Polymerization of Styrene Using Bis(β-ketoamino)nickel(II)/Methylaluminoxane Catalytic Systems

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ABSTRACT: Styrene (St) was polymerized in toluene solution by using bis(β-ketoamino)nickel(II) complex as the catalyst precursor and methylaluminoxane (MAO) as the cocatalyst. The polymerization conditions, such as Al : Ni ratio, monomer concentration, reaction temperature, and polymerization time, were studied in detail. Both of the bis(β-ketoamino)nickel(II)/MAO catalytic systems exhibited higher activity for polymerization of styrene, and polymerization gave moderate molecular weight of polystyrene with relatively narrow molecular weight distribution ($M_w/M_n < 1.6$). The obtained polymer was confirmed to be atactic polystyrene by analyzing the stereo-triad distributions mm, mr, and rr of aromatic carbon C^1 in NMR spectrum of the polymer. The mechanism of the polymerization was also discussed and a metal–carbon coordination mechanism was proposed. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 500–509, 2007

Key words: late-transition-metal; catalytic polymerization; styrene; tacticity; polymerization mechanism

INTRODUCTION

Transition metal complexes, as styrene polymerization catalysts, have received considerable attention since Ziegler–Natta catalysts, based on $TiCl_4$/$Al(CH_2CH_3)_3$, were used to synthesize a stereoregular isotactic polystyrene (iPS).[1,2] The first syndiotactic polystyrene (sPS) was synthesized by using a homogeneous organometallic catalytic system on the basis of titanium compounds and methylalumoxane.[3,4] Recently, various systems based on late transition metal complex catalysts has been explored for styrene (St) polymerization. For example, cationic η^3-allylnickel complexes alone[5,6] or modified by phosphine and phosphite ligands[6,7] as well as a few other systems (e.g., cationic η^3-benzylic nickel complexes[8]) are active homogeneous catalysts for the low molecular weight polymerization of styrene through a simple cationic mechanism.[5–8] Neutral alkyl nickel complexes alone[9–12] or activated by addition of electron-poor additives[12,13], as well as homogeneous organometallic catalytic systems containing methylaluminoxane (MAO) (e.g., $Ni(acac)_2$/$MAO^{14–16}$) are known to produce nonstereospecic polystyrene, and a coordination mechanism was proposed.[12,13] Since 1995, an increasing number of late transition metals in conjunction with different organic halides and ligands have been known to be able to catalyze the atom transfer radical polymerization of styrene.[17–27] Neutral nickel and palladium σ-acetylide complexes,[28] and a series of cationic palladium and nickel-based acetylide complexes $(PR'_3)_2M(C{\equiv}CR)_2$ [M=Pd, Ni, R'=Ph$_3$, n-Bu$_3$; R=Ph, CH$_2$OH, CH$_2$OOCCH$_3$, CH$_2$OOCPh, CH$_2$OOCPhOH-o, C$\equiv$CC$_6$H$_4$C$\equiv$CH, etc.] as a high active initiators for polymerization of styrene showed catalytic activity in the polymerization of styrene.[29,30] Recently, a new family of catalytic systems based on indenyl nickel complexes and AgBPh$_4$ (or NaBPh$_4$, or AgBF$_4$) and PPh$_3$ have been reported for styrene polymerization.[31–34] Groux and Zargarian first reported that (Ind)(PR$_3$)Ni—X (Ind = indenyl and its substituted derivatives; R = Ph, Me, Cy, Bu, etc.; X = halide, alkyl, alkynes,

imidate, thiolate, etc.) can act as effective precatalysts in polymerization of styrene, and they proposed that a cationic species $[Ind(PPh_3)Ni]^+$ generated *in situ* is the active center for these reactions, such as a $(\eta^3, \eta^0$-Ind-$CH_2CH_2NMe_2)Ni(PPh_3)Cl/AgBF_4/PPh_3$ system that a chelating amino-indenyl cationic nickel complex *in situ* generated from $(\eta^3, \eta^0$-Ind-$CH_2CH_2NMe_2)Ni(PPh_3)Cl$ and $AgPh_4$ (or $AgBF_4$) for styrene polymerization.[31] [(1-Me-Ind)Ni(PPh_3)Cl/AgBF_4/PPh_3] catalytic system for styrene oligomerization in 90% yield, and a bis(phosphine) cationic species $[(1-Me-Ind)Ni(PPh_3)PPh_3]^+$ was obtained when equimolar quantities of $[(1-Me-Ind)Ni(PPh_3)Cl$ and $AgBF_4$ and PPh_3 are stirred in CH_2Cl_2,[32] and similar results were also observed when PPh_3 was added to the mixture of $(\eta^3, \eta^0$-Ind-CH_2CH_2N-$Pr_2)Ni(PPh_3)Cl$ and $NaBPh_4$ (>90%).[33] Sun et. al. have also reported that cationic nickel complexes $(\eta$-1-R-Ind)Ni(PPh_3)Cl)$ (R = cyclopentyl or benzyl), $NaBPh_4$, and PPh_3 showed high catalytic activity for the polymerization of styrene in toluene and gave rise to a syndio-rich atactic polystyrene (aPS).[34] However, insufficient data reports have been published on the use of late transition metal complexes with MAO as cocatalyst for styrene polymerization.

The present study aims at investigating the effects of some polymerization parameters on styrene polymerization using bis(β-ketoamino)nickel(II)/MAO catalytic systems. A particular objective is to study the influence of electronic versus steric effects of these nickel complexes on such styrene polymerization.

EXPERIMENTAL

Materials

All manipulations involving air- and moisture-sensitive compounds were performed under a dried and purified argon atmosphere standard glove box and Schlenk techniques. Toluene was dried over sodium/benzophenone and distilled under argon prior to use. Other solvents were purified using standard procedures. Styrene (St) was purchased from Shanghai reagent factory and purified by washing twice with aqueous sodium hydroxide (5 wt %) and twice with water for removing inhibitors, followed by drying over anhydrous $MgSO_4$ and distillation over CaH_2 under argon atmosphere at reduced pressure. Hydroquinone was purchased from Shanghai fine chemical science and technology. MAO was prepared by the hydrolysis of trimethylaluminum (TMA) with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene with initial $[H_2O]/[TMA]$ molar ratio of 1.3, according to literature.[35] The excess $Al_2(SO_4)_3$ was separated by filtration.

Preparation of bis-(β-ketoamino)nickel(II) complex

Bis-(β-ketoamino)nickel(II) complexes $Ni[CH_3C(O)CHC(NR)CH_3]_2$ (R = phenyl, **1** and R = naphthyl, **2**), which here employed to act as catalysts for polymerization of styrene after activation with MAO, were synthesized according to the method reported in our previous work.[36] The complexes were prepared by two-step procedures, which consisted of a condensation reaction between a β-diketo compound and one equivalent of an aromatic amine to afford the respective β-ketoamine ligands, which were subsequently deprotoned by using *tert*-BuOK strong alkali, and exposure to the desired nickel for complexation by mixing with $[Et_4N]_2[NiBr_4]$ in *tert*-BuOH solvent.

Polymerization of styrene

All procedures for polymerization were carried out under purified nitrogen atmosphere. A typical polymerization procedure is as follows: the appropriate MAO solid and 10 mL of toluene as solvent were added in turn into a 50 mL two-necked round-bottomed flask containing a magnetic stir bar, shaken to obtain a homogeneous solution, and then 10 mL of styrene monomer was injected. After an appropriate amount of fresh Ni(II) catalyst solution (in toluene, 0.005 mol/L) was injected into the reaction solution, the mixture stood at a constant temperature for a definite reaction time. The polymerization was stopped by addition of ethanol/HCl 5% (v/v). The resulting precipitation was collected, filtered, washed with EtOH for several times, and then dried in vacuum at 50°C to a constant weight. The polymerization yield was determined by gravimetry. Unless otherwise stated, the total reaction volume was kept at 21 mL by varying of the amount of toluene, if necessary. Series experiments of effects of hydroquinone were carried out by adding different amounts of hydroquinone to **1**/MAO system prior to the initiation of the styrene polymerization.

Characterization of polystyrene

The molecular weights (M_w and M_n) and molar mass distributions (M_w/M_n) of the polymers were measured by gel permeation chromatography using a Waters 1515 HPLC instrument equipped with a 2414 differential refractometer and a set of Styragel MIXED-C columns (Styragel Waters HR4E and HR5E) to separate molecular weight ranging from 10^2 to 10^6. The oven temperature was set at 40°C. THF was used as the eluent and the flow rate was 1 mL/min. Monodispersed polystyrene (PSt) standards (Aldrich Chemical) were used to generate the calibration curve. The proton and carbon nuclear magnetic resonance
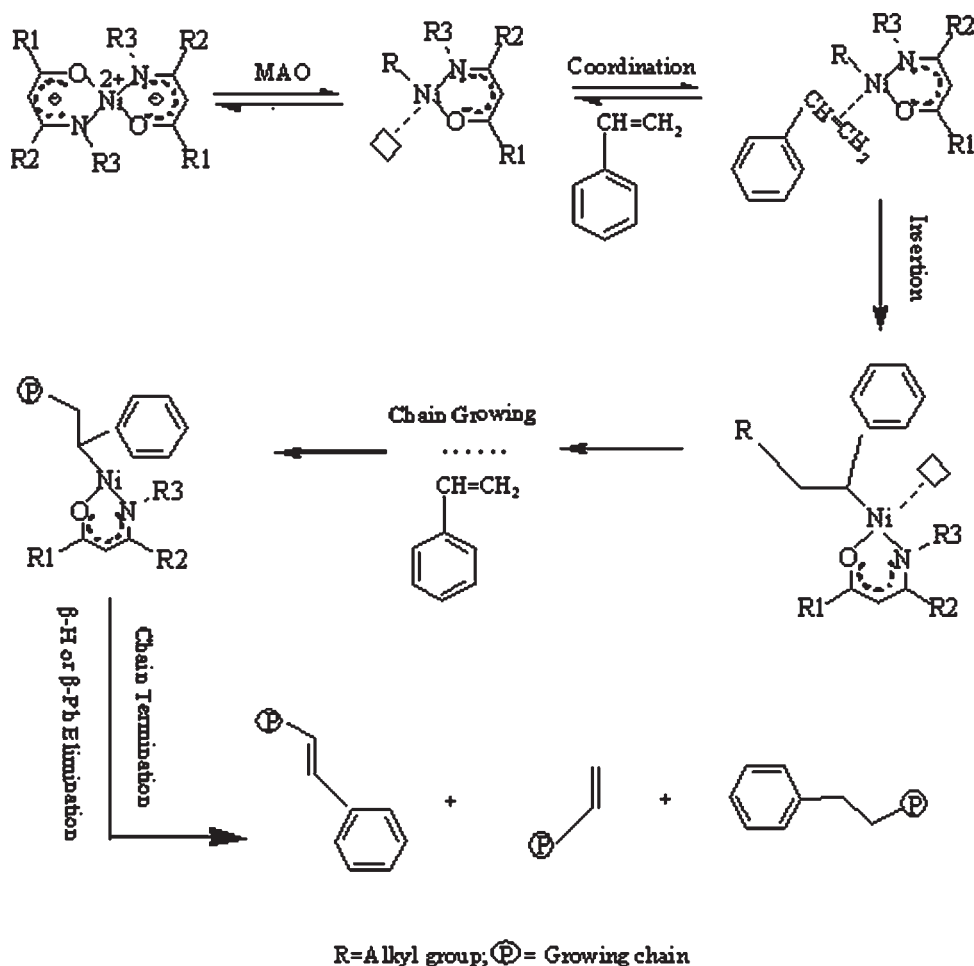
Scheme 1 The proposed mechanism of styrene polymerization catalyzed by bis(β-ketoamine)nickel(II)/methylaluminoxane (MAO) systems.

(^{1}H and ^{13}C NMR) spectra of polymer were recorded on a Bruker ARX 400 NMR spectrometer at room temperature using chloroform-*d* as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal reference. The infrared (IR) spectra were measured on a Shimadzu IRPrestige-21 FTIR spectrophotometer using the KBr method. The thermal properties of polystyrene were determined by a Perkin–Elmer differential scanning calorimeter (DSC 7) with a constant heating/cooling rate of 10°C/min.

RESULTS AND DISCUSSION

Complexes **1** or **2** and MAO were firstly conducted by mixing styrene with either bis(β-ketoamino)nickel (II) or MAO alone or without both bis(β-ketoamino)-nickel(II) and MAO at 60°C for 1 h. It was found that styrene did not polymerize in each cases described above. However, together with MAO, they all show high catalytic activity for styrene polymerization. The results of the above experiments results showed that complex **1** or **2** without MAO is inert toward styrene polymerization, while the addition of

moderate MAO is of benefit to form the cationic species. In this study, therefore, nickel complex is the single catalyst precursor, and MAO is the cocatalyst and plays an important role in promoting the polymerization of styrene. It indicates undoubtedly that the present styrene polymerization with bis(β-ketoamino)-nickel(II)/MAO systems in toluene proceeds by a coordination mechanism, and the metal–carbon bond can form the cationic species in the present polymerization. The proposed mechanism is that a rapid methylation of Ni compound by MAO takes place, and the active species arises from a ligand transfer reaction between the Ni alkyls and MAO, and then the resulting active cationic complex was inserted by styrene monomer, and the chain propagation was proceeded by successively inserting monomer and terminated by β-H or β–Ph eliminating (Scheme 1).

Effects of hydroquinone

A series of experiments were carried out by adding different amount of hydroquinone to **1**/MAO system prior to the initiation of the styrene polymerization.

Effects of Hydroquinone on Polymerization of Styrene Catalyzed by 1/MAO System

| Run	Styrene (mol/L)	Catalyst (10^{-4} mol/L)	MAO (mol/L)	Hydroquinone (mol/L)	Activity in 10^6 g PS (mol Ni h)$^{-1}$	M_w	M_w/M_n
1	4.12	2.33	0.13	0	1.501	32,049	1.51
2	4.12	2.33	0.13	0.13	0.874	49,835	2.15
3	4.12	2.33	0.13	0.22	0.553	56,867	2.41
4	4.12	2.33	0.13	0.43	0.036	53,182	2.52

Polymerization conditions: $T_p = 60°C$; $V_p = 21$ mL; $t_p = 60$ min.

The results are summarized in Table I. Although the polymerization containing hydroquinone was not completely stopped after 1 h, the polymerization conversion as well as catalyst activities decreased deeply. When fourfold of hydroquinone/MAO was used, the polymerization was stopped completely and no polymer was obtained after 1 h. The fact that equivalent molar ratio of hydroquinone and MAO will result in complete ineffectiveness of catalyst systems indicate that that the peculiarly active Al—CH₃ bonds in the original MAO are completely killed by the reaction with hydroquinone. These results seem to be similar to those results of ethylene and propylene homopolymerization or copolymerization catalyzed by Et(Ind)₂ZrCl₂/MAO/hydroquinone system.[37] Soga and coworkers suggested that MAO reacted with *p*-hydroquinone to obtain a toluene-insoluble modified MAO, and the modified MAO alone cannot activate the zirconocene catalyst, and the Al—CH₃ part of the structure in MAO takes part in the activation of metallocene catalysts.[37] Our observations can also suggest that MAO is co-oligomerized with *p*-hydroquinone, and there exist peculiarly active Al—CH₃ bonds in the original MAO with which hydroquinone reacts selectively (Scheme 2). There are also the possibilities that a portion of hydroquinone is consumed by the reaction with a trace amount of Al(CH₃)₃ contained in MAO and besides the edges of ''oligo-MAO''. In addition, with increase in the amount of hydroquinone the molecular weight of the polystyrene increased. The fact strongly indicates that hydroquinone is not acted as a chain-transfer agent. Hydroquinone decreases the rate of chain growth as well as chain termination, but has much influence on the rate of chain growth than on that of chain termination.

Effects of Al : Ni molar ratio

In this study, nickel complex is the single catalyst precursor and MAO is the cocatalyst, and it plays an important role in promoting the polymerization of styrene. As shown in Figures 1 and 2, the catalyst activities as well as molecular weights of resulted polymers depend significantly on the Al/Ni molar ratio; the catalyst activities for both **1**/MAO and **2**/MAO systems rapidly increase at first with an increase in the Al/Ni molar ratio and then level off at about constant values. The results indicate that the present styrene polymerization mainly be catalyzed by the cationic active species generated by MAO/Ni compound. Too low Al/Ni molar ratio or MAO amount will be depleted by the impurity of polymerization system, and the left over amount will not form enough active species with reaction Ni compound. With the Al : Ni molar increase, the concentration of the active Ni^{2+} will rapidly increase and will be saturated after the Ni compound reacted completely with MAO. Contrarily, the molecular weight of polymer increases at first with an increase in the Al/Ni molar ratio, and then decreases gradually. MAO is known to contain TMA both in a form coordinated to MAO and as free TMA. Excess of MAO will lead to a dramatic decrease in polymer molecular weight because of the chain transfer reaction to MAO and TMA.
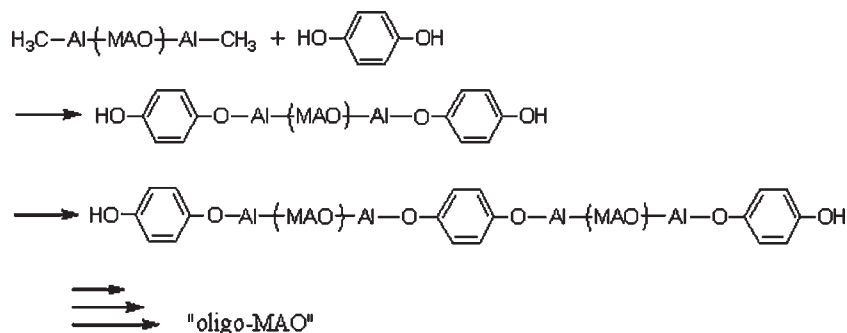
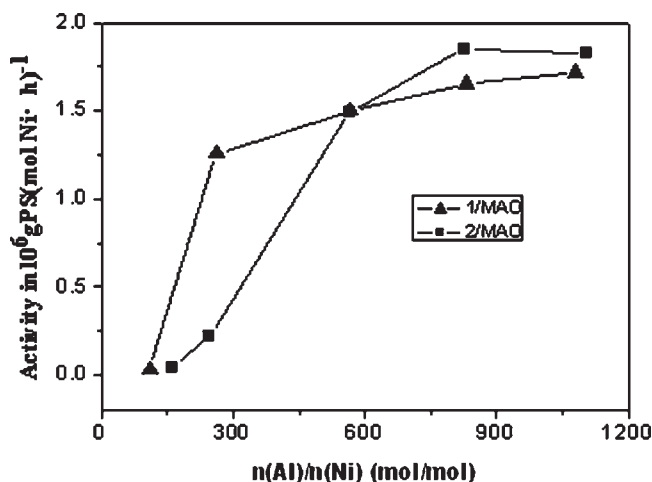**Scheme 2** The reaction of MAO with *p*-hydroquinone.

Figure 1 The effect of Al:Ni molar ratio on the catalytic activity (PDI = 1.41–1.57). Polymerization conditions: $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; $C_{[St]}$ = 4.12 mol/L; T_p = 60°C; t_p = 1 h; V_p = 21 mL.

Figure 3 The effect of polymerization temperature on the catalytic activity (PDI = 1.36–1.56). Polymerization conditions: $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; n(Al)/n(Ni) = 565; $C_{[St]}$ = 4.12 mol/L; t_p = 1 h; V_p = 21 mL.

Effects of polymerization temperature

Polymerizations of styrene with **1**/MAO and **2**/MAO catalytic systems were performed in toluene at different polymerization temperature (T_p), with constant ratios of monomer to Ni complex and MAO to Ni complex. As shown in Figure 3, both **1**/MAO and **2**/MAO are able to proceed at the scope of temperature from 0 to 80°C in toluene, and exhibited high catalytic activities. The catalytic activities obviously depend on polymerization temperature. With increase of polymerization temperature, the catalyst activity increases rapidly first, but higher temperature led to the decrease of the activities. The highest activities value can be achieved at about 40°C for **1**/MAO system and 60°C for **2**/MAO system, respectively. In addition, as shown in Figure 4, the poly-

mer molecular weights were also strongly affected by the polymerization temperature. The molecular weights (M_w) of the polymer decrease monotonously with polymerization temperature increasing, but molecular weight distribution is not changed, and is relatively narrow (M_w/M_n < 1.6). It may be because of significant increase in the chain transfer and chain termination rate at higher temperature.

Comparing the activities of catalysts **1** and **2** at different reaction conditions, it can be found that the activities of complex **2** is apparently higher than that of complex **1** at 0°C. However, the polymerization yields and catalyst activities of **1**/MAO system is higher than those of **2**/MAO system above 20°C (at 60°C their catalytic activity is comparable with each
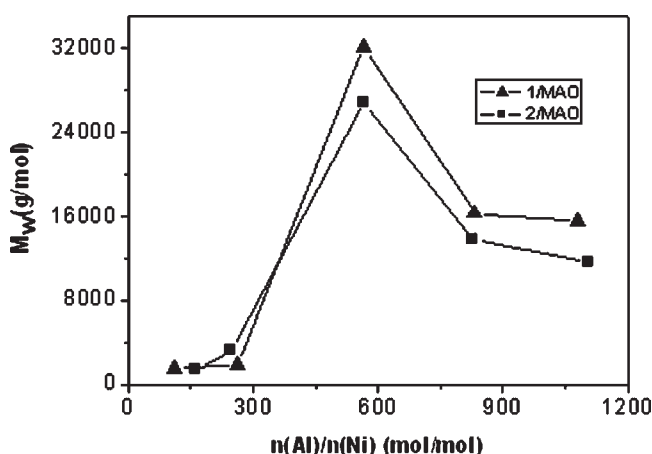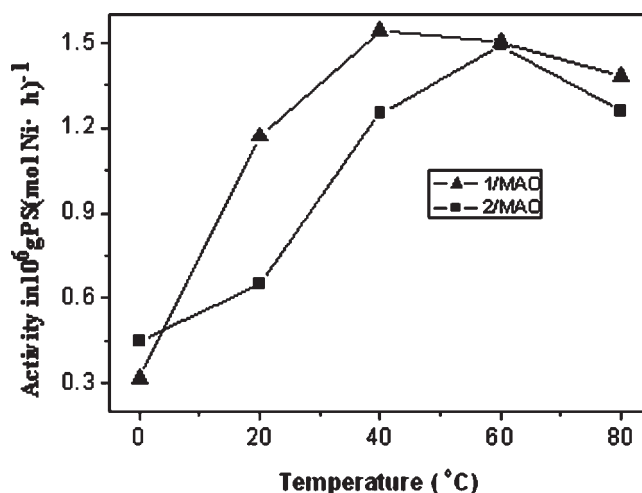

Figure 2 The effect of Al : Ni molar ratio on the polymer molecular weight (PDI = 1.41–1.57). Polymerization conditions: $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; $C_{[St]}$ = 4.12 mol/L; T_p = 60°C; t_p = 1 h; V_p = 21 mL.
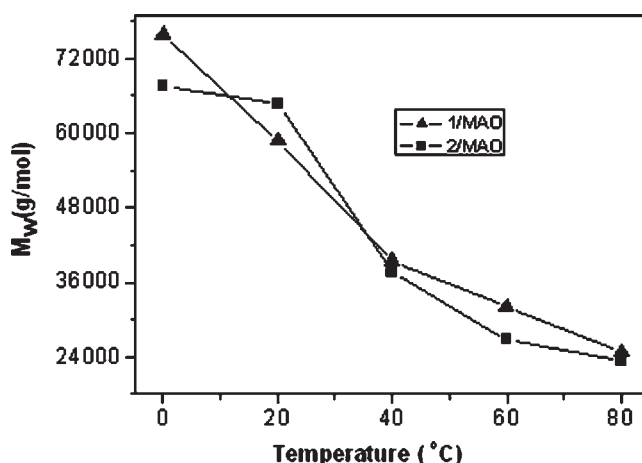

Figure 4 The effect of polymerization temperature on the polymer molecular weights (PDI = 1.36–1.56). Polymerization conditions: $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; n(Al)/n(Ni) = 565; $C_{[St]}$ = 4.12 mol/L; t_p = 1 h; V_p = 21 mL.
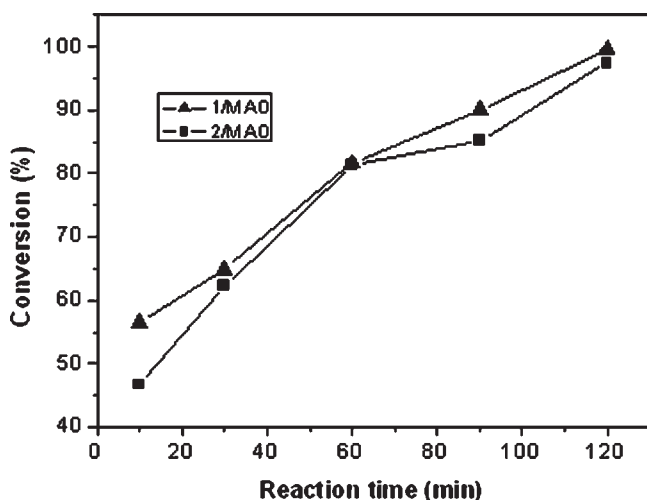
Figure 5 Effects of polymerization time on the polymer yields (PDI = 1.41–1.54). Polymerization conditions: $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; $n(Al)/n(Ni)$ = 565; $C_{[St]}$ = 4.12 mol/L; T_p = 60°C; V_p = 21 mL.

other). This fact indicates that the active species loss rate depends on the temperature condition and a close relationship between structure–activity of these nickel complexes. It is well known that steric bulk and electronic effects of the ligand could control the activation of the catalysts for olefin polymerization. Ni compound **2** with the chelating naphthyl ring substituent connected with the imino group has more steric bulk and a stronger electronic conjugation over a wider range than Ni compound **1** with the unique steric effect phenyl ring. Compared with the steric effect, the chelating phenyl ring on ligand with the unique steric effect seem to play an important role in stabilizing the active species generated from the reaction between the Ni compound precur-

sors and MAO. As a result, the active species would become much more stable. Compared with the electron effect, Ni compound **2** with the chelating naphthyl ring has stronger electronic conjugation over a wider range, which reduces the electron cloud density of Ni^{2+} (active species) and strengthen Ni—C bond, and thus is unfavorable to the coordination of monomer to Ni^{2+} active species.

Effects of polymerization time

Figures 5 and 6 illustrate the effect of polymerization time on the conversions and molecular weights of polymers. Considerable effects of polymerization time on the conversions were observed. As expected, with prolonging polymerization time, the polymerization conversions increased progressively and the increase tends to the highest value because of the decreasing on monomer concentration during the reaction. The dependencies of the weight–average molecular weights on the polymerization time can be also seen for both catalytic systems. The molecular weight of PS nonlinearly increased with prolonging polymerization time, while the molecular weight polydispersity maintained at around 1.4–1.5.

Effects of monomer concentration

Considerable effects of the molar ratio of monomer to catalyst on the catalyst activities and the molecular weight of polymer were also observed. The effects of molar ratio of monomer to catalyst on the styrene polymerizations were illustrated in Figures 7 and 8. The catalytic activity of styrene polymerization increased rapidly with increasing the styrene/Ni molar ratio (monomer concentration). On one
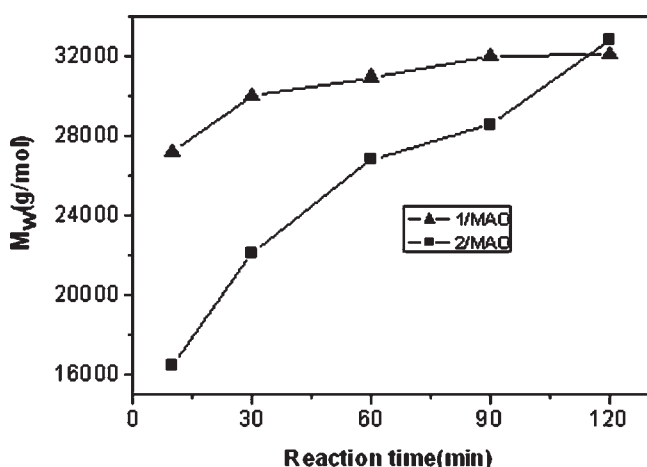

Figure 6 Effects of polymerization time on the polymer molecular weights (PDI = 1.41–1.54). Polymerization conditions: $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; $n(Al)/n(Ni)$ = 565; $C_{[St]}$ = 4.12 mol/L; T_p = 60°C; V_p = 21 mL.
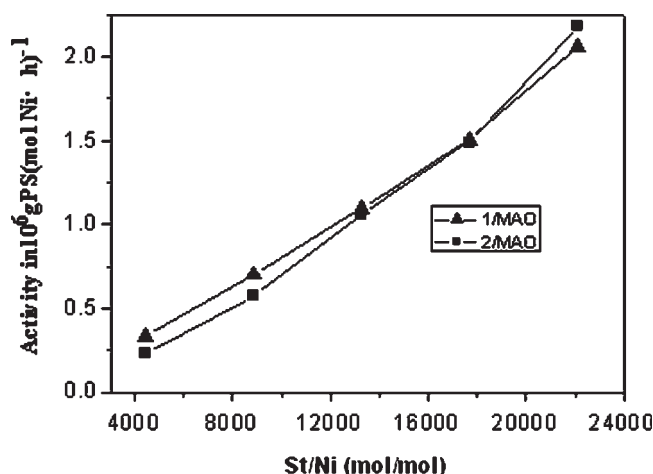

Figure 7 Effects of monomer concentration on catalytic activity (PDI = 1.35–1.57). Polymerization conditions: $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; $n(Al)/n(Ni)$ = 565; T_p = 60°C; t_p = 1 h; V_p = 21 mL.
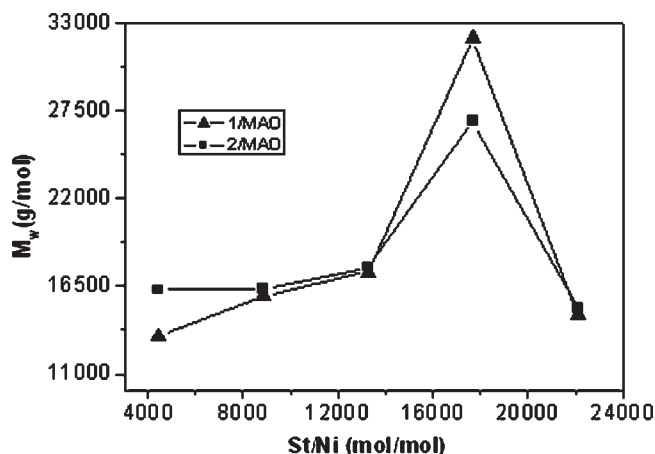
Figure 8 Effects of monomer concentration on polymer molecular weights (PDI = 1.35–1.57). Polymerization conditions: $C_{[Ni]} = 2.33 \times 10^{-4}$ mol/L; $n(Al)/n(Ni) = 565$; $T_p = 60°C$; $t_p = 1$ h; $V_p = 21$ mL.

hand, the catalytic activity of styrene polymerization fall because of monomer rapid depletion at low monomer concentration, and on the other hand, the phenyl ring of toluene can also coordinate to Ni^{2+} cationic species. This coordination, which competes with the monomer, will lead to the drop in activity. Contrarily, the molecular weights (M_w) of PS obtained increased rapidly with increasing monomer concentration and then decrease gradually in the range of the conditions studied. To get the products with high conversion and high molecular weight, the optimum molar ratio of monomer to catalyst are considered to be ca.18,000 for both of the catalytic systems.

Tacticity of the synthesized polymers

The FTIR spectra of polymers obtained by both catalytic systems are similar. Figure 9 is the typical IR spectrum of polymer obtained by **2**/MAO system. As expected, the FTIR spectra of the polymer show typical bands attributable to polystyrene. There are no obvious absorption bands appearing at 1217.6 and 1220 cm^{-1}, which are assigned to the characteristic signal of the sPS.[38,39] However, absorption band at 1070 cm^{-1}, which is assigned to the characteristic signal of the aPS, was observed. The results indicated that those catalytic systems can efficiently polymerize styrene to give aPS. The exact microstructure of the polymer needs to be confirmed by ^{1}H and ^{13}C NMR information.

Figures 10 and 11 show typical ^{1}H and ^{13}C NMR spectra for PS obtained from the **2**/MAO catalyst system at 60°C and determined at room temperature in CDCl$_3$ solution. As seen in Figure 10, in the 0.8–7.8 ppm range, three groups of hydrogen protons appear, which are assigned to the hydrogen protons

on aromatic carbon hydrogen (H^2, H^3, and H^4), hydrogen proton on methine carbon (H^5), and hydrogen proton on methylene carbon (H^6) in the PS units, respectively. The chemical shift signals appearing around 1.746–1.875, 1.875–2.058, and 2.11–2.28 ppm can be assigned to the syndiotactic (rr), heterotactic triad (mr), and isotactic (mm) triad of methine carbon hydrogen proton (H^5) resonances. The stereotriad distributions of mm, mr, and rr, calculated from the triad resonance integral,[40] are [mm] = 21%, [mr] = 33%, and [rr] = 46%.

There are six typical carbons with different chemical environment in polystyrene, which consist of aromatic carbon C^1, C^2, C^3, C^4, and methine carbon C^5 and methylene carbon C^6. The aromatic carbon C^1 is very sensitive to the space configuration, and can generally be considered as the most important characteristic resonance for differentiating the stereoregularity of polymer microstructure by analyzing in term of triads.[38] According to the reported results,[38,41] abroad signals at the range of 145–147 ppm, attributable to the aromatic carbon C^1, indicate an aPS. A sharp peak at 146.2, attributable to the aromatic carbon C^1, indicates an iPS and a sharp peak at 145.6 indicates a sPS.

Figure 11 shows the typical ^{13}C NMR spectra of PS obtained by **2**/MAO catalytic system at 60°C, which were determined at room temperature in CDCl$_3$ solution. The present spectra show characteristically broad signals of actactic polystyrene in the range of ca. 145.1–146.17 ppm. The peaks at δ = 143.0–143.567 ppm, δ = 142.206–143.0 ppm, and δ = 144.0–144.87 ppm are assigned to heterotactic triad (mr), isotactic (mm), and syndiotactic (rr), respectively. The stereo-triad distributions of mm, mr, and
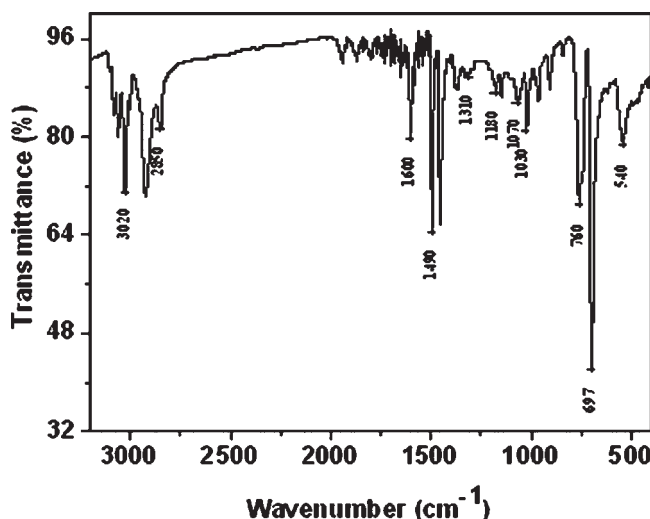

Figure 9 FTIR spectrum of polystyrene obtained by **2**/MAO catalytic system and polymerization conditions: $C_{[Ni]} = 2.33 \times 10^{-4}$ mol/L; $n(Al)/n(Ni) = 565$; $C_{[St]} = 4.12$ mol/L; $T_p = 60°C$; $t_p = 1$ h).
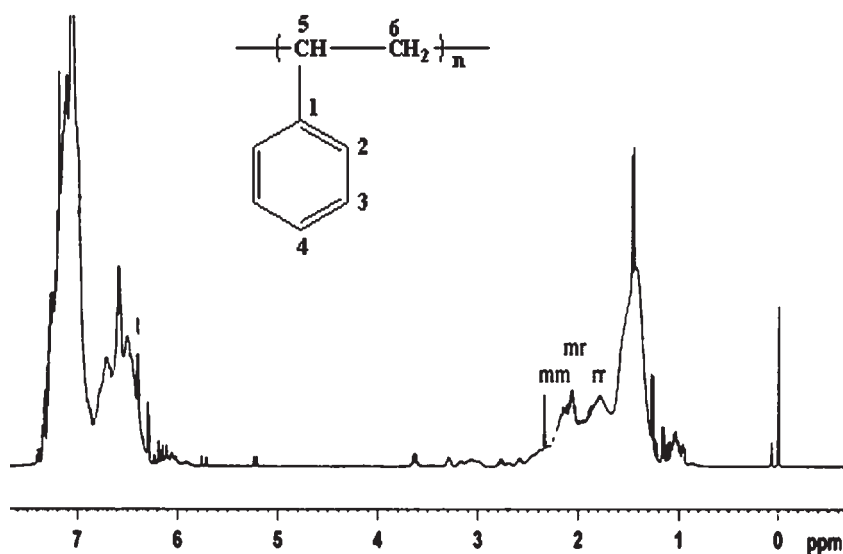
Figure 10 ^{1}H-NMR spectrum of polystyrene obtained by **2**/MAO catalytic system and polymerization conditions is $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; n(Al)/n(Ni) = 565; $C_{[St]}$ = 4.12 mol/L; T_p = 60°C; t_p = 1 h).

rr, calculated from the triad resonance integral, are [rr] = 44.8%, [mm] = 22.8%, [mr] = 32.4% for **1**/MAO and [rr] = 47.1%, [mm] = 27.1%, [mr] = 25.8%

for **2**/MAO, respectively. The results suggested that the polystyrene obtained by both catalytic systems is a atactic polymer (aPS).
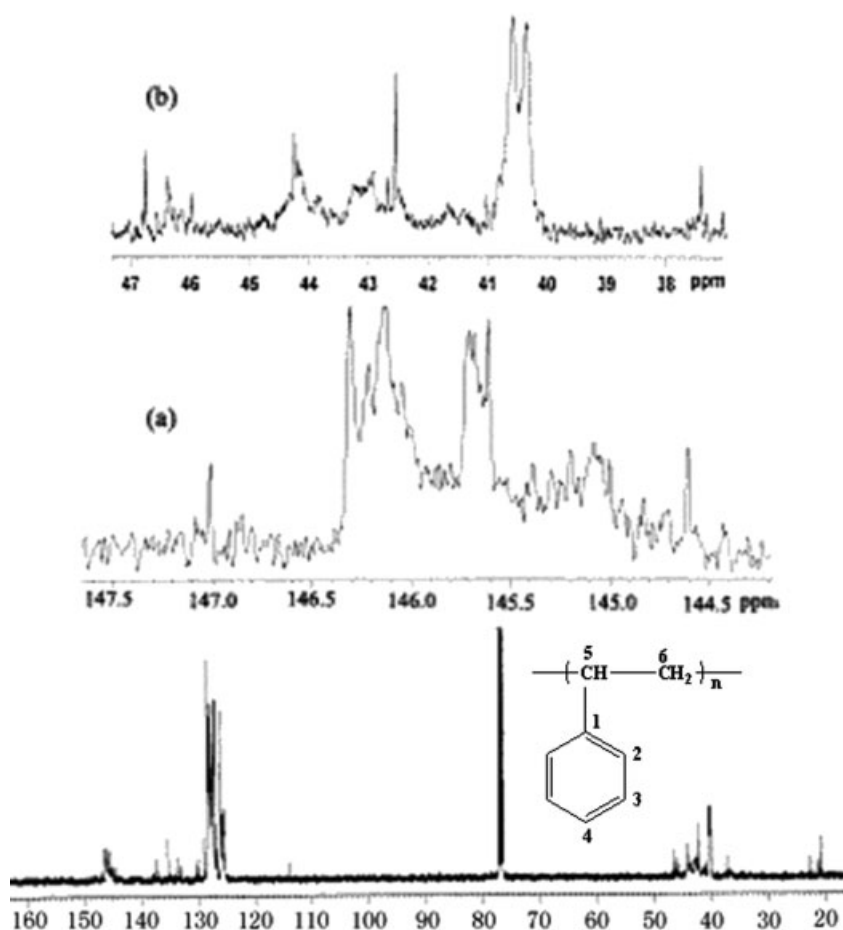

Figure 11 ^{13}C NMR spectrum of polystyrene obtained by **2**/MAO catalytic system and polymerization conditions is $C_{[Ni]}$ = 2.33 × 10^{-4} mol/L; n(Al)/n(Ni) = 565; $C_{[St]}$ = 4.12 mol/L; T_p = 60°C; t_p = 1 h).
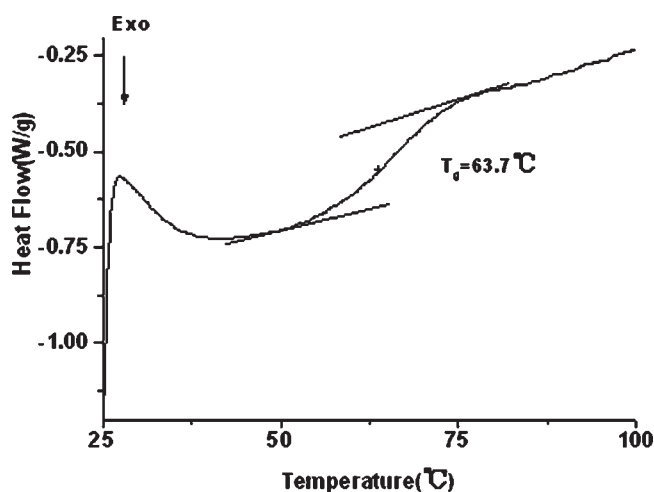
Figure 12 DSC curve of PS of polystyrene obtained by **2**/MAO catalytic system and polymerization conditions is $C_{[Ni]} = 2.33 \times 10^{-4}$ mol/L; $n(Al)/n(Ni) = 565$; $C_{[St]} = 4.12$ mol/L; $T_p = 60°C$; $t_p = 1$ h).

The resonances of methine carbon C^5 and methene carbon C^6 were split completely and can determine the fine structure of polystyrene. According to the literature,[42] the chemical shift of methine carbon C^5 and methene carbon C^6 are 40.3 and 43.67 ppm, respectively. The peak of methene carbon C^6 is split to be three main peaks due to influence of different configuration. The peaks consist of heterotactic triad (mr): $\delta = 43.0$–43.567 ppm; isotactic (mm): $\delta = 42.206$–43.0 ppm; and syndiotactic triad (rr): $\delta = 44.0$–44.87 ppm, respectively. The stereo-triad distributions of mm, mr, and rr, calculated from the triad resonance integral, are [rr] = 44.3%, [mm] = 24.4%, and [mr] = 31.3%.

Figure 12 shows the DSC curve of the polystyrene obtained with **2**/MAO catalytic system at 60°C. According to the literature, the melting point and glass transition temperature are $T_m = 240°C$ and $T_g = 101°C$ for iPS, but $T_m = 270°C$ for sPS.[38,42] In this curve, only low glass transition temperature at 63.7°C is found, which indicates a typical aPS. Moderate molecular weight gives rise to a T_g of the resulted polymer, which is significantly lower than that of commercial aPS. In addition, all polymers obtained by above catalytic systems are soluble in organic solvent, such as chloroform, 2-butanone, acetone, THF, chlorobenzene, and o-dichlorobenzene. This fact further indicates that all polystyrenes obtained above catalytic systems were atactic structure.

CONCLUSIONS

Bis(β-ketoamine)nickel(II)/MAO catalytic systems have been used to initiate polymerization of styrene (St) in toluene solution. The addition of hydroquinone gave rise to the decrease of catalytic activity

and increase of molecular weight of polystyrene (PS) because the hydroquinone acted as deactivator of catalyst but not chain-transfer agent in polymerization. Both of the bis(β-ketoamino)nickel(II) /MAO catalytic systems exhibited higher activity for polymerization of styrene, and polymerization gave moderate molecular weight of polystyrene with relative narrow molecular weight distribution ($M_w/M_n < 1.6$). For both catalytic systems, the catalyst activities rapidly increase at first with an increase in the Al/Ni molar ratio and then level off at about constant values. Both catalytic systems are able to proceed at the scope of temperature from 0 to 80°C in toluene, and exhibited high catalytic activities. The obtained polymer was confirmed to be aPS, and a metal–carbon coordination mechanism was proposed.

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