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Structures and styrene polymerization activities of a series of nickel complexes bearing ligands of pyrazolone derivatives

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A series of nickel complexes with β-ketoamine ligands based on pyrazolone derivatives were synthesized by condensing pyrazolone with aniline, 2-chloroaniline or naphthylamine and then reacting the produced β-ketoamine with nickel halide. The solid-state structures of these three complexes were determined by single-crystal X-ray diffraction. The bis(β-ketoamine)nickel complexes are all air-stable and can act as highly active catalyst precursors for styrene polymerization with activation of methylaluminoxane under mild reaction conditions. The activity of the catalyst for styrene polymerization is as high as 2.10×10^5 g polymer/mol Ni h. Both steric and electronic effects were found to be important and influential for catalytic activity. Copyright © 2005 John Wiley & Sons, Ltd.

KEYWORDS: crystal structure; β-ketoamine; nickel complexes; styrene; polymerization

INTRODUCTION

Styrene is one of the few monomers able to polymerize through all the known polymerization mechanisms, i.e. radical, anionic, cationic and coordinated mechanisms. More interestingly, the polymerization of styrene monomer can lead to the formation of three tactic structures in the resulting polymers, including isotactic, syndiotactic and atactic polystyrenes.[1–7] The stereoregular conformation in the polymer architecture imparts crystallinity and hence elevates the physical properties in the resulting styrene polymers.

Recently, there has been an intense search for new-generation catalysts for the polymerization of olefin and other unsaturated monomer in both academic and industrial research laboratories, especially those containing late transition metals.[8–12] Organometallic nickel complexes have also been studied to catalyze the styrene polymerization.[13,14] Our group has reported that a nickel complex bearing β-ketoamine ligand can catalyze norbornene vinylic polymerization.[15] With the aim of studying the catalytic properties of the late metal complexes for styrene polymerization, three nickel pyrazolone complexes were prepared and used as catalyst precursors for the polymerization of styrene with the activation of methylaluminoxane (MAO).

EXPERIMENTAL

Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk techniques. Solvents were purified using standard procedures. Reagents 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and aniline (AR), 2-chloroaniline (AR), naphthylamine (AR) were obtained from China National Medicine Group, Shanghai Chemical Reagent Company and used without further purification. Styrene from Aldrich was dried with potassium and distilled. Anhydrous toluene was obtained by distillation over Na. MAO was prepared by the hydrolysis of trimethylaluminum with $Al_2(SO_4)_3.18H_2O$ in toluene with an H_2O : Al molar ratio of 1.3 : 1.

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Measurements

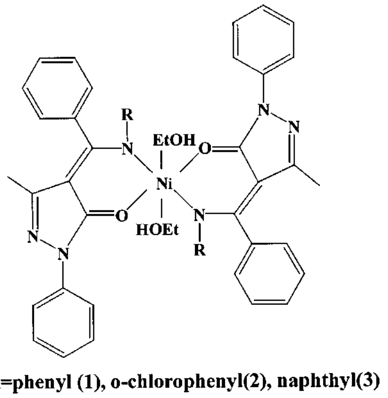
Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240C elementary analyzer. Infrared spectra were recorded on a Bruker EQUINOX55 FT-IR spectrophotometer in the region of 4000–400 cm^{-1} in KBr pellets. ^{1}H and ^{13}C NMR spectra were measured on a Varian Unity INOVA 400NB instrument using $CDCl_3$ as solvent and TMS as internal standard at room temperature. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distributions of the polymers were performed on a Waters Breeze system with THF as the eluent at 40 °C using standard polystyrene as the reference. Melting points were recorded on a Tormas model 40 micro hot stage and uncorrected.

Crystal structure determination

Single crystal X-ray diffraction data of complexes **1**, **2** and **3** were collected on a Bruker Smart 1000 CCD diffractometer at room temperature, Mo Kα radiation, 2θ range 3.6–56.0° (Table 1). The structures were solved by direct methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against F^2 using SHELXTL[16] with anisotropic thermal parameters for all the non-hydrogen atoms. Absorption corrections were applied using SADABS.[17]

Syntheses of Ni(II) complexes

The syntheses of the L**1**, L**2** and L**3** were according to the literature methods.[18–20] Complexes **1**–**3** were synthesized according to the following procedure. The general structures of these complexes are shown in Scheme 1.



Scheme 1. Structures of these bis-(β-ketoamine)–nickel (II) complexes.

Table 1. Crystal data and refinement complex **1**, **2** and **3**

Complex	1	2	3
Formula	$C_{50}H_{48}NiN_6O_4$	$C_{50}H_{46}Cl_2NiN_6O_4$	$C_{58}H_{52}NiN_6O_4$
Formula weight	855.65	924.54	955.77
Cell setting	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$	$C2/c$
a (Å)	24.797(3)	25.050(3)	25.834(3)
b (Å)	10.752(1)	10.806(2)	10.904(1)
c (Å)	17.185(2)	17.260(2)	17.362(2)
α (deg)	90	90	90
β (deg)	107.911(2)	106.117(2)	102.922(2)
$\gamma/°$	90	90	90
V (Å^3)	4359.7(9)	4488.5(10)	4767.0(10)
Z	4	4	4
D_C (mg/m^3)	1.304	1.368	1.332
μ(mm^{-1})	0.50	0.604	0.46
F(000)	1800	1928	2008
Crystal size	0.50 × 0.30 × 0.17	0.36 × 0.36 × 0.21	0.42 × 0.36 × 0.30
θ_{max} (deg)	27.1	25.00	27.11
Limiting indices (h, k, l)	$-31 \rightarrow 15$	$-18 \rightarrow 29$	$-32 \rightarrow 32$
	$-13 \rightarrow 13$	$-12 \rightarrow 12$	$-13 \rightarrow 13$
	$-19 \rightarrow 22$	$-20 \rightarrow 20$	$-22 \rightarrow 21$
No. reflections	12 486	10 980	19 853
No. $I > 2\sigma(I)$ reflections	4769	3938	5239
No. parameters	281	300	317
Goodness-of-fit	1.00	1.07	1.04
Final R indices [$I > 2\sigma(I)$]	0.044, 0.109	0.056, 0.151	0.047, 0.129
R indices (all data)	0.078, 0.123	0.086, 0.173	0.069, 0.142
Largest diff. peak and hole (e/Å^3)	0.45 and −0.42	0.51 and −0.35	0.80 and −0.29

*Complex **1** [Ni(L**1**)$_2$(CH$_3$CH$_2$OH)$_2$]*

A CH_2Cl_2 solution (5 ml) containing L**1** (42 mg, 0.12 mmol) and Et_3N (17 μl, 0.12 mmol) was stirred for 10 min at room temperature, then a solution of $NiCl_2$ (7.8 mg, 0.06 mmol) in EtOH (5 ml) was added and the mixture stirred for 20 min. The resulting clear brown solution was filtered and left to stand at room temperature for several days to give black crystalline products at 65% yield. Calculated for $C_{50}H_{48}NiN_6O_4$: C 70.19, H 5.65 and N 9.82%; found: C 70.08, H 5.78 and N 9.63%. ^{1}H NMR ($CDCl_3$),δ(ppm): 6.256 (2H, phenyl); 6.812 (2H, phenyl); 7.371 (2H, phenyl), 1.375 (3H, $-CH_3$).

*Complex **2** [Ni(L**2**)$_2$(CH$_3$CH$_2$OH)$_2$]*

Complex **2** was prepared by a similar procedure to complex **1**. Yield: 68%. Calculated for C $C_{50}H_{46}Cl_2NiN_6O_4$: C 64.96, H 5.01 and N 9.09%; found: C 65.18, H 5.63 and N 9.30%. ^{1}H NMR ($CDCl_3$), δ(ppm): 6.832 (1H, *o*-chlorophenyl); 7.124 (1H, *o*-chlorophenyl); 1.510 (3H, $-CH_3$).

*Complex **3** [Ni(L**3**)$_2$(CH$_3$CH$_2$OH)$_2$]*

Complex **3** was prepared by a similar procedure to complex **1**. Yield: 71%. Calculated for $C_{58}H_{52}Ni\,N_6O_4$: C 72.89, H 5.48 and N 8.79%; found: C 72.55, H 5.30 and N 8.89%. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.425 (2H, naphthyl); 7.147 (2H, naphthyl); 1.523 (3H, $-CH_3$)

Typical polymerization procedure

All procedures for polymerization were carried out under purified nitrogen. A typical polymerization procedure is as follows: MAO (0.5 mmol) was added to a Schlenk flask under an inert atmosphere with 10 ml solution of styrene (48.08 mmol, 5.0 g) in toluene, and 9 ml of toluene. The reaction was started by the addition of 1 ml of a fresh catalyst solution (toluene, 1×10^{-6} mol catalyst) at 60 °C. After 1 h, the reaction mixture was poured into an excess of ethanol acidified with 5% HCl (molar ratio), which was washed with ethanol, filtered, dried under vacuum at 80 °C for 48 h, weighed, and finally characterized by ^{13}C NMR and gel permeation chromatography (GPC). The whole reaction volume is 20 ml unless otherwise stated.

RESULTS AND DISCUSSION

Syntheses and structures of complexes

L**1**–L**3** were very soluble in CH_2Cl_2 and $CHCl_3$, but moderately soluble in hot MeOH and EtOH. When the deprotonated (by triethylamine) ligand was allowed to react with $Ni(NO_3)_2$ or $NiCl_2$ in either 2 : 1 or 1 : 1 molar ratio, the same crystalline products were obtained as identified by X-ray diffraction studies, which suggests that the composition of the products is sensitive neither to the type of anion nor to the ligand-to-metal ratio under these reaction conditions.

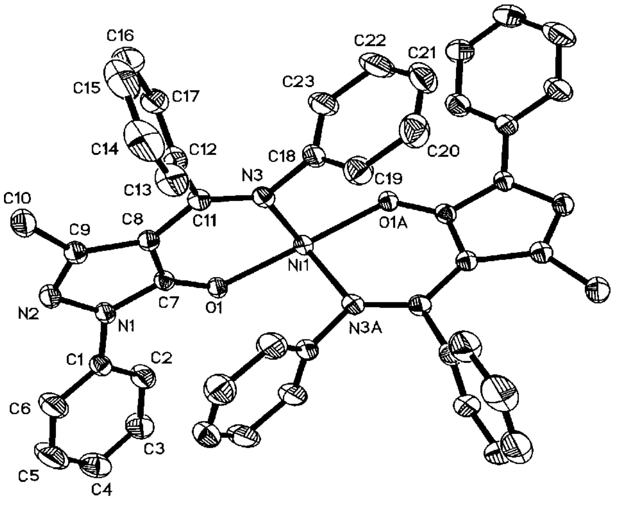


Figure 1. ORTEP plots of complex **1** showing the atom-labeling scheme. Hydrogen atoms and two ethanol molecules are omitted for clarity.

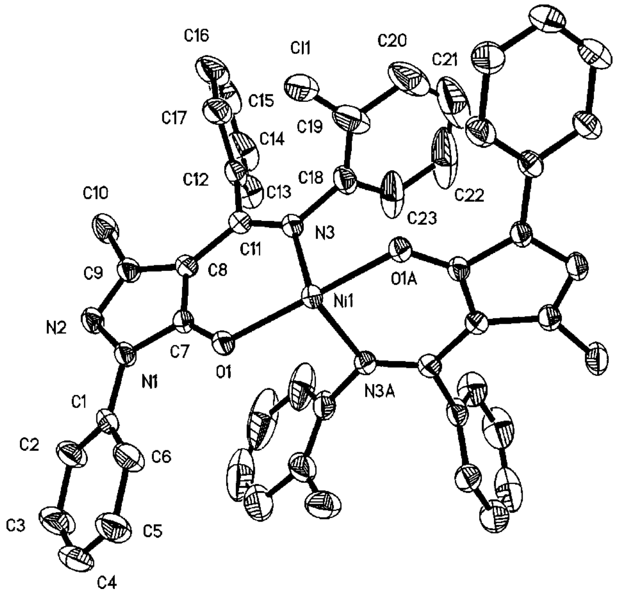


Figure 2. ORTEP plots of complex **2** showing the atom-labeling scheme. Hydrogen atoms and two ethanol molecules are omitted for clarity.

The crystal structures of **1**–**3** are shown in Figs 1– 3, respectively; the similar monomer in solid state, and selected atomic distances and bond angles are listed in Table 2.

In these complexes, the six-coordinate nickle atom is arranged in a distorted octahedral geometry where the two L*n* ligands act as monoanionic bidentate N,O-chelators lying in the *trans*-conformation to create two stable six-membered chelate rings (NiOCCCN). The metal–ligand bond lengths of Ni–O [1.992(1) Å for **1**, 1.988(2) Å for **2,** and 1.982(1) Å for **3**] were slightly shorter than the metal–solvate bond length of

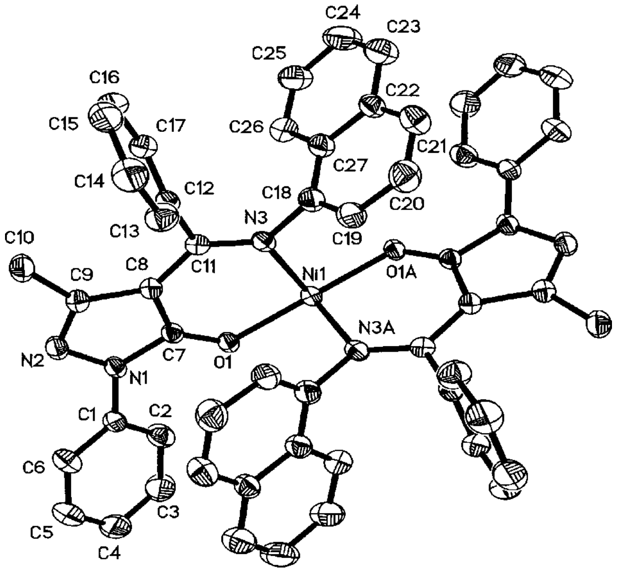


Figure 3. ORTEP plots of complex **3** showing the atom-labeling scheme. Hydrogen atoms and two ethanol molecules are omitted for clarity.

Ni–O [2.185(2) Å for **1**, 2.201(3) Å for **2**, and 2.229(2) Å for **3**] and Ni–N [2.077(2) Å for **1**, 2.101(3) Å for **2**, and 2.092(2) Å for **3**] and significantly longer than the respective Ni–O and Ni–N bond distances of the known nickel complexes with bidentate N,O-chelator ligands.[21–23] The distance of the Ni(II) ion in **1** to the two least square chelate planes defined by O1–C7–C8–C11–N3 and O2–C30–C31–C34–N6 was 0.025 Å. Similar distances were 0.055 Å in **2** and 0.042 Å in **3**. A sequence seemed to occur with the series **1**, **3** and **4**, where the aforementioned Ni-to-chelate distances were in the order **2** < **3** < **1**. On consideration of the relationship of crystal structure vs catalytic activity (see next section), a fact was disclosed that the more electron withdrawing substituents there were, such as in **2**, higher activity than with bigger steric substituent in **3** on the R group of the ligand was observed. This was accompanied by a larger Ni-to-chelate distance.

Table 2. Selected interatomic distances (Å) and bond or dihedral angles (°) for complexes **1**, **2** and **3**

	1	**2**	**3**
Ni(1)–O(1)	1.992(1)	1.988(2)	1.982(1)
Ni(1)–N(3)	2.077(2)	2.101(3)	2.092(2)
Ni(1)–O(2)	2.185(2)	2.201(3)	2.229(2)
O(1)[a]–Ni(1)–O(1)	170.2(1)	172.8(2)	171.0(1)
N(3)[a]–Ni(1)–N(3)	94.1(1)	96.9(2)	94.8(1)
N(3)–Ni(1)–O(1)	91.5(1)	91.7(1)	92.5(1)
C(11)–N(3)–C(18)	118.6(2)	118.2(3)	118.3(2)
N(3)–C(11)–C(8)–C(7)–O(1) vs Ni(1)–N(3)–O(1)	1.0	2.2	1.7
N(3)–C(11)–C(8)–C(7)–O(1) vs C(7)–C(8)–C(9)–N(2)–N(1)	3.5	3.0	4.1
N(2)–C(9)–C(8)–C(7)–N(1) vs C(1)–C(2)–C(3)–C(4)–C(5)–C(6)	151.5	152.2	152.4

Symmetry transformations used to generate equivalent atoms: [a] $-x+1, y, -z+3/2$.

These solid-state structural results imply that both steric and electronic effects are important for good catalytic activity. Interestingly enough, there were weak intramolecular or intermolecular π–π interactions, although there were several aromatic planes; the shortest $\pi \cdots \pi$ centroid to centroid distances for intramolecular or intermolecular planes were 3.71, 4.34 and 3.73 Å or 3.55, 3.61 and 3.62 Å for complexes **1**, **2**, and **3**, respectively.

Polymerization of styrene

All of the nickel catalysts precursors can be activated with MAO for styrene polymerization. These complexes are extremely stable in the air, and can still maintain high activity after being exposed to air for several weeks. The polymers were isolated as white solids and characterized by GPC in THF using polystyrene as stander. Microstructural analysis of the PS was carried out using IR spectra and NMR. The results of the polymerization are summarized in Table 3. It was

Table 3. Styrene homopolymerization by the different pyrazolone-based nickel (II) catalyst[a]

Run	Complex	Al : Ni (mol ratio)	Polymer yield (g)	Activity[b]	$M_n{}^c/10^4$	$M_w{}^c/10^4$	MWD
1	None	—	0.13	—	0.97	5.26	5.42
2	**1**	800	0.84	1.68	1.50	3.47	2.31
3	**1**	400	0.32	0.64	1.83	3.79	2.07
4	**2**	800	1.05	2.10	1.56	3.28	2.10
5	**2**	400	0.51	1.02	1.76	3.91	2.22
6	**3**	800	0.56	1.12	1.78	4.22	2.37
7	**3**	400	0.19	0.38	2.34	4.56	1.95

[a] Conditions: 20 ml toluene, 60 °C, 5 ml styrene, $M_{Ni} = 5 \times 10^{-6}$ mol, reaction for 1 h.
[b] Activity in 10^5 g of polymer/(mol of Ni h).
[c] Molecular weights of the polymers were determined by a Waters Breeze system at 40 °C in THF with polystyrene as standard.

assumed that the ethanol molecules in the complexes were consumed by MAO as a first step. Then the Ni complexes were activated with MAO to form catalytic species for styrene polymerization. With the activation of methylaluminoxane, a blank styrene polymerization was performed without nickel complexes. The low yield of completely atactic polystyrene confirmed the previously reported result connecting the ability of MAO to initiate ionic polymerization of vinyl monomers.[24] The catalytic activity of these catalysts could reach 2.10×10^5 g polymer/(mol of Ni h), even if the AlNi molar ratio was not very high (Al : Ni = 800). Under the same conditions, the catalytic activities obtained with complex **3**-MAO were the lowest in these series of nickel complexes. By introducing the chloro groups on the phenoxy moiety of the nickel complex **2**, the electron density on the metal center should be reduced. Therefore, it could increase the coordination propensity of the electron-rich monomers, such as styrene.[25,26] Moreover, that steric effects of the ligands play an important role in giving higher activity. On the basis of the obtained results, the complex **3**-MAO has lower activity than the complex **1**-MAO. The introduction of the bulky naphthyl group, the extended electronic conjugation for naphthyl ring, should be unfavorable for insertion of any monomer, such as styrene. However the bulky naphthyl group gave an obvious increase in the molecular weight. We attribute this to reduction of β-hydrogen elimination by steric hindrance.[25]

The results from styrene polymerizations using complex **2** under different molar ratios of MAO to the Ni complex (Al : Ni) are shown as Fig. 4. The monomer conversion and catalytic activity monotonically increased with increases in Al : Ni from 200 to 800. However, the monomer conversion and catalytic activity decreased when the Al : Ni molar ratio increased to 1000. With increases in the Al : Ni ratio, a prominent decrease in molecular weight was observed. As we know, Me_3Al is usually contained in MAO in certain amounts. Besides the chain transfer to monomer and the chain termination via β-H elimination, the chain transfer should also be caused by Me_3Al.[27] The reason for the influence of the Al : Ni molar ratio on the number-average molecular weight of polymers may be the increase in the chain transfer to Me_3Al with the increasing Al : Ni molar ratio.

As shown in Fig. 5, the polymerization temperature can also affect the catalytic activities and the M_w of the polymers greatly. When the reaction temperature increased from 20 to 80 °C, a prominent increase in activity was obtained, but with significant decreases in molecular weight. However, increasing the reaction temperature from 80 to 100 °C caused a slight decrease in activity. These facts indicate that part of the catalytic species is deactivated gradually at higher temperatures. Finally, the evolution of the polymerization yield with time was examined. The results are shown as Fig. 6. As discussed in the literature,[15] the polymer yield

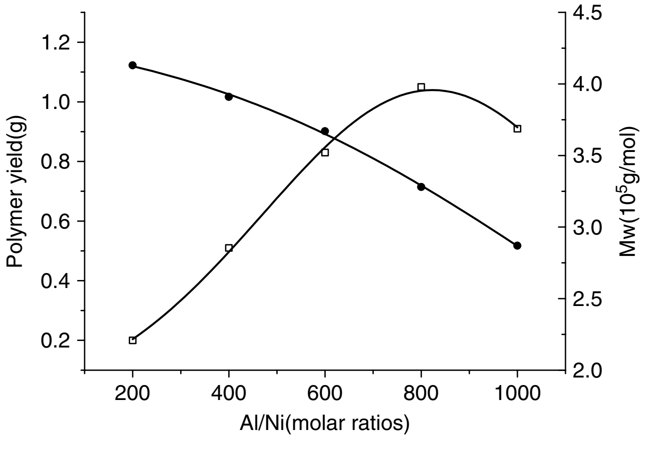


Figure 4. Plot of polymer yield (□) and M_w (●) vs Al : Ni molar ratio (complex **2**). $M_{Ni} = 5 \times 10^{-6}$mol, 60 °C, $V_{total} = 25$ ml, reaction time = 1 h.

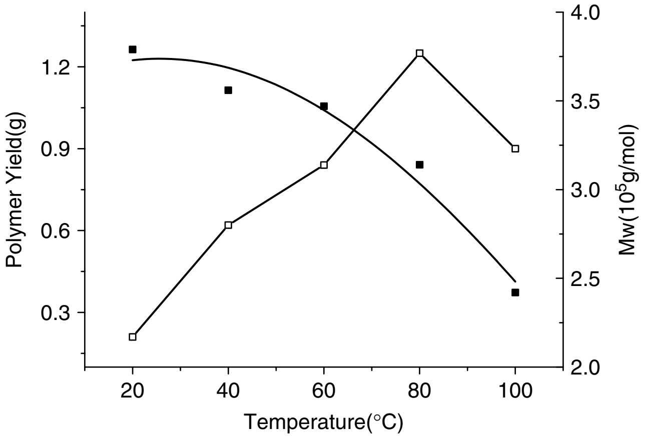


Figure 5. Plot of polymer yield (□) and M_w (■) vs polymerization temperature (complex **1**). [Ni] : [Al] = 1 : 800 (molar ratio), $M_{Ni} = 5 \times 10^{-6}$ mol, $V_{total} = 25$ ml.

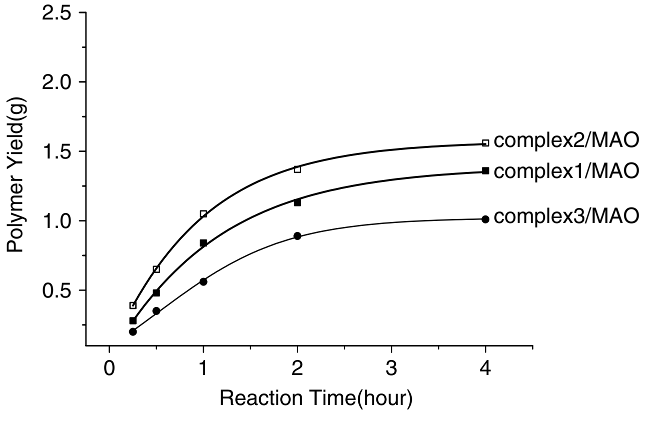


Figure 6. Plot of polymer yield vs polymerization time. [Ni] : [Al] = 1 : 800 (molar ratio), $M_{Ni} = 5 \times 10^{-6}$ mol, 60 °C, $V_{total} = 25$ ml.

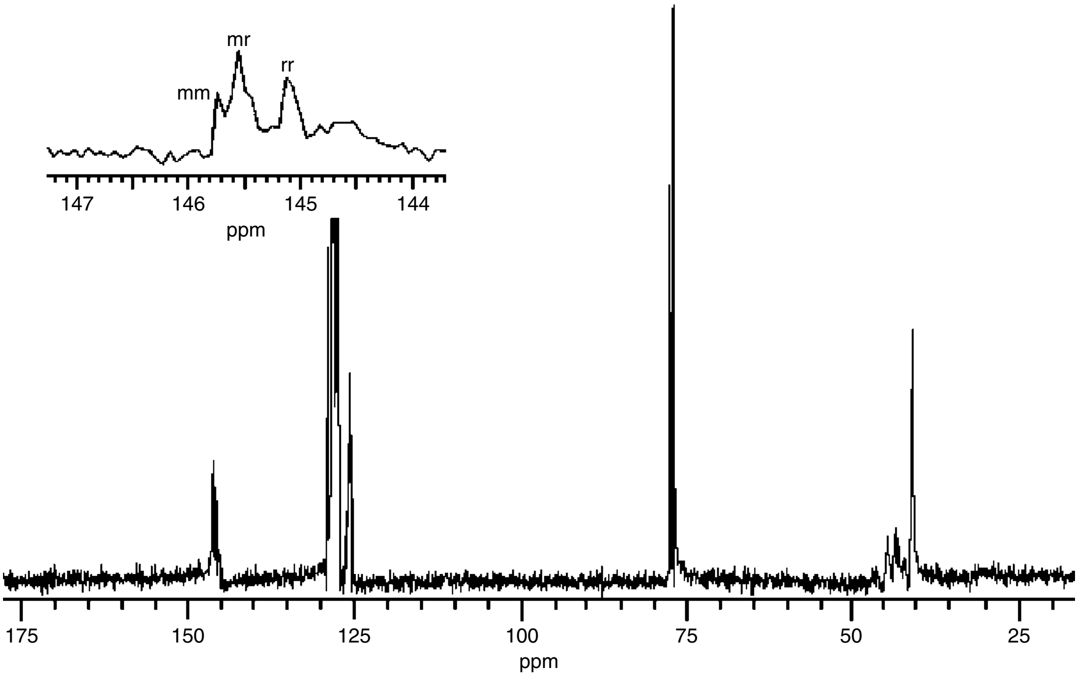


Figure 7. ^{13}C NMR spectrum of polystyrene prepared by complex **3**/MAO at 60 °C.

should increase monotonically with increasing time. The polymerization activities would reach their highest values at an early stage and then decrease rapidly with time.

The polystyrenes obtained with these catalysts showed moderate molecular weights ($M_n > 1.50 \times 10^4$ g/mol, $M_w > 3.28 \times 10^4$ g/mol). The molecular weight distributions for the polystyrenes ($M_w/M_n = 1.95–2.37$) promoted by the complexes indicate the presence of a single active species in the polymerization process. As shown in Fig. 7, the ^{13}C NMR spectra showed the stereochemistry of the polystyrene. The aromatic C-1 spectrum was analyzed in term of triads. Three main peaks with small peaks and shoulders were observed. The three main peaks, at 145.12, 145.54 and 145.75 ppm, are assigned to syndiotactic (rr), heterotactic (mr) and isotactic triads (mm),[28–30] respectively. It is obvious that the relative amounts of the mr triad were much higher than those of the other triads in the polystyrene obtained. This fact indicates that the polystyrenes obtained by this series of nickel catalysts are syndio-rich atactic polymers. Similarly, the IR spectra of the polymers also support the stereoregularity of the polystyrene. All the polystyrenes obtained here are readily soluble in acetone, tetrahydrofuran and chloroform, which also indicate low stereoregularity.

CONCLUSIONS

The synthesized nickel complexes with β-ketoamine ligands based on pyrazolone derivatives were moderately active in styrene polymerization. The catalytic activity and polystyrene characteristics were significantly affected by the structure of the nickel complex and the reaction parameters. The ^{13}C NMR and FTIR data show that the polystyrene obtained using these nickel catalysts is a syndio-rich atactic polymer. Further investigations focusing on the relationships of the complex structure and the activity are now in progress.

Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center; CCDC reference numbers for **1**, **2** and **3** are 232 629, 276 359 and 232 630 respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ UK (Fax:+44-1223-336033; email: deposit@ccdc.cam.ac.uk or www: www.ccdc.cam.ac.uk).

Acknowledgments

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