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Homo- and copolymerization of norbornene with styrene catalyzed by a series of copper(II) complexes in the presence of methylaluminoxane

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Vinyl-type polymerization of norbornene as well as random copolymerization of norbornene with styrene was studied using a series of copper complexes-MAO. The precatalysts used here are copper complexes with β-ketoamine ligands based on pyrazolone derivatives and the molecular structure of complex 4 was determined using X-ray analysis. All of these catalyst systems are moderately active for the vinyl-type polymerization of norbornene and random copolymerization of norbornene with styrene. The random copolymers obtained suggest that only one type of active species is present. Gel permeation chromatography (GPC) and NMR indicate that the copolymers are 'true' copolymers. The copolymerization reactivity ratios ($r_{\mathrm{NBE}} = 20.11$ and $r_{\mathrm{Sty}} = 0.035$) indicate 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. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: β-ketoamine; copper complexes; catalyst; olefin; norbornene; styrene; polymerization

INTRODUCTION

In the past two decades, metallocenes have revolutionized the commercial polymerization of olefins. There has been considerable recent activity in the area of late transition metal polymerization catalysis, especially for the Fe, Co, Ni and Pd catalysts in both academic and industrial research fields.[1–3] Compared with the metallocenes based on early transition metals, the late transition metal catalysts are less oxophilic and thus less easily poisoned by polar monomer contaminants.[4–6] Among these, copper(II) complexes present some unique properties in both homo- and copolymerization of olefins with functional monomers.[7–10] Copper alkene chemistry has been well developed in the literature,[11–15] but Cu(II) complexes used as catalysts have not been thoroughly investigated. There were a few reports that benzamidinate[16] and benzimidazolyl[17,18] copper(II) complexes were used for ethylene polymerization but with low catalytic activities. Copper (II) catalysts based on α-diimine ligands produce very-high-molecular-weight polyethylene with moderate activity.[19]

There are, however, still no reports of copper(II) catalysts based on N,O-chelate ligands for the copolymerization of norbornene and styrene. Complexes containing ligands of the N,O-chelate family are of particular interest. For example, Ni-based systems are very effective catalysts in α-olefin and polar olefin polymerizations.[20–24] β-Ketoamines are important members of this general family[25] because of their ease of preparation and modification of both steric and/or electronic effects.

On the other hand, late-transition-metal complexes of pyrazolone derivatives have been used in many fields, such as the luminescence effects and biological activities,[26–29,33] probably due to their easy synthesis and tolerance for polar substances. However, to our knowledge, there are still no reports about copper complexes with pyrazolone ligand being used for olefin copolymerization. Herein, a series of copper(II) complexes based on β-ketoamine ligands are

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investigated and used for the homopolymerization and the copolymerization of norbornene and styrene in the presence of methylaluminoxane.

RESULTS AND DISCUSSION

The relationships of the complex structure are very close to the catalytic activity. Furthermore, catalytic activity and polymer yield can be affected over a wide scope by the variable reaction parameters. Following a typical copolymerization procedure, a random copolymer of norbornene and styrene was successfully obtained.

Structure of complex 4

The structure of **4** is shown in Fig. 1 and the crystallographic data and refinement parameters for complex **4** are presented in Table 1. Comparing the molecular structure of complex **4** with complex **1**, we find that, in these two complexes, the coordination geometries are very similar to each other in solid state. Both show the same four-coordinate environment where the two L ligands act as monoanionic bidentate N,O-chelators and lie in the *trans*-conformation to create two stable delocalized six-membered chelate rings (CuOCCCN).

The metal–ligand bond length of Cu–N [1.973(2) Å] for complex **1** is slightly less than the Cu–N [1.981(2) Å] bond length for complex **4**. A distinctly different mean deviation from O1–C1–C2–C3–N1 (0.0332 Å for **1** and 0.0625 Å for **4**) is observed. The influence of the naphthyl's greater steric hindrance may be the reason for the different configurations of these complexes. Correlation of the crystal structure with catalytic activity (see next section) indicates that, with a larger R group substituent, such as in **4**, higher activity is observed.

Table 1. Crystallographic data and structure refinement details for **4**

Complex	4
Formula	$C_{54}H_{40}CuN_6O_2$
Formula weight	868.46
T (K)	292(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
Crystal size (mm)	0.47 × 0.25 × 0.22
a (Å)	11.821(1)
b (Å)	13.486(2)
c (Å)	14.003(2)
α (°)	86.188(2)
β (°)	78.662(2)
γ (°)	85.568(2)
V (Å^3)	2179.2(4)
Z	2
D_{calc} (g cm^{-3})	1.324
μ (Mo Kα)/mm^{-1}	0.551
Reflections collected	24 391
Refl. obs. $I > 2\sigma(I)$	9411
Max. 2θ (°)	54.00
R_{int}	0.0199
R_1 [$I > 2\sigma(I)$]	0.0574
wR_2 (all data)	0.1414
Largest difference peak and hole (e$^-$ Å^{-3})	0.685 and −0.371

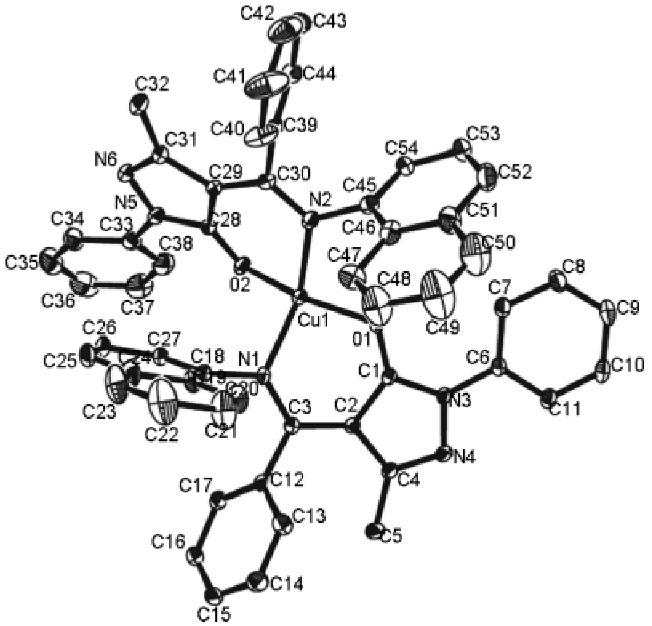


Figure 1. ORTEP plots of complex **4** showing the atom-labeling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Cu(1)–O(1), 1.904(2); Cu(1)–N(1), 1.981(2); Cu(1)–O(2), 1.911(2); Cu(1)–N(2), 2.005(2); O(1)–Cu(1)–N(1), 94.6(1); O(2)–Cu(1)–N(2), 92.8(1); O(1)–Cu(1)–O(2), 152.4(1); N(1)–Cu(1)–N(2), 140.0(1).

Norbornene homopolymerization

The polymerization results using the Cu(II) β-ketoamine complexes **1–5** activated with MAO are summarized in Table 2. Under the same polymerization conditions, the

Table 2. Norbornene polymerization with different catalysts[a]

Run	Complex	Polymer yield (g)	Activity[b]	M_n[c] (10^5 g/ mol)	M_w (10^5 g/ mol)	M_w/M_n
1	1	0.085	0.42	2.79	7.25	2.60
2	2	0.135	0.67	2.91	7.87	2.70
3	3	0.237	1.18	2.84	7.52	2.65
4	4	0.552	2.76	3.20	8.46	2.64
5	5	0.373	1.87	2.86	7.32	2.56

[a] Conditions: 20 ml toluene solution, 60 °C, 5 g norbornene, reaction time = 4 h, [Al] : [Cu] = 300, $m_{\mathrm{Cu}} = 5.0 \times 10^{-6}$ mol.
[b] Activity in 10^4 g of polymer/(mol Cu·h).
[c] Molecular weights of the polymers were determined using a Waters Breeze system at 40 °C in chlorobenzene with polystyrene standards.

structures of the Cu(II) complexes greatly affect the polymer yields and the catalytic activity. Comparison of the activities for the norbornene polymerization of the five complexes provides a catalytic activity sequence of **4** > **3** > **2** > **1**, which implies that the steric effects of the ligands play an important role in giving higher activity. The highest activity of 2.76×10^4 *g*-polymer/molCu h is obtained with the complex-**4**–MAO system. This activity is attributed to both the steric bulk and the conjugating effects of the large naphthyl ring. In addition to the bulkiness of the naphthyl group, the greater electronic conjugation for the naphthyl ring should be favorable for stabilizing the insertion transition state when the aryl ring orients itself in a coplanar fashion with the diimine chelating ring in the course of propagations, resulting in lowering the propagation barrier[34] and increasing the activity. Furthermore, complex **5** with a *p*-nitro substituent on the phenyl ring is three times more active than **2**, caused by the electron-withdrawing *p*-NO_2 group affording a more electron-deficient active Cu(II) center.

Similar electronic effects were also observed by Younkin[35] for the salicylaldiminato Ni(II) complexes in the polymerization of ethylene. Comparison with Ni(II) β-ketoamine complexes prepared by our group[36] shows that the catalytic activities of the nickel complex–MAO is several hundred times higher than that of the copper complex–MAO under similar polymerization conditions. This fact implies that the chain propagation rate of nickel catalyzing polymerization is much faster than with copper. This phenomenon can be attributed to the different metals. In addition, comparing the M_n of PNBE obtained by copper catalyst with the M_n of PNBE obtained by nickel catalyst, we find that the polymer M_n obtained by copper catalyst is lower. This fact indicates that the catalytic species in the copper system has a relative shorter active time than that in the nickel system. Therefore, the active chain in the copper system would terminate faster than that in the nickel system.

The influence of the [Al] : [Cu] ratio on the polymerization yield is summarized in Fig. 2. The monomer conversion and catalytic activity increase monotonically with increases in the Al : Cu rate from 300 to 700. As shown in Fig. 3, polymerization temperature affects the catalytic activities and M_w of the polymers greatly. Increases in reaction temperature from 0 to 80 °C give increases in activity, but significant decreases in molecular weights.

The polynorbornenes obtained with these catalysts show high molecular weights ($M_n > 3.20 \times 10^5$ g/mol, $M_w > 8.46 \times 10^5$ g/mol). The molecular weight distributions of the polynorbornenes ($M_w/M_n < 3$) promoted by the complexes indicate the presence of a single active species in the polymerization process.

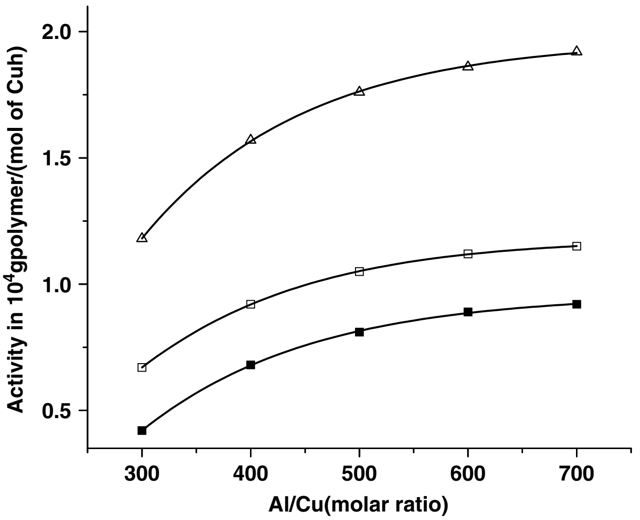


Figure 2. Evolution of catalytic activity with [Al] : [Cu] ratio (■, catalyst 1; □, catalyst 2; △, catalyst 3). Conditions: 20 ml toluene solution, 60 °C, 5 g norbornene, reaction time = 4 h, $m_{Cu} = 5.0 \times 10^{-6}$ mol, solvent: toluene.

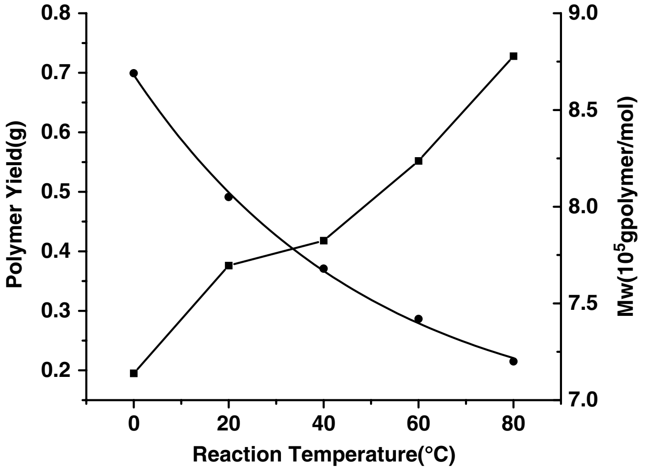


Figure 3. Plot of polymer yield (■) and M_w (●) vs polymerization temperature (complex **4**–MAO). Conditions: 20 ml toluene solution, 5 g norbornene, reaction time = 4 h, [Al] : [Cu] = 300, $m_{Cu} = 5.0 \times 10^{-6}$ mol.

As shown in Fig. 4, the ^1H NMR spectra show the absence of double bonds in the polymers, indicating that polymerization occurs via a vinyl-type mechanism. Similarly, the IR spectra of the polymers also prove the occurrence of vinyl-type polymerization rather than ring-opening metathesis polymerization, which would afford a double-bond-containing polymer showing peaks at 996 and 735 cm^{-1}.[37] All the polynorbornenes synthesized here are easily soluble in cyclohexane, chlorobenzene and *o*-dichlorobenzene, indicating low stereoregularity. What is more, analysis by wide-angle X-ray diffraction shows an amorphous material.

Copolymerization of norbornene and styrene

Late metal catalytic systems have been reported to act as initiators for the copolymerization of norbornene with

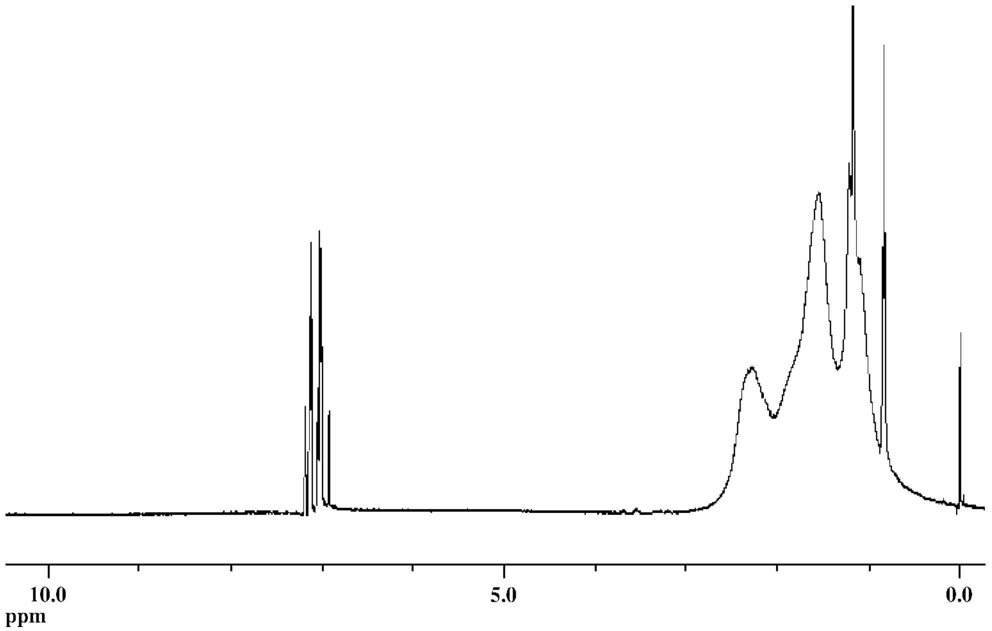


Figure 4. ^{1}H NMR spectrum of polynorbornene obtained by complex **2**–MAO system.

styrene using Ni(stear)$_2$: MAO,[38] Ni(acac)$_2$: MAO[39] and Ni-Pd(diimine) : MAO[40] systems, and Ni compounds involving O-donated ligands.[41] To our knowledge, this is the first report on norbornene and styrene copolymerization using copper complex–MAO catalytic systems.

The copolymerization of styrene (Sty) and norbornene (NBE) in the presence of the copper(II) complex–MAO system was investigated. The basic mechanism of norbornene homopolymerization and copolymerization with styrene are shown in Scheme 1.[40] ^{13}C NMR spectra of the resulting copolymers obtained from complex **5**– MAO showed the superposition of the respective homopolymers as expected (Fig. 5).[41] A series of experiments was performed varying the initial comonomer feed ratios. The copolymerization results catalyzed by the complex **1**–**5**–MAO system are presented in Table 3. As may be observed, the copolymerization catalytic activity sequence is the same as for norbornene homopolymerization. The M_w values decrease with decreases in the copolymerization rate. This indicates that norbornene insertion is the dominant rate-controlling process. Unimodal molar mass distributions with narrow molecular weight distributions (M_w/M_n close to 2) of all the copolymers indicate that the copolymerization occurs at the single active site and the polymer is a 'true' copolymer without homopolymers.[41]

Table 3. Copolymerization of styrene and norbornene in the presence of the complex **1**–**5**–MAO catalytic system[a]

Complex	Yield (%)	Found Sty(%)	Found NBE(%)	M_n[b] (10^4 g/mol)	M_w (10^4 g/mol)	M_w/M_n
1	1.7	40.3	59.7	0.55	1.53	2.78
2	3.2	28.5	71.5	0.85	2.23	2.62
3	5.7	20.9	79.1	1.13	2.76	2.44
4	11.5	5.2	94.8	1.62	4.34	2.68
5	8.6	15.6	84.4	1.36	2.95	2.17

[a] Conditions: 20 ml toluene solution, [Sty] = 0.02 mol, [NBE] = 0.04 mol, [Al] : [Cu] = 600, $m_{\mathrm{Cu}} = 5.0 \times 10^{-6}$ mol, temperature 60 °C for 12 h.

[b] Molecular weights of the polymers were determined using a Waters Breeze system at 40 °C in tetrahydrofuran with polystyrene standards.

As observed in Fig. 6, the copolymerization rates as well as the M_w values decrease with an increase in styrene content in the monomer feed. The monomer reactivity ratios of norbornene and styrene were obtained from the Fineman–Ross plot (Fig. 5) as $r_{\mathrm{norbornene}} = 20.11$, $r_{\mathrm{styrene}} = 0.035$. The result is very similar to that for the nickel stearate–MAO system ($r_{\mathrm{styrene}} = 0.02, r_{\mathrm{norbornene}} = 20.8$), which results in a lower styrene incorporation ratio by the nickel stearate–MAO system under polymerization conditions.[39] 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.

The thermostability of the homo- and copolymers were investigated by TGA. The copolymers exhibit higher decomposition temperatures (425–465 °C) than the homopolymer of styrene (~390 °C). This suggests that the norbornene segment in the copolymer improves its thermostability relative to polystyrene. THF is a good solvent for polystyrene, but a bad one for polynorbornene. However, the copolymers are easily dissolved in chloroform or THF. The solubility of

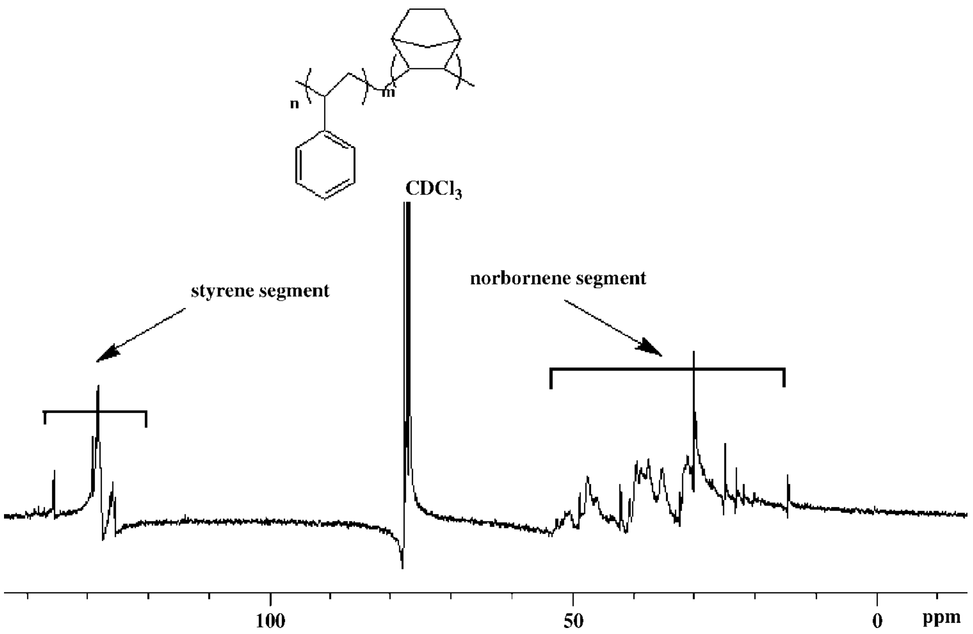


Figure 5. ^{13}C NMR spectrum of poly(norbornene-ran-styrene) obtained by complex **5**–MAO system.

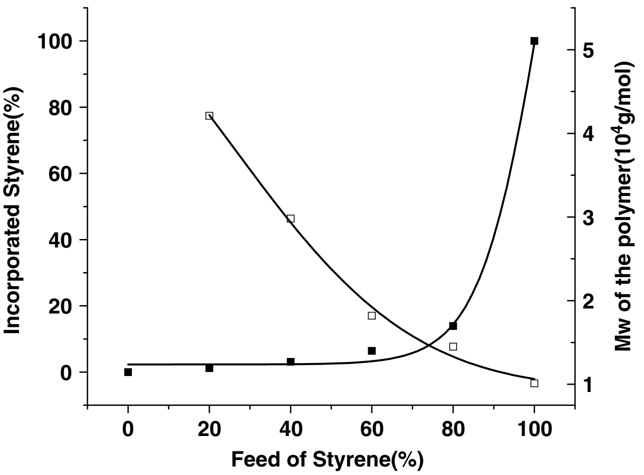


Figure 6. Plot of M_w (□) and percentage incorporated styrene (■) vs feed of styrene (complex **4**–MAO). Conditions: 20 ml toluene solution, [Sty] + [NBE] = 0.06 mol, [Al] : [Cu] = 600, $m_{Cu} = 5.0 \times 10^{-6}$ mol, temperature 60 °C for 12 h.

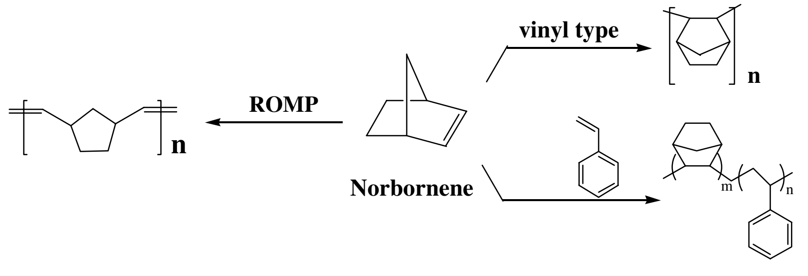
the polynorbornene segment has been significantly improved by copolymerization. These results suggest that the introduction of styrene segments in the copolymer improves its processability relative to polynorbornene. Study of polar and nonpolar monomer homo- and copolymerization is currently under investigation.

EXPERIMENTAL

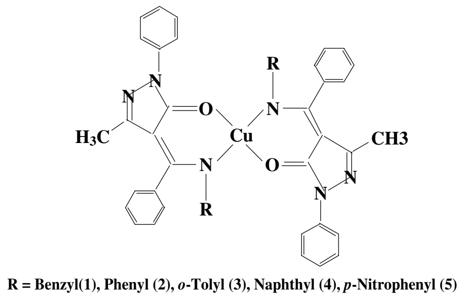
All manipulations were carried out under an atmosphere of inert gases using standard Schlenk techniques.

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. The 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone and the benzylamine, aniline, *o*-methylaniline, naphthylamine and *p*-nitroaniline (AR) were



Scheme 1. The basic mechanism of norbornene homopolymerization and copolymerization with styrene.



Scheme 2. The structure of bis-(β-ketoamine)–copper(II) complexes.

obtained from China National Medicine Group Shanghai Chemical Reagent Company and used without further purification.

The structures of these Cu(II) complexes are shown in Scheme 2. They were synthesized by an improved literature procedure.[30–32] Among these Cu complexes, the preparation of Cu(L4)$_2$•2H$_2$O has been reported.[33] The molecular structure of Cu(L1)$_2$ has been reported by our group.[31] Norbornene from Aldrich was dried with metal kalium and distilled, and then dissolved in toluene to make a 0.4 g/ml solution. Anhydrous toluene was obtained by distillation over metallic Na. MAO was prepared by the hydrolysis of trimethylaluminum with $Al_2(SO_4)_3$•18H_2O in toluene with a H_2O : Al molar ratio of 1.3 : 1.

Measurements

Infrared spectra were recorded on polymer–KBr pellets with a Bruker Equinox55 FT-IR spectrophotometer in the region 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) or o-$C_6D_4Cl_2$ (for PNBE) solution using tetramethylsilane as the 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 and chlorobenzene 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 50 ml/min and a heating rate of 10 °C/min.

Single-crystal studies on complex **4** were collected on a Bruker SMART CCD diffractometer at room temperature, Mo Kα, 2θ range 3.6–54.0°. The structure was solved by direct methods followed by difference Fourier synthesis, and then refined by full-matrix least-squares techniques against F^2 using SHELXTL[42] with anisotropic thermal parameters for all the non-hydrogen atoms. Absorption corrections were applied using SADABS.[43] All the hydrogen atoms were placed in calculated positions and refined isotropically using a riding model.

General polymerization procedure

Catalytic polymerization of norbornene was carried out in a Fisher–Porter glass reactor and protected by nitrogen. MAO (0.5 mmol, solid powder) was added into a Schlenk flask with a magnetic stirrer. Norbornene (53.2 mmol, 5.0 g) in 10 ml toluene and 9 ml of toluene were then added. The reaction was started by the addition of 1 ml of freshly prepared Cu-complex solution (5.0×10^{-6} M in toluene) at 60 °C. After 1 h, the reaction mixture was poured into excess ethanol acidified with 5% HCl. The polymer was washed with ethanol and then dried under vacuum at 80 °C for 48 h.

CONCLUSIONS

Bis(β-ketoamine)copper(II) complexes based on pyrazolone derivatives can be activated by MAO to efficiently catalyze norbornene polymerization via a vinyl addition mechanism with moderate catalytic activities. The molecular weight distributions of the polynorbornenes ($M_w/M_n < 3$) produced by all the catalysts indicate the presence of a single active species in the polymerization process.

Random copolymers of norbornene and styrene were successful synthesized using a series of copper(II) complex catalyst–MAO systems. 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 ($r_{\text{norbornene}} = 20.11$ and $r_{\text{Sty}} = 0.035$) indicates a much higher reactivity of norbornene, which is interpreted by a coordination mechanism. The study of the polar and nonpolar monomer homo- and copolymerization currently being investigated.

Acknowledgement

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Supplementary materials

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center; the CCDC reference number for **4** is 294972. 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).

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