

Polymerization of Styrene Using Pyrazolyimine Nickel (II)/Methylaluminoxane Catalytic Systems

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ABSTRACT: The polymerization of styrene with two pyrazolyimine nickel (II) complexes of (2-(C₃HN₂Me₂-3, 5)(C(Ph) = N(4-R₂C₆H₂(R₁)₂-2, 6)NiBr₂ (Complex 1, R₁ = ⁱPr, R₂ = H; Complex 2, R₁ = H, R₂ = NO₂)) activated by methylaluminoxane was studied. The influences of polymerization parameters such as polymerization temperature, Al/Ni molar ratio, and reaction time on catalytic activity and molecular weight of the polystyrene (PS) were investigated in detail. The electron-withdrawing of nitro group in Complex 2 could not enhance the catalytic activity for styrene polymerization; however, the molecular weights of polymers were increased. Both of the two cata-

lytic systems exhibited high activity [up to 8.45 × 10⁵ gPS/(mol Ni h)] for styrene polymerization and provide PS with moderate to low-molecular weights ($M_w = 2.21 \times 10^4 \sim 5.71 \times 10^3$ g/mol) and narrower molecular weight distributions about 2.0. The obtained PS were characterized by means of IR, ¹H NMR, and ¹³C NMR techniques. The results indicated that the PS was atactic polymer. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 121–125, 2012

Key words: pyrazolyimine nickel (II); complexes; methylaluminoxane; styrene polymerization; atactic polymer

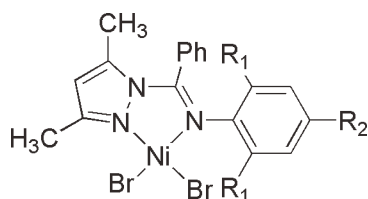
INTRODUCTION

During the past decades, the utilization of soluble transition metal complexes for styrene polymerization has received considerable attention.¹ 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,^{2–4} and each has led to polystyrenes (PS) with different stereoregularities. Ziegler-Natta catalysts based on titanium tetrachloride and aluminum alkyls yielded isotactic PS,^{5–7} however, titanium complexes/methylaluminoxane (MAO) catalytic systems obtained syndiotactic PS.^{8–13} Recently, various systems based on nickel complexes have been explored for styrene polymerization. For example, cationic η^3 -allylnickel complexes alone^{14,15} or modified by phosphine and phosphate ligands^{14,16,17} as well as cationic η^3 -benzyl nickel complexes¹⁸ were active homogeneous catalysts for the low-molecular weight polymerization of styrene by simple cationic mechanism. Neutral allylnickel complexes alone^{19–22} or with the activation of electron-poor additives can produce nonstereospecific PS, and a coordination mechanism was proposed.^{20,23}

Neutral σ -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.²⁴ The latest contribution showed that styrene polymerization with α -diimine nickel catalyst led to atactic polymer.²⁵ The catalytic behavior of the anilido-imino nickel complexes/MAO systems for styrene polymerization was investigated.²⁶ End group analysis of the polymer confirmed a coordination mechanism, and atactic PS was obtained. Moreover, styrene polymerization with using β -diketiminato nickel (II) complexes with activation of MAO was reported and the resulting PS also was atactic polymer.²⁷

Previously, we have reported the synthesis, molecular structure of nickel (II) complexes of (2-(C₃HN₂Me₂-3, 5)(C(Ph) = N(4-R₂C₆H₂ (R₁)₂-2, 6)NiBr₂ [Complex 1, R₁ = ⁱPr, R₂ = H; Complex 2, R₁ = H, R₂ = NO₂]) (Scheme 1) and their catalytic behavior toward norbornene with the activation of MAO.^{28,29} The purpose of this work is to further study the catalytic activity in styrene polymerization using these two nickel complexes with activation of MAO. Influence of polymerization conditions, such as polymerization temperature, Al/Ni molar ratio, and reaction time on catalytic activity were investigated in detail. And the results of IR, ¹H NMR, and ¹³C NMR indicated that the PS was atactic polymer.

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Complex 1 $R_1=i\text{-Pr}$, $R_2=\text{H}$

Complex 2 $R_1=\text{H}$, $R_2=\text{NO}_2$

Scheme 1 The structures of two pyrazolylimine nickel (II) complexes.

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. MAO was prepared by partial hydrolysis of trimethylaluminum (TMA) in toluene at $0\text{--}60^\circ\text{C}$ with H_2O from $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$. The pyrazolylimine ligands and corresponding nickel complexes were prepared according to our previous methods.²⁸

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 (MWD) of the polymers were performed on a Waters Breeze instrument using THF as eluent at 40°C and standard PS as reference. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1600 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury-Plus 300 NMR spec-

trometer at room temperature using CDCl_3 as solvent and TMS as internal standard.

RESULTS AND DISCUSSION

Polymerization of styrene

The two pyrazolylimine nickel (II) Complexes 1 and 2 showed good catalytic activities for styrene polymerization using MAO as cocatalyst over a wide range of polymerization temperature. The molecular weights of all PSs were moderate to low between 10^4 g/mol and 10^3 g/mol ($M_w = 2.21 \times 10^4$ to 5.71×10^3 g/mol), and the 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 MWD 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 two catalytic systems exhibited high activity over a wide temperature range of $30\text{--}70^\circ\text{C}$. The catalytic activities of two complexes increase first and then decrease with polymerization temperature increasing. As for the catalytic activity, the optimum reaction temperature for Complex 1 is 40°C and for Complex 2 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 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.

The pyrazolylimine nickel Complex 2 bearing nitro group displays lower catalytic activity toward styrene polymerization [Table I, 40°C , 2.04×10^5 gPS/(mol Ni h); 50°C , 2.78×10^5 gPS/(mol Ni h); 60°C , 5.36×10^5 gPS/(mol Ni h)] than the pyrazolylimine nickel Complex 1 bearing diisopropyl groups [Table I, 40°C , 8.45×10^5 gPS/(mol Ni h); 50°C , 7.48×10^5 gPS/(mol Ni h); 60°C , 7.29×10^5 gPS/(mol Ni h)]. The steric effect of isopropyl group would decrease catalytic activity, and in the general catalytic systems for olefin polymerization, the electron-withdrawing effect of nitro group would enhance catalytic activity. However, the activity of Complex 2 with nitro group is lower than Complex 1 with isopropyl group, so, it could be concluded that the introduction of an electron-withdrawing group into pyrazolylimine ligand could not increase the

TABLE I
Influences of Temperature on Styrene Polymerization with Complex 1/MAO and Complex 2/MAO Catalytic Systems^a

Complex	Entry	T_p (°C)	Activity ^b	Yield (%)	M_w^c	M_w/M_n
1	1	30	3.45	38.0	9.26	1.66
1	2	40	8.45	93.0	6.87	1.79
1	3	50	7.48	82.3	5.94	1.90
1	4	60	7.29	80.2	5.71	2.63
2	5	40	2.04	22.4	22.12	2.16
2	6	50	2.78	30.6	21.41	2.27
2	7	60	5.36	59.0	17.93	2.30
2	8	70	5.10	56.1	14.42	2.34

^a Polymerization conditions: precursor catalyst concentration: $[\text{Ni}] = 3.0 \times 10^{-4}$ mol/L; styrene addition: 6 mL; Al/Ni = 600; reaction time: 1 h; solvent: toluene; total volume: 20 mL.

^b In units of 10^5 gPS/(mol Ni·h).

^c In units of 10^3 g/mol.

catalytic activity. High catalytic activity means fast rate of chain propagation, while fast chain propagation is often gone with faster chain-transfer reaction.³⁰ This cause that the molecular weights of the polymers obtained with Complex 1 [Table I, 40°C, 6.87×10^3 g/mol; 50°C, 5.94×10^3 g/mol; 60°C, 5.71×10^3 g/mol] lower than Complex 2 (Table I, 40°C, 2.21×10^4 g/mol; 50°C, 2.14×10^4 g/mol; 60°C, 1.79×10^3 g/mol).

Al/Ni molar ratio played an important role in affecting the catalytic activities. As shown in Table II, the both two catalytic systems showed similar tendency. When the molar ratio of Al and Ni was low, the catalytic systems could not generate enough active species to polymerize styrene effectively because of the small amount of MAO. The polymer yield and the catalytic activity increased with the increasing of MAO amount until the Al/Ni molar

TABLE II
Influences of Al/Ni Molar Ratio on Styrene Polymerization with Complex 1/MAO and Complex 2/MAO Catalytic Systems^a

Complex	Entry	Al/Ni	Activity ^b	Yield (%)	M_w^c	M_w/M_n
1	1	400	3.82	42.0	7.05	1.75
1	2	600	8.45	93.0	6.87	1.79
1	3	800	8.22	90.4	6.37	1.85
1	4	1000	7.34	80.8	6.21	1.81
2	7	400	2.12	23.3	19.51	2.17
2	5	600	5.36	59.0	17.93	2.30
2	6	800	6.21	68.3	17.17	2.39
2	8	1000	4.95	54.5	14.68	2.51

^a Polymerization conditions: precursor catalyst concentration: $[\text{Ni}] = 3.0 \times 10^{-4}$ mol/L; styrene addition: 6 mL; polymerization temperature: Complex 1, 40°C; Complex 2, 60°C; reaction time: 1 h; solvent: toluene; total volume: 20 mL.

^b In units of 10^5 gPS/(mol Ni·h).

^c In units of 10^3 g/mol.

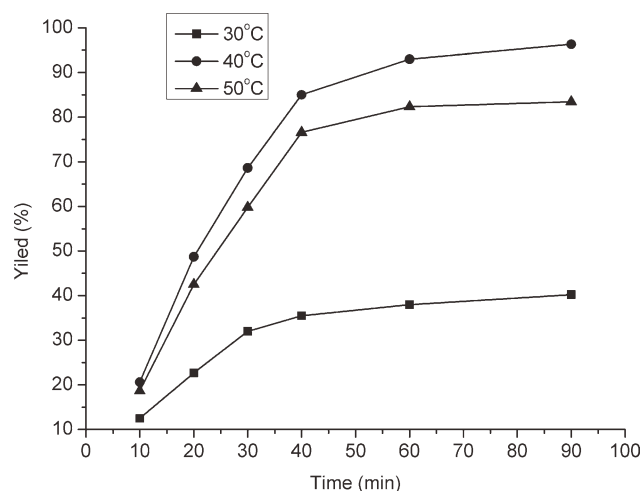


Figure 1 Influence of the reaction time on the styrene polymerization with Complex 1/MAO catalytic system at 30, 40, and 50°C. Polymerization conditions: precursor catalyst concentration: $[\text{Ni}] = 3.0 \times 10^{-4}$ mol/L; styrene addition: 6 mL; Al/Ni = 600; solvent: toluene; total volume: 20 mL.

ratio was optimum for styrene polymerization, and then decreased respectively, with further enlarging MAO ratio. When the Al/Ni molar ratio was up to the optimum value (600 for Complex 1/MAO and 800 for Complex 2/MAO), there were maximum active species in the both catalytic systems, and the polymer yield and catalytic activities were the highest. And the highest catalytic activity up to 8.45×10^5 gPS/(mol Ni h) could be observed in Complex 1/MAO catalytic system (Entry 2 in Table II). If the molar ratio of Al and Ni was higher than 600 for Complex 1/MAO and 800 for Complex 2/MAO, excessive MAO existed in the catalytic systems. However, TMA, present in MAO, is a kind of strong reducing agent, which could be a disadvantageous influencing factor to the stability of Ni (II) with the result that the catalytic activity decreased. In

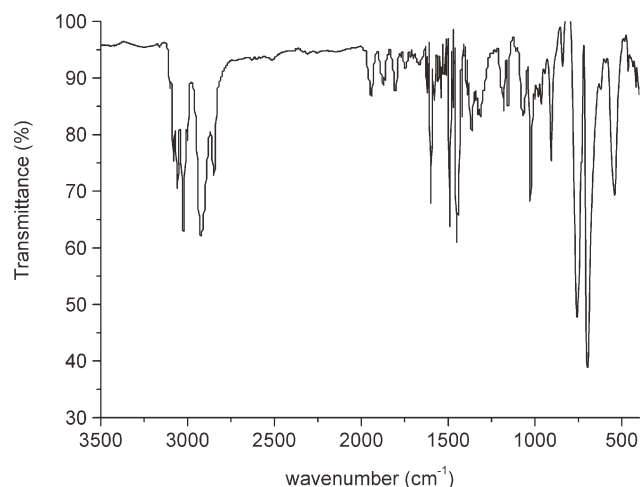


Figure 2 FTIR spectrum of polystyrene obtained by Complex 1/MAO catalytic system (Entry 2 in Table I).

addition, the Al/Ni molar ratio also affected the molecular weight of the polymers, because MAO, a cocatalyst, was used to activate pyrazolyimine nickel complexes on the one hand, however, it may be a transfer agent for these catalytic systems on the other hand.

Complex 1/MAO catalytic system was chosen for kinetic study on styrene polymerization at 30, 40, and 50°C, respectively. As shown in Figure 1, the polymer yields increased with the reaction time prolonging, and two distinct periods can be observed in the polymerization process. In the first period, about 10–40 min, the polymer yields increased rapidly. In the second period, the polymer yields increased very slightly and leveled off probably due to the consuming of monomer and active species. This result suggested that the active species can be produced rapidly at the original stage of the polymerization, and then being stabilized at 30, 40, and 50°C, respectively.

Microstructure analysis of PS

All of the obtained polymers were completely soluble in many organic solvents, such as chloroform, 2-butanone, acetone, and THF, indicating that atactic PS with low stereoregularity was obtained. The microstructure of a representative PS sample obtained from Entry 2 in Table I was characterized by IR, ^1H NMR, and ^{13}C NMR. IR spectrum (Fig. 2) revealed that there are no obvious absorption bands appearing at 1217.6 and 1220 cm^{-1} , which are assigned to the characteristic signal of sPS.^{31,32} However, the presence of absorption at 1070 cm^{-1} in the IR spectrum supports that atactic PS was observed.

^1H NMR and ^{13}C NMR spectra shown in Figures 3 and 4, respectively, also further confirmed that the resulting PS was atactic polymer. As displayed in Figure 3, three groups of hydrogen proton signals were

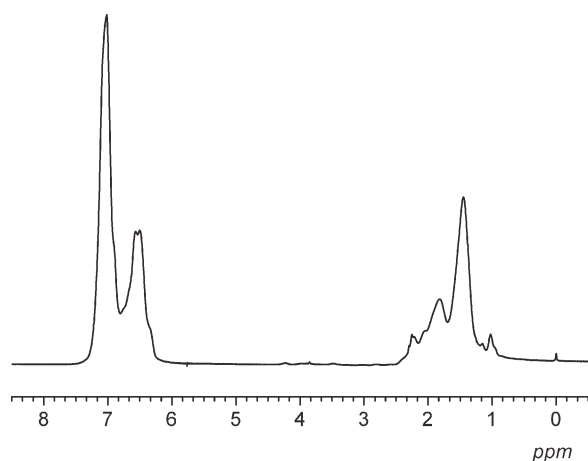


Figure 3 ^1H NMR spectrum of polystyrene in CDCl_3 obtained by Complex 1/MAO catalytic system (Entry 2 in Table I).

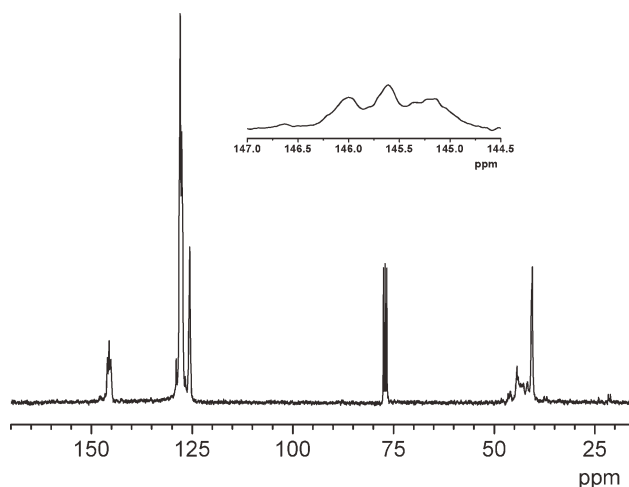


Figure 4 ^{13}C NMR spectrum of polystyrene in CDCl_3 obtained by Complex 1/MAO catalytic system (Entry 2 in Table I).

found. Chemical shifts at 6.50~7.02 ppm are aromatic hydrogen signals, those at 1.84~2.26 ppm are methine hydrogen signals, and those at 1.00~1.44 ppm are methylene hydrogen signals in PS. ^{13}C NMR spectrum of the PS was analyzed for aromatic C-1 in the terms of triads (see Fig. 4). Three main peaks at 146.0 ppm, 145.2 ppm, and 144.2 ppm were assigned to isotactic triad (mm), heterotactic triad (mr), and syndiotactic triad (rr), respectively.^{33–35} The stereo-triad distributions of mm, mr, and rr, calculated from the triad resonance integral, are [mm] = 27.9%, [mr] = 31.8%, [rr] = 40.3%.

CONCLUSIONS

The two pyrazolyimine nickel (II) complexes exhibited good activity for styrene polymerization in the presence of MAO. The catalytic activity, molecular weight, and MWD could be controlled over a wide range by variation of the polymerization parameters. Under appropriate conditions, the catalytic activity could be up to 8.45×10^5 gPS/(mol Ni h) (Complex 1: polymerization temperature = 40°C, Al/Ni molar ratio = 600), and the molecular weights of all PSs were between 2.21×10^4 g/mol and 5.71×10^3 g/mol. Also, the MWD of obtained PSs was between 1.66 and 2.63, implied styrene was polymerized by single active species. The electron-withdrawing of nitro group in Complex 2 could not enhance the catalytic activity for styrene polymerization; however, the molecular weights of polymers were increased. The results of IR, ^1H NMR, and ^{13}C NMR indicated that obtained polymer was atactic PS.

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