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Copolymerization of Norbornene and Styrene Catalyzed by a Series of Bis(β-ketoamine) Nickel(II) Complexes in the Presence of Methylaluminoxane

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Summary

Random copolymerization of norbornene with styrene was studied by using a series of late metal catalysts/MAO. The precatalysts used here are nickel complexes with b-ketoamine ligands based on pyrazolone derivatives. The copolymers obtained here suggest that only one type of active species is present. Copolymers were characterized by ^{13}C NMR, Gel permeation chromatography (GPC), thermogravimetric analysis (TGA) and FT-IR spectra. The analyses of the product by ^{1}H NMR and ^{13}C NMR spectra gave the verification of ''true'' random vinyl addition copolymer. Varying the monomer feed ratio controlled the composition of the copolymers. A copolymerization reactivity ratio (r_{NBE} = 20.35 and r_{Sty} = 0.027) indicates a much higher reactivity of norbornene, which suggests a coordination polymerization mechanism. The solubility and processability of the copolymers are improved relative to polynorbornene and the thermostability of the copolymers is improved relative to polystyrene.

Keywords

Nickel catalyst; copolymerization; norbornene; styrene; MAO

Introduction

Interests in polymers of cyclic olefins such as bicyclo[2.2.1]hept-2-ene (norbornene) have increased dramatically over the past decade. Among these, norbornene is known to polymerize by ring-opening metathesis, cationic or radical polymerization, and vinylic polymerization (olefin addition polymerization) [1-4]. The vinylic polymerization of norbornene, yielding a 2,3-connected, rotationally strongly constrained vinyl-type polynorbornene, has been considerably attracted because of the vinyl homopolymers exhibit high decomposition temperatures, increased thermal stability, dielectric properties, and unusual transport properties, and they are attractive materials for microelectronics, optical applications, and for other potential uses in packing and gas separation [5,6]. The vinyl polymers of norbornene can be obtained by transition metal complexes based on titanium, zirconium, nickel, palladium, chromium, cobalt, and iron [7-9]. So far, catalyst selection for the vinyl polymerization of norbornene is still a hot topic. Many nickel and palladium catalytic systems have been reported as being highly active for the polymerization of norbornene. However, the homopolymers are brittle materials at room temperature and their solubility in common solvents, as well as their processability, is rather poor. The copolymerization of norbornene with other traditional vinyl monomers is the usually applied method of forming stable norbornene copolymers. The copolymers present not only have improved solubility and processability relative to homopolymers of norbornene but they also have improved thermal stability and optical properties relative to homopolymers of the comonomer. The catalytic copolymerization of norbornene with styrene has been less reported. Recently, Only a few catalytic systems are reported as initiators for the copolymerization of norbornene with styrene using $Ni(stear)_2$/MAO [10], $Ni(acac)_2$/MAO [11], Ni-Pd(diimine)/MAO [12] and Ni compounds involving N- or O-donated ligands[13] systems.

On the other hand, the late-transition-metal complexes of pyrazolone derivatives have been used in many fields, such as the luminescence effects and biological activities [14], probably due to their easy synthesis and tolerance for polar substances. However, to our knowledge, there are still no reports about nickel complexes with pyrazolone ligand being used for olefin copolymerization. Herein, a series of nickel (II) complexes based on β-ketoamine ligands are used for the copolymerization of norbornene and styrene in the presence of methylaluminoxane. The copolymerization reactivity ratios were determined. The composition and microstructure of the copolymers were also studied by means of gel permeation chromatography (GPC), FTIR and ^{1}H NMR spectroscopies, thermogravimetric analysis (TGA).

Experimental

Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuoline techniques. Solvents were purified using standard procedures. Norbornene (from Aldrich) was distilled over potassium and then dissolved in dried toluene to give 0.4 g/mL solution. Styrene was dried over CaH_2, and then freshly distilled under vacuo prior to use. Methylaluminoxane (MAO) was prepared by partial hydrolysis trimethylaluminum (TMA) with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene at 0-60°C as water source. The initial $[H_2O]/[TMA]$ molar ratio was 1.3. Nickel(II) complexes were synthesized according to our previous work [15-16].

Instruments

Infrared spectra were recorded on polymer-KBr pellets with a Bruker EQUINOX55 FT-IR spectrophotometer in the region of 4000 ~ 400 cm^{-1}. ^{1}H and ^{13}C NMR spectra were obtained using an INOVA 500 Hz at room temperature in $CDCl_3$ (for copolymer) solution using tetramethylsilane as internal standard. Gel permeation chromatography (GPC) analyses of the molecular weight molecular and weight distributions of the polymers were performed on a Waters Breeze system with tetrahydrofuran as the eluent at 40°C using standard polystyrene as the reference.

TGA data were measured with a TG-290C thermal analysis system instrument, under dry nitrogen with a flow rate of 50ml/min and a heating rate of 10°C/min.

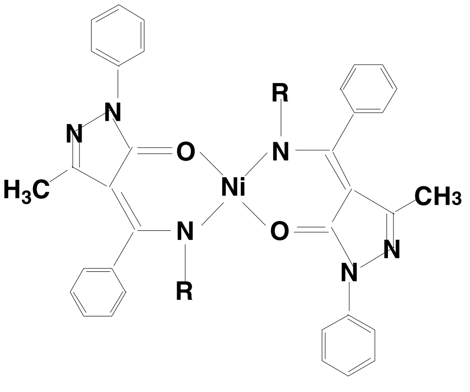
General Polymerization Procedure

Catalytic copolymerization of norbornene and styrene has been carried out in a Fisher-Porter glass reactor and protected by nitrogen. MAO (0.5 mmol, solid powder) was added into an Schlenk flask with a magnetic stirrer. Norbornene (0.04 mol, 3.76 g) and styrene (0.02 mol, 2.04g) in 10 ml toluene and 9 ml of toluene were added later. The reaction was started by the addition of one ml of a freshly prepared Ni-complex solution (5.0×10^{-6}M in toluene) at 60°C. After 1 hr, the reaction mixture was poured into excess of ethanol acidified with 5% HCl. The polymer was washed with ethanol and then dried under vacuum at 80°C for 48h.

Results and discussion

Heretofore, late metal catalytic systems have been reported to act as initiators for the copolymerization of norbornene with styrene using Ni(stear)$_2$/MAO [10], Ni(acac)$_2$/MAO [11], Ni-Pd(diimine)/MAO[12] systems, and Ni compounds involving O-donated ligands [13]. To our knowledge, this is the first report on norbornene and styrene copolymerization using bis(β-ketoamine) nickel(II) complex/MAO catalytic systems.

Copolymerization of norbornene and styrene with bis-(β-ketoamine)nickel(II) (1–5) (As shown in Scheme **1**) complexes in combination with MAO were carried out.



R = Benzyl(1), Phenyl (2), *o*-Tolyl (3), Naphthyl (4), *p*-Nitrophenyl (5)

Scheme 1. Structure of nickel(II) complexes

As reported by our group, the same Ni(II)-based β-ketoamine complex in combination with MAO has shown very high activity in norbornene polymerization of up to 3.38×10^{7} g/(molNi.h), giving vinyl addition polynorbornenes insoluble in common solvents such as tetrahydrofuran, chloroform, and toluene [15]. Crude polymers were extracted by boiling solvents chloroform. It is known that polystyrene is completely soluble in chloroform whereas polynorbornene is insoluble. On the other hand, chloroform would dissolve copolymer of styrene and norbornene. As discussed in the following text, it has a small quantity of styrene segment in the copolymer. Therefore, the soluble fraction in chloroform is 'pure' copolymer. After extraction, the soluble fraction is trace. The percentages for the soluble and insoluble fractions obtained after extraction of the crude polymer with the boiling chloroform for the different nickel complexes is shown in Table **1**. This fact indicates the homopolymerization of norbornene and styrene is infrequent. The main process is copolymerization of norbornene and styrene.

Table 1. The percentages for the soluble and insoluble fractions obtained after extraction of the crude polymer with the boiling chloroform for the different nickel complexes

Complex	Copolymer(g)	PNBE(g)
1	0.63	trace
2	0.72	trace
3	1.23	0.13
4	2.69	0.19
5	1.97	0.14

[a] Conditions: 20ml toluene, [St]=0.02mol, [NBE]=0.04mol, [Al]/[Ni]=300, m_{Ni}=5.0x10^{-6}mol, temperature 60°C for 12h.

As shown in Table **2**, the catalytic activity sequence was found to be 4 > 5 > 3> 2 > 1. This is coherent to the expected steric effects of the ketoamine ligand, which are in the order 4 > 3> 2> 1. It is evident that steric bulk has an effect on the activities. Bigger substituent on the imino group favor higher catalytic activity. Among these nickel β-ketoamine catalysts, complex **4** with naphthyl on the imino group exhibited the highest activity, and complex **1** with benzyl substituent on the imino group showed the lowest activity. Furthermore, complex **5**, having a strong electron-withdrawing group of p-nitrophenyl, exhibits higher activity than complex **2**, caused by the electron-withdrawing p-NO_2 group affording a more electron-deficient active Ni(II) center. This result has a good agreement with reported norbornene homopolymerization data [15].

Table 2. Copolymerization of styrene and norbornene in the presence of the complex **1-5**/MAO catalytic system[a]

Complex	Yield in %	Activity[b]	Found in polymer		Mn[c] (10^4g/mol)	Mw (10^4g/mol)	Mw/Mn
			St (%)	NBE(%)			
1	10.7	1.04	27.8	72.2	0.52	1.77	3.41
2	12.3	1.20	26.7	73.3	0.55	1.89	3.44
3	21.7	2.12	23.3	76.7	0.87	2.12	2.44
4	45.9	4.48	6.9	93.1	1.88	4.75	2.53
5	33.6	3.28	16.5	83.5	1.25	2.75	2.20

[a]. Conditions: 20ml toluene, [St]=0.02mol, [NBE]=0.04mol, [Al]/[Ni]=300, m_{Ni}=5.0x10^{-6}mol, temperature 60°C for 12h.

[b]. Activity in 10^4g of polymer/(mol of Ni·h).

[c]. Molecular weights of the polymers were determined by a Waters Breeze system at 40°C in tetrahydrofuran with polystyrene as standard.

As may be observed, the Mw values decrease with decreases of the copolymerization rate. This indicates that norbornene insertion is the dominant rate controlling process. Unimodal molar mass distributions with narrow molecular weight distributions (Mw/Mn close to 2) of all the copolymers indicates that the copolymerization occurs at the single active site and the polymer is a 'true' copolymer without homopolymers [8].

The ^{1}H NMR spectra of copolymers incorporated with more than 30 mol% styrene were obtained in $CDCl_3$. The ^{1}H NMR spectrum of a styrene-norbornene copolymer containing 37.7 mol% of styrene is compared to a pure polystyrene in Figure **1**. In the case of the polystyrene, Figure **1**b, the aromatic region is composed of two distinct peaks attributed to meta and para protons (d=6.9 ppm), and ortho ones (d =6.5 ppm). In the case of copolymers, Figure **1**a, two peaks one 7.1 ppm (meta and para protons) and the other 6.5 ppm (ortho protons) are also observed for all the aromatic protons. Compared to Figure **1**b, the two peaks shift to low field is weakened sharply with the decrease of styrene feed content. The results are similar to those obtained for the bridged dinuclear diimine nickel and palladium complexes/MAO catalytic system [8]. This result also confirms that the polymers prepared by random copolymerization are really copolymers.

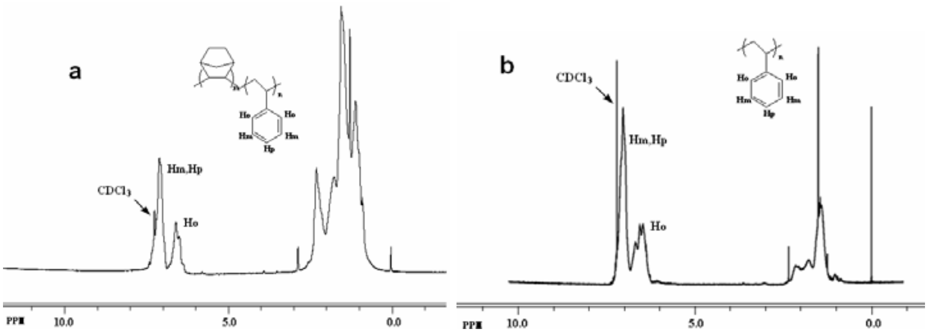


Figure 1. a.^{1}H NMR of Copolymer (the soluble fraction in boiling chloroform) obtained by nickel complex **4**/MAO catalytic system at 60°C. (M_{St}=37.7%) Conditions: 20ml toluene, [St]=0.03mol,[NBE]=0.03mol, [Al]/[Ni]=300, $m_{Ni}=5.0\times10^{-6}$mol, temperature 60°C for 12h. **b.** ^{1}H NMR of polystyrene obtained by nickel complex **4**/MAO catalytic system at 60°C.

^{13}C NMR spectra of the resulting copolymers obtained from complex **2**/MAO showed the superposition of respective homopolymers as expected (Figure **2**) [13]. From the spectra, the backbone carbon, bridgehead carbon, bridge carbons and aromatic cycle carbon could be found. As discussed before, the polymers are really copolymers.

The ^{13}C NMR spectra also support for this conclusion.

The variation of the copolymer composition, determined by ^{1}H NMR and Gel permeation chromatography (GPC), versus the comonomer feed is shown in Figure **3**. The copolymerization rates as well as the Mw values decrease with an increase in styrene content in the monomer feed. As it can be seen, the styrene incorporation increases with the styrene content in monomer feed and the incorporation rate into the copolymer chains is much slower than that of norbornene. The monomer reactivity ratios of norbornene and styrene were obtained from the Fineman–Ross plot to be $r_{norbornene}$ =20.35, $r_{styrene}$=0.027. The result is very similar to that for the nickel

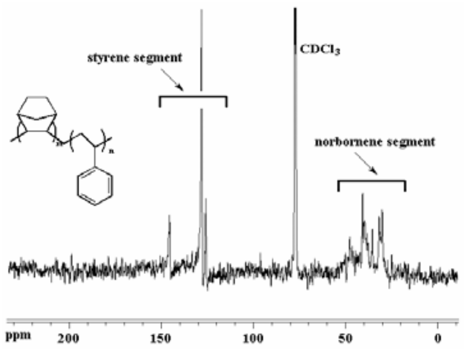


Figure 2. ^{13}C NMR spectrum of Copolymer (the soluble fraction in boiling chloroform) obtained by complex **2**/MAO system. (M$_{St}$=30.3%)

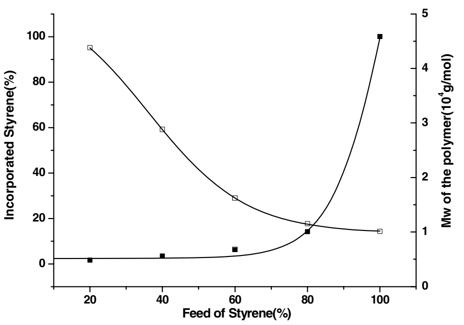
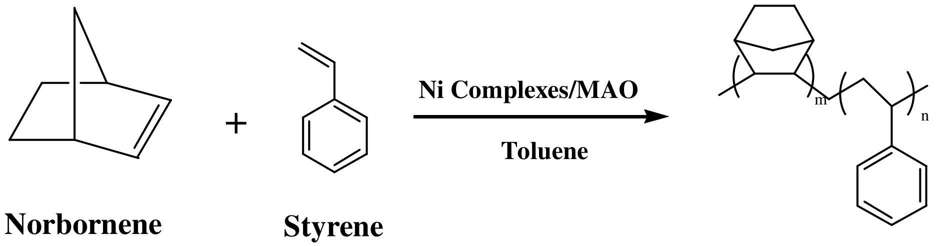


Figure 3. Plot of Mw (□) and Incorporated Styrene %(■) versus Feed of Styrene (complex 4/MAO). Conditions: 20ml toluene,[St]+[NBE] =0.06mol, [Al]/[Ni]=300, mNi=5.0×10^{-6}mol, temperature 60°C for 12h.

stearate/MAO system ($r_{styrene}$=0.02, $r_{norbornene}$=20.8), which results in the lower styrene incorporation ratio by the nickel stearate/MAO system under polymerization conditions [10]. The much higher reactivity of norbornene illustrates that the monomer reactivity order is rather unusual and is obviously not in agreement with a free radical or cationic type polymerization but supports a coordination type mechanism.



Scheme 2. Copolymerization of NBE with St catalyzed by Ni complexes/MAO systems

As shown in Figure **4**, the FTIR spectra of the copolymers of different compositions show the absence of the vibration bands of carbon–carbon double bonds at 1620–1680 cm^{-1}. It indicates that the norbornene was copolymerized with styrene by the nickel complex in the presence of MAO by vinyl addition. This fact also confirms the copolymerization mechanism as shown in Scheme **2**.

The FTIR spectra of norbornene-styrene copolymers exhibit an increase in the intensity of the bands related to the phenyl ring, i.e., at 698, 755, 1605, 1495, and 1453 cm^{-1}, and phenyl ring overtones and combinations at 1942, 1874, 1805, and 1750 cm^{-1}, with the styrene feed content.

The thermostability of the copolymers was investigated by TGA as shown in Figure **5**. The copolymers exhibit higher decomposition temperatures (428°–470°C) than the homopolymers of styrene (≈ 390°C). This suggests that the norbornene segment in the copolymer improves its thermostability relative to polystyrene. From this Figure, the

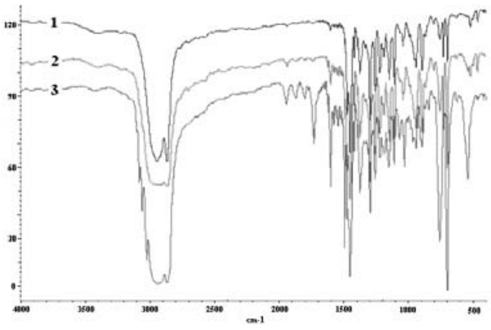


Figure 4. FTIR spectra of Copolymer (the soluble fraction in boiling chloroform) obtained by nickel complex 4/MAO catalytic system at different monomer ratios. M_{NBE}:M_{St}=12:1 (1); 8:1 (2); 4:1 (3)

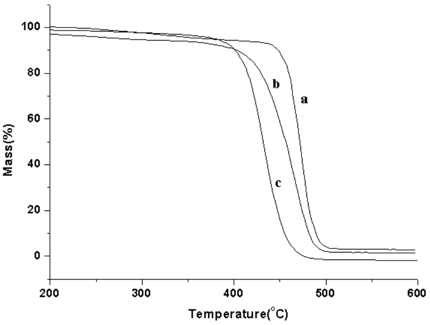


Figure 5. TG Curves of polynorbornene (**a**) and copolymers containing St 7 mol% (**b**) and copolymers containing St 37.7 mol % (**c**) obtained by complex **4**/MAO system.

copolymer of higher decomposition temperatures contains more norbornene segment in it. It indicates that the more introduction of norbornene segment could be more helpful for the copolymer thermostability than the less.

THF is a good solvent for polystyrene, while a bad one for polynorbornene. However, the copolymers are easily dissolved in chloroform or THF. The solubility of polynorbornene segment has been significantly improved by copolymerization. These results suggest that the introduction of styrene segments in the copolymer improves its processability relative to polynorbornene.

Conclusions

Bis(β-ketoamine)nickel (II) complexes based on pyrazolone derivatives can be activated by MAO to efficiently catalyze random copolymerization of norbornene and styrene. Unimodal molar mass distributions with the narrow molecular weight distributions indicate that the copolymerization occurs at the single active site and the polymer is a 'true' copolymer. Determination of reactivity ratios ($r_{\mathrm{norbornene}}$ = 20.35 and r_{Sty} = 0.027) indicates a much higher reactivity of norbornene, which is interpreted by a coordination mechanism. The characterizations of composition and microstructure also approve those improvements of solubility and processability relative to homopolymers.

The study for the polar and unpolar monomer homo- and copolymerization is our current investigation.

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