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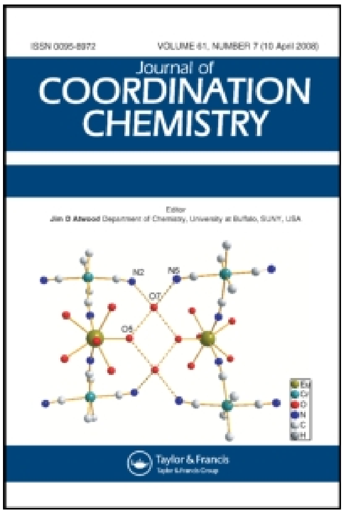

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A copper complex with β-ketoamine ligand based on pyrazolone derivative: synthesis, crystal structure and catalysis for norbornene polymerization

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A copper complex with β-ketoamine ligand based on pyrazolone derivative: synthesis, crystal structure and catalysis for norbornene polymerization

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A copper complex with β-ketoamine ligand based on a pyrazolone derivative was synthesized by condensing pyrazolone with 3-methylaniline and then reacting the produced β-ketoamine with copper halide. The solid-state structure of the complex was determined by single-crystal X-ray diffraction. The *bis*(β-ketoamine) copper complex shows moderate activity to catalyze the vinyl polymerization of norbornene with activation of methylaluminoxane under mild reaction conditions. The activity of the catalyst for norbornene polymerization is as high as 2.88×10^4 g polymer/mol Cu h. The polymer yield and catalytic activity can be controlled over a wide range by the variation of reaction parameters.

Keywords: β-Ketoamine; Copper complex; Crystal; Olefin polymerization; Norbornene

1. Introduction

In recent years, there has been much study of late transition metal catalysts for olefin homo- and copolymerization [1–4]. Compared with metallocenes based on early transition metals, the late transition metal catalysts are less oxophilic and thus less easily poisoned by polar monomer contaminants [5–8]. Among these late transition metals, copper presents some interesting properties in olefins polymerization [9, 10]. Several series of copper complexes bearing benzamidinate ligands [11], benzimidazolyl ligands [12] and α-diimine [9] ligands have been reported for ethylene polymerization upon activation with methylaluminoxane. Complexes containing N,O-chelating ligand are particularly interesting for catalysis by mixed-donor-ligand-complexes, such as the Ni-based systems shown to be effective in ethylene polymerization [13]. β-Ketoamines are important members of the family of N,O bidentate ligands [14] because of their ease of preparation and simple modification of both steric and/or electronic effects.

Late-transition-metal complexes of pyrazolone derivatives have been used in many fields [15, 16], such as luminescence effects [17] and biological activities [18, 19], probably due to their ease of preparation and tolerance for polar substances.

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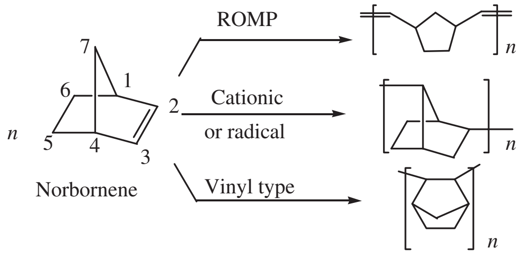

Scheme 1. The basic mechanism of norbornene homopolymerization.

There are few reports of copper complexes with pyrazolone derivatives used for olefin polymerization.

Norbornene can be polymerized in three different ways leading to different polymer structures (scheme 1). The most studied processes are the ring-opening metathesis polymerization (ROMP) and the vinyl addition polymerization. The nature of the copper(II) complex bearing a N,O-chelate ligand for the polymerization of norbornene is not reported. With the aim of studying the catalytic properties of this complex for olefin polymerization, a copper complex with pyrazolone derivatives as ligand has been prepared and applied as catalyst precursors for the polymerization of norbornene after activation by methylaluminoxane (MAO). Reaction conditions are found to be important and influential toward the catalytic activity.

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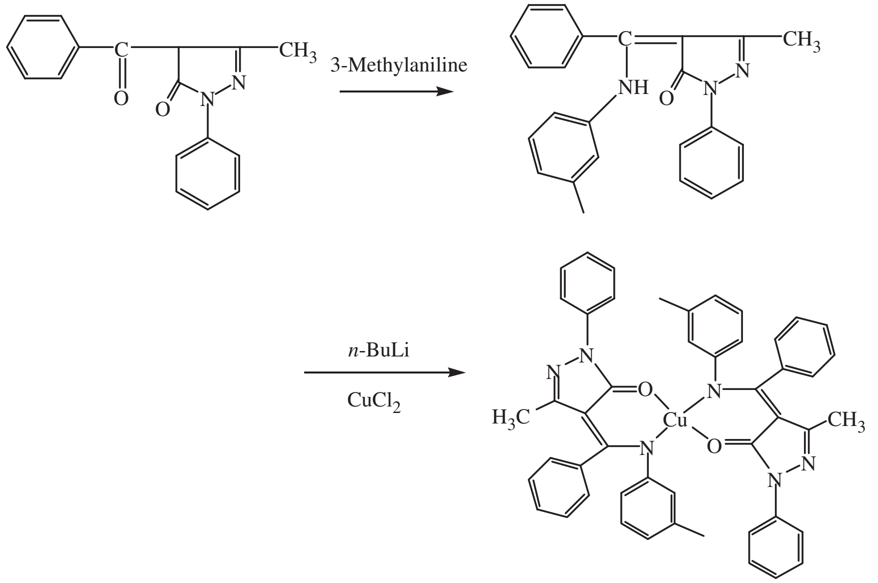
2. General procedures and materials

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 3-methylaniline (AR) were obtained from China National Medicine Group, Shanghai Chemical Reagent Company and used without further purification. The Cu(II) complex was synthesized by a procedure as shown in scheme 2, an improved procedure of the literature [15–17]. Norbornene from Aldrich was dried with potassium metal and distilled, and then dissolved in toluene to make a 0.4 g mL^{-1} solution. Anhydrous toluene was obtained by distillation over sodium metal. MAO was prepared by the hydrolysis of trimethylaluminum with $Al_2(SO_4)_3 \cdot 18H_2O$ in toluene with the H_2O/Al molar ratio of 1.3 : 1.

2.1. *Preparation of* bis*[5-methyl-2-phenyl-4-(3-tolyliminophenylmethylene) pyrazol-3-ato]copper(II)*

The ligand of 5-methyl-2-phenyl-4-[(Z)-3-tolylamino-phenylmethylene]pyrazol-3(2H)-one was reported by our group [20]. A solution containing one equiv. of **L** (1.25 g, 3.40 mmol) and lithium *n*-butyl (3.40–3.50 mmol) in toluene (50 mL) was cooled to −70°C and stirred for ca 8 h. When the temperature rises to room temperature, 0.5 equiv. of $CuCl_2$ (0.235 g, 1.75 mmol) was added to the reaction system,



Scheme 2. Synthesis of the ligands β-ketoamine and the *bis*-(β-ketoamine)-copper(II) complex.

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which was heated to 60°C and kept stirring for one day. After removal of the solvent from the reaction system in vacuum, the crude product was extracted by CH_2Cl_2 and washed by *n*-hexane. After filtration and removal of the solvent from the residues, the powder of *bis*[5-methyl-2-phenyl-4-(3-tolyliminophenylmethylene)pyrazol-3-ato]copper(II) was obtained. Yield: 0.975 g, 72%. Elemental analysis, calculated for $C_{48}H_{40}N_6CuO_2$: C, 72.39; H, 5.06, N, 10.55%; Found: C, 72.48; H, 5.19; N, 10.78; m.p.: >320°C. The single-crystals (black) of CuL_2 were grown in ethanol, and the ORTEP plot of structure in figure 1 (CCDC reference number is 295533).

3. Measurements

FT-IR spectra were recorded on a Bruker EQUINOX 55 Spectrometer. NMR spectra were carried out on an INOVA 500 Hz at room temperature in $CDCl_3$ solution using TMS as internal standard. Gel permeation chromatography (GPC) analyses of the molecular and weight distributions of the polymers were performed on a Waters Breeze system with 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. The reflection data of complex were collected on a Bruker SMART CCD diffractometer at room temperature, Mo-Kα, 2θ range 2.6–54.0°. The structure was solved by Direct methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against F^2 using SHELXTL [21a] with anisotropic thermal parameters for all the non-hydrogen atoms. Absorption corrections were applied using SADABS [21b]. All the hydrogen atoms were placed in calculated positions and refined isotropically using a riding model.

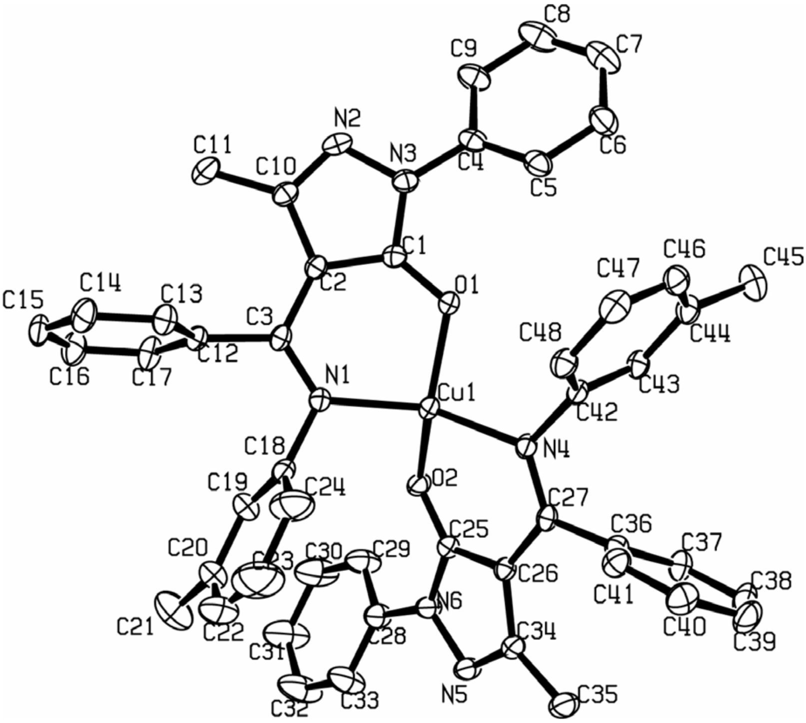

Figure 1. ORTEP plots of complex showing the atom-labeling scheme. Thermal ellipsoids at the 30% level are shown. Hydrogen atoms are omitted for clarity.

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4. General polymerization procedure

MAO (0.5 mmol) was added under an inert gas atmosphere into an Schlenk flask with a magnetic stirrer. Norbornene (53.2 mmol, 5.0 g) in 10 mL toluene and 9 mL of toluene were added later. The reaction was started by the addition of 1 mL of a freshly prepared Cu-complex solution (5.0×10^{-6} M in toluene) at 60°C. After 1 h, the reaction mixture was poured into an excess of ethanol acidified with 5% HCl. The polymer was washed with ethanol and then dried under vacuum at 80°C for 48 h.

5. Results and discussion

5.1. *Structure of complex*

The structure of the complex is shown in figure 1 and the crystallographic data and refinement parameters are presented in table 1. The molecular structure of ligand (5-methyl-2-phenyl-4-[(Z)-3-tolylamino-phenylmethylene]pyrazol-3(2H)-one) has been reported by our group [20]. The N,O-chelate ligand is an example of a class of potential bidentate chelating ligands that is synthesized from the condensation of

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Table 1. Crystallographic data for complex.

Empirical formula	$C_{48}H_{40}CuN_6O_2$
Formula weight	796.40
Crystal size (mm^3)	0.52 × 0.38 × 0.26
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	19.3558(17)
b (Å)	10.0509(9)
c (Å)	22.121(2)
β (°)	100.511(2)
V (Å^3)	4231.2(7)
Z	4
D_{Calcd} (g cm^{-3})	1.250
μ (Mo-Kα) (mm^{-1})	0.562
T(K)	292(2)
θ range (°)	1.29–27.00
Reflections collected	9220
Unique reflections	5122
R_1 ($I > 2\sigma$)	0.0568
wR_2 (all data)	0.1789
Goodness-of-fit on F^2	0.740
Largest diff. peak and hole (e Å^{-3})	0.353 and −0.546

Table 2. Selected bond lengths (Å) and angles (°) for complex.

Bond	Length	Bond	Angle
Cu(1)–O(1)	1.915(2)	O(1)–Cu(1)–O(2)	144.78(10)
Cu(1)–O(2)	1.916(2)	O(1)–Cu(1)–N(1)	95.32(11)
Cu(1)–N(1)	1.968(3)	O(2)–Cu(1)–N(1)	93.15(11)
Cu(1)–N(4)	1.985(3)	O(1)–Cu(1)–N(4)	97.27(10)
N(4)–C(27)	1.324(4)	O(2)–Cu(1)–N(4)	94.77(10)
N(4)–C(42)	1.436(4)	N(1)–Cu(1)–N(4)	145.49(12)
O(2)–C(25)	1.283(4)	C(27)–N(4)–C(42)	119.1(3)
O(1)–C(1)	1.286(4)	C(27)–N(4)–Cu(1)	123.3(2)
N(3)–C(1)	1.364(4)	C(42)–N(4)–Cu(1)	117.6(2)
N(3)–N(2)	1.391(4)	C(25)–O(2)–Cu(1)	117.9(2)
N(3)–C(4)	1.418(4)	C(1)–O(1)–Cu(1)	119.3(2)
N(1)–C(3)	1.304(4)	C(1)–N(3)–N(2)	111.0(3)
N(1)–C(18)	1.440(5)	C(1)–N(3)–C(4)	129.3(3)
C(1)–C(2)	1.408(4)	N(2)–N(3)–C(4)	119.7(3)
C(10)–C(2)	1.437(5)	C(44)–C(43)–C(42)	121.8(3)
C(25)–C(26)	1.409(4)	N(4)–C(27)–C(26)	121.5(3)

commercially available 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone with the primary amine, 3-methylaniline. In the copper(II) derivative, two deprotonated ligands chelate to the metal through their amido N and carbonyl O atoms (figure 1). For both six-membered chelate rings, the five C, N and O atoms are coplanar however, the Cu atom lies out of the plane. The Cu1/N1/O1 lies 13.9° out of the O1/C1/C2/C3/N1 plane, Cu1/N4/O2 lies 24.4° out of the O2/C25/C26/C27/N4 plane, in the opposite direction. The four-coordinate geometry of copper is best regarded as distorted square planar. The carbonyl C=O bond distances [1.286 (4) and 1.283 (4) Å] are lengthened relative to that [1.247 (2) Å] in the free ligand [22]; similarly, the exocyclic C=O double bond is also lengthened, so that the negative charge formally residing on the amide N is better regarded as being delocalized over the five-atom unit (table 2).

Table 3. Norbornene polymerization with this copper catalyst.[a]

Run	Reaction time (h)	Polymer yield (g)	Activity[b]	Mn[c]/10^5	Mw/10^5	MWD
1	0.5	0.072	2.88	4.26	9.41	2.21
2	1	0.102	2.04	3.89	9.22	2.37
3	2	0.153	1.53	4.06	8.62	2.12
4	4	0.225	1.13	4.43	8.34	1.88

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

The structure of a similar organic compound, 4-[(1-naphthylamino)phenylmethylene]-5-methyl-2-phenylpyrazol-3-one, has been authenticated [23]. In addition, a structure of this compound as a 2 : 1 complex with silver hexafluorophosphate is known. In this salt, the Ag is coordinated by two ligands through the N-atom sites of the pyrazolyl rings [24].

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6. Catalytic olefin polymerization

The Cu(II) complex exhibited moderate catalytic activity for norbornene polymerization in the presence of MAO; the results are summarized in table 3. With the activation of methylaluminoxane, a blank norbornene polymerization was performed under the same conditions without copper complex. The low yield of polynorbornene confirms the previously reported result connecting the ability of copper complex to initiate polymerization of norbornene. Comparison to Ni(II) β-ketoamine complexes prepared by our group [25] show the catalytic activity of the nickel complex/MAO is several hundred times higher than the copper complex/MAO under similar polymerization conditions. This implies the chain propagation rate of the nickel catalyzing polymerization was much faster than that of the copper. This distinct difference of the nickel and copper complexes bearing analogous β-ketoamine ligand could be attributed to the different metals. Interestingly, the catalytic activities of Co(II) β-ketoamine complexes/MAO was equivalent to the copper complex/MAO [26], showing the chain propagation rate of the copper polymerization was as much as that of the cobalt polymerization.

The polynorbornenes obtained with these catalysts showed high molecular weights (Mn $> 3 \times 10^5$ g mol^{-1}, Mw $> 8 \times 10^5$ g mol^{-1}). The narrow molecular weight distributions of the polynorbornenes (Mw/Mn = 1.88–2.37) promoted by the complexes indicate the presence of a single active species in the polymerization process. As shown in figure 2, the ^{1}H NMR spectra show no double bond in the polymers, indicating the polymerization occurs through a vinyl-type mechanism. Similarly, the IR spectra of the polymers also indicate a vinyl-type polymerization rather than ring-opening metathesis polymerization which would afford a double-bond-containing polymer showing an IR absorptions at 996 and 735 cm^{-1} [27]. As shown in figure 5, the resonances of methenes and methines appear at 29.4–33.5 ppm for carbon-5 and carbon-6, 35.5–38.6 ppm for carbon-7, 38.6–42.4 ppm for carbon-1 and carbon-4, and 46.8–54 ppm for carbon-2 and carbon-3. The ^{13}C NMR spectrum is similar to that

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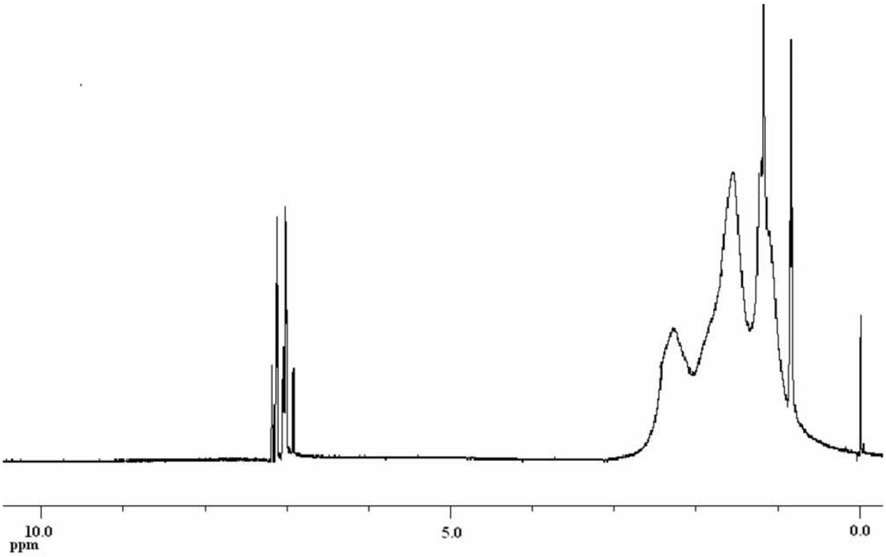

Figure 2. ^{1}H NMR spectrum of polynorbornene obtained by complex/MAO system.

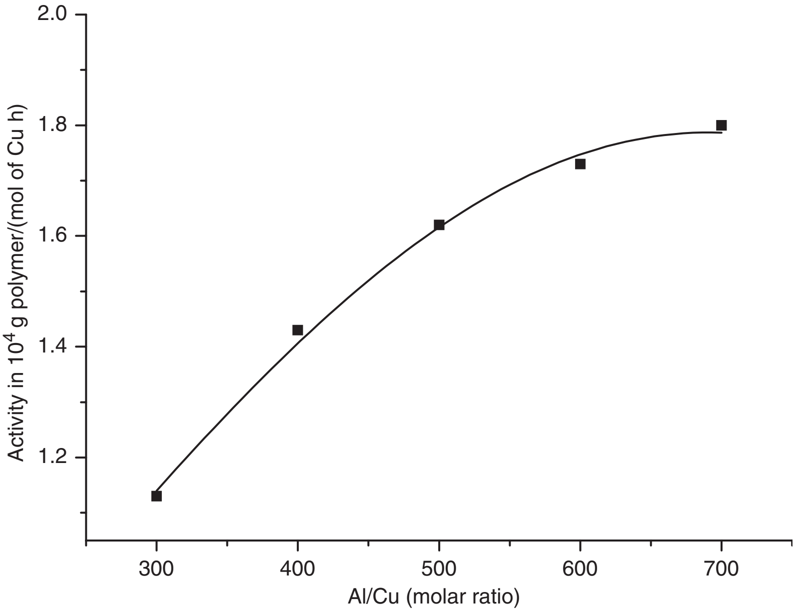

Figure 3. Evolution of catalytic activity with [Al]/[Cu] ratio. Conditions: 20 mL toluene, 60°C, 5 g norbornene, reaction time = 4 h, $m_{Cu} = 5.0 \times 10^{-6}$ mol, solvent: toluene.

reported by Greiner's and Wu's groups [27, 28]. These data further confirm that the polynorbornenes obtained were the products of vinylic polymerization. All the polynorbornenes obtained here are easily soluble in cyclohexane, chlorobenzene and *o*-dichlorobenzene, indicating low stereoregularity. Figure 6 shows the WAXD spectra of polynorbornene. This spectrum displays two broad halos at 2θ of 10.2 and 19.1 that

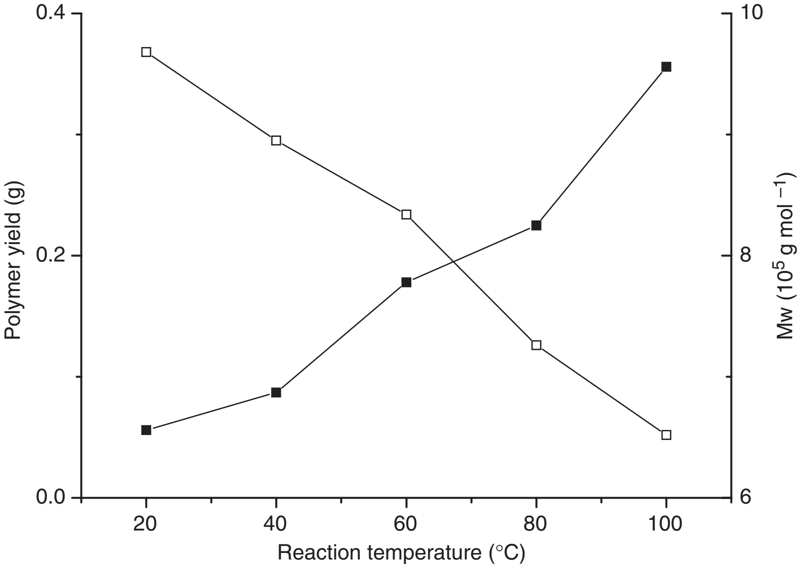

Figure 4. Plot of polymer yield (■) and Mw (□) *vs*. polymerization temperature. Conditions: 20 mL toluene, 5 g norbornene, reaction time = 4 h, [Al]/[Cu] = 300, $m_{Cu} = 5.0 \times 10^{-6}$ mol.

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can be attributed to short-range order. This is in agreement with the results reported by Zhao *et al.* [29]. No traces of Bragg reflections, characteristic of crystalline regions, are revealed. The polynorbornene is also non-crystalline.

The reaction parameters can affect the catalytic activity, polymer yield and polymer molecular weight remarkably. As shown in table 3, with increasing time, the polymer yield should increase monotonically with time. The polymerization activities reach their highest values at an early stage and then decrease rapidly with time, indicating that the character of the catalytic system changed rapidly. The reason for activity decreasing with time is that the catalytic species are deactivated gradually. The results from norbornene polymerizations under different molar ratios of MAO to the Cu complex (Al/Cu) are summarized in figure 3. The monomer conversion and catalytic activity monotonously increase with an increase of Al/Cu from 300 to 700. As shown in figure 4, the polymerization temperature can also affect the catalytic activities and the Mw of the polymers greatly. When the reaction temperature increased from 0 to 100°C, a prominent increase in activity was obtained, but with significant decreases in molecular weight.

7. Conclusions

bis(β-Ketoamine)copper(II) complex based on a pyrazolone derivative can be activated by MAO to efficiently catalyze norbornene polymerization following the vinyl addition mechanism at moderate catalytic activities. The narrow molecular weight distributions of the polynorbornenes (Mw/Mn = 1.88–2.37) produced by all the catalysts indicate the presence of a single active species in the polymerization process.

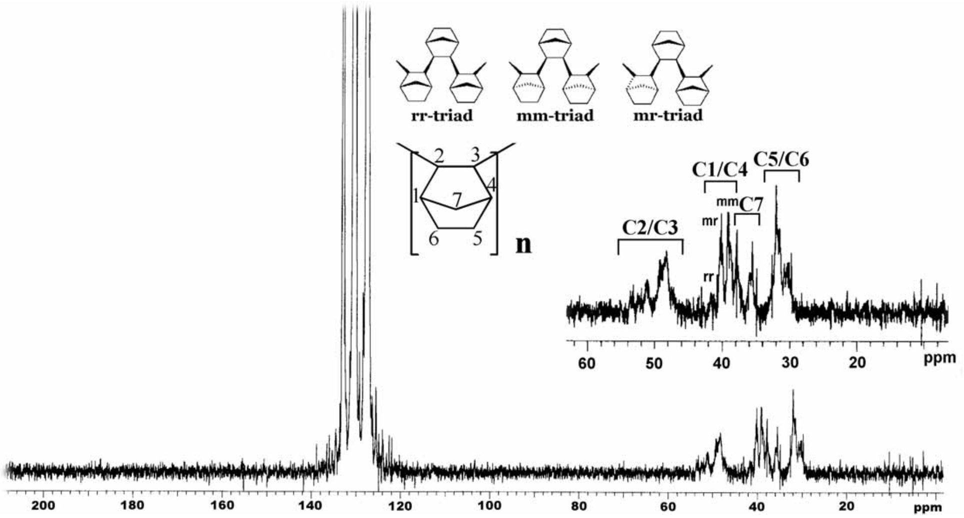

Figure 5. ^{13}C NMR spectrum of polynorbornene prepared by complex/MAO at 60°C.

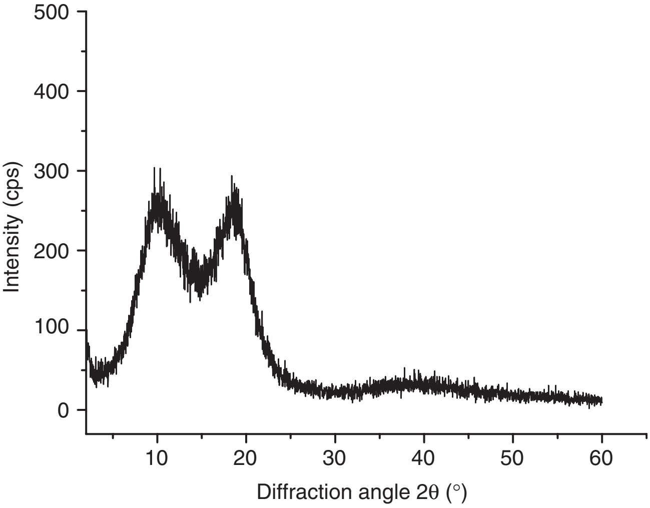

Figure 6. WAXD diagram of PNBE obtained by complex/MAO at 60°C.

The polymer yield can be controlled over a wide scope by variation of reaction parameters. The obtained polynorbornenes have low stereo regularity study of polymerization of polar and non-polar monomers is under investigation.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre; CCDC reference number for complex is 295533.

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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; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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