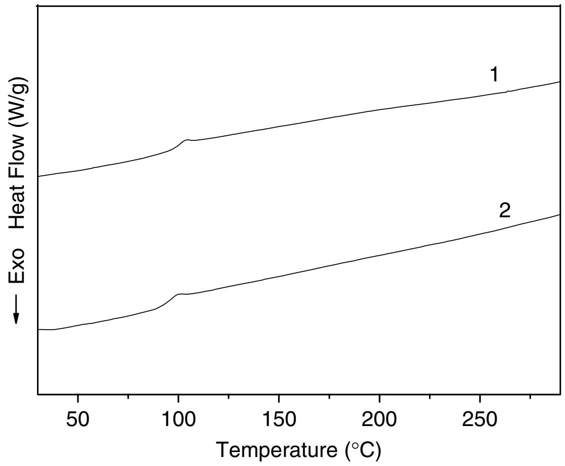

Figure 4. DSC curve of polystyrene obtained by **3**/MAO catalytic system at different temperature (30 °C, **1**; 70 °C, **2**).

mr and rr, are [mm] = 52.4%, [mr] = 27.6% and [rr] = 20.0%, calculated from the triad resonance integral for **3**/MAO. The results suggested that the polymers obtained by the β-diketiminate nickel/MAO catalytic systems are iso-rich atactic polystyrenes.

In the DSC curves of polystyrene obtained by **3**/MAO (Fig. 4), the glass transition temperature (T_g = 103 °C for curve 1, and T_g = 98 °C for curve 2) was obtained from both curves. No sharp melting peak above 200 °C was observed, indicating that the polystyrenes are amorphous. The melting points 270 and 240 °C were reported to appear in the syndiotactic and isotactic polystyrene, respectively.[6,39] The higher T_g value of curve 1 than 2 is the result of lower molecular weight of **2** than **1**. No melting point was observed for polystyrenes prepared at different temperatures, suggesting that the obtained polymers were atactic polystyrenes. Moreover, polystyrenes obtained from these catalytic systems were soluble in acetone, tetrahydrofuran, chloroform and chlorobenzene, which also indicates that low stereoregularity polystyrenes were produced.

Conclusions

The nickel (II) complexes of β-diketiminate ligands exhibited good activity for styrene polymerization in the presence of MAO. The steric hindrance had a pronounced effect on styrene polymerization rates. Ligands with electron-withdrawing substituents had increased catalytic activity. The activity of the catalysts increased with increasing Al : Ni molar ratio. With an increase in the reaction temperature, the catalytic activities for styrene polymerization increased first, and then decreased due to the decomposition of the active species at high temperature. The molecular weight of the polymer increased with a decrease in the temperature. Microstructure analysis of the obtained polymer showed that iso-rich atactic polystyrenes were produced with the catalytic systems.

Acknowledgments

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