

Bis(β -ketoamino)copper(II)/Methylaluminoxane Systems for Homo- and Copolymerizations of Methyl Acrylate and 1-Hexene

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ABSTRACT: Two bis(β -ketoamino)copper [ArNC(CH₃)CHC(CH₃)O]₂Cu (**1**, Ar = 2,6-dimethylphenyl; **2**, Ar = 2,6-diisopropylphenyl) complexes were synthesized and characterized. Homo- and copolymerizations of methyl acrylate (MA) and 1-hexene with bis(β -ketoamino)copper(II) complexes activated with methylaluminoxane (MAO) were investigated in detail. MA was polymerized in high conversion (>72%) to produce the *syndio*-rich atactic poly(methyl acrylate), but 1-hexene was not polymerized with copper complexes/MAO. Copolymerizations of MA and 1-hexene with **1,2**/MAO produced

acrylate-enriched copolymers (MA > 80%) with isolated hexenes in the backbone. The calculation of reactivity ratios showed that $r(\text{MA})$ is 8.47 and $r(\text{hexene})$ is near to 0 determined by a Fineman-Ross method. The polymerization mechanism was discussed, and an insertion-triggered radical mechanism was also proposed. © 2010 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 48: 1113–1121, 2010

KEYWORDS: copolymerization; monomers; organometallic catalysts; radical polymerization

INTRODUCTION The copolymerization of olefins with polar monomers by organometallic catalysts has been an interesting goal. In particular, the copolymerization of olefins with acrylate monomers can produce new special materials: the thermal stability, the hydrophobic character derived from the C—C backbone, and the adhesive power introduced with the ester groups.^{1–3} In the last few years, late transition metal nickel and palladium complexes have been developed for the direct copolymerization of ethylene and polar monomers because of their greater functional group tolerance.^{4–14} However, the majority of the catalytic systems reported up to now generally produce copolymers with low incorporation of polar monomer and with low molecular weights and branched structures.

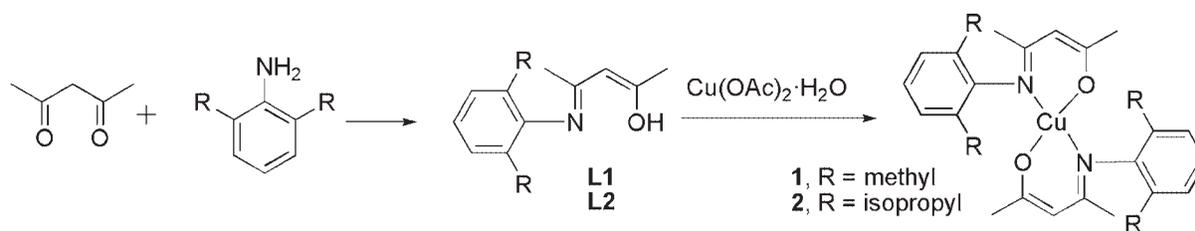
In addition to nickel- and palladium-based catalyst, copper-based systems have also been reported for homo- and copolymerization of alkenes with polar monomers. The researchers of Exxon-Mobil first investigated the activity of methylaluminoxane (MAO)-activated copper(II) systems.^{15–18} Subsequently, several other reports have emerged of LCuCl₂ or L₂Cu (L: ligand) complexes using α -diimine,¹⁹ pyrazolylpyrimidine,²⁰ and pyrazolylquinoline²¹ ligands that are also active for ethylene polymerization with MAO as activator. In particular, Stibrany et al. reported good activity of bis(benzimidazole)copper(II)/MAO systems for the homo- and copolymerizations of ethylene and methyl acrylate (MA).^{22,23} Carlini

and coworkers reported bis(salicylaldimine)copper(II) complexes, when activated with MAO, catalyzed the homo- and copolymerizations of ethylene and methyl methacrylate (MMA).²⁴ The activity of MAO-activated [1,2-bis(4,4-dimethyl-2-oxazolin-2-yl)ethane]copper(II) dichloride (Cu(D-MOX)Cl₂) for the polymerization of acrylates and their copolymerization with ethylene was also reported by Sen and coworkers,²⁵ who investigated the reaction mechanism. Foley and coworkers recently found that salicylaldimine or α -diimine copper species cannot be an active catalyst for ethylene polymerization under mild conditions due to ligand transfer to aluminum, and the resulting LAlMe₂/LAlMe⁺ complexes are likely the active species.²⁶

Generally, the poly(methyl acrylate)s (PMAs) produced by these copper(II)/MAO systems are atactic. The introduction of ethylene into the MA or MMA homopolymerization system resulted in the formation of acrylate-rich copolymers in greatly reduced yields. Unlike Brookhart-type palladium α -diimine catalyst,^{4,5} these systems produced highly linear copolymers with high acrylate incorporation. Additionally, the level of alkene incorporation in the copolymers was similar to that reported for well documented radical polymerization systems. Besides, some copper complexes bearing [N,O] ligands have been developed for norbornene polymerization.^{27–31} To date, reports on olefin polymerization systems based on copper are scarce, and polymerization mechanism

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SCHEME 1 Synthesis of copper complexes.

is not clearly deduced. Except for the atom transfer radical polymerization systems, a noteworthy current limitation for copper-based catalytic systems is the absence of copolymerization of α -olefins and acrylate monomers.

In this article, novel bis(β -ketoamino)copper(II) complexes were chosen and synthesized as precursors because these copper precursors are stable, cheap, and easy to be prepared. Homo- and copolymerizations of MA and 1-hexene with novel bis(β -ketoamino)copper(II) complexes in combination with MAO were investigated. The influences of the reaction parameters on polymerization behavior were evaluated, and the microstructures of the resulting polymers were also characterized. Moreover, the polymerization mechanism using bis(β -ketoamino)copper complexes/MAO systems was also analyzed and commented.

RESULTS AND DISCUSSION

Synthesis of Copper Complexes and Molecular Structure

The synthetic route of the copper complexes is shown in Scheme 1. β -Ketoamino ligands **L1** and **L2** were prepared by condensation of acetylacetone and the corresponding substituted aniline following previously reported method.³² The desired bulky copper complexes **1** and **2** were synthesized under mild conditions in high yields (>80%) by the reaction of $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ with 2 equiv of the β -diketiminato ligands in methanol.

^1H NMR analysis failed because of the paramagnetic character of the Cu(II) complex, which is similar to other copper(II) complexes bearing [N,O] ligands.^{28–31} Therefore, the IR and elemental analysis were measured to confirm the structures of copper complexes **1** and **2**. The elemental analysis results revealed that the components of two complexes were in accord with the formula CuL_2 . Both **1** and **2** are stable in air, and they are soluble in CH_2Cl_2 , tetrahydrofuran (THF), and toluene, and sparingly soluble in methanol and hydrocarbons.

Crystal suitable for X-ray crystallography of **2** was obtained by slow evaporation from methanol/toluene solution. ORTEP diagram is shown in Figure 1 along with selected bond lengths and bond angles.³³ Complex **2** shows the four-coordinate environment around the copper atom where the two ligands act as bidentate N,O-chelators and lie in the *trans* conformation to create two slightly distorted six-membered coordination planes. It is well known that four-coordinated Cu(II) complexes are usually characterized by a square planar coordination that may be distorted to pseudotetrahedral

geometry.³⁴ Unlike copper complex $\text{Cu}[(\text{CH}_3)_3\text{CC}(\text{NH})\text{CH}_2\text{C}(\text{O})\text{C}(\text{CH}_3)_2]$ adopting square planar geometry,³⁵ bulky copper complex **2** can be described as a distorted square planar coordination geometry, which may result from the steric hindrance of the substituents on the imine moieties. The dihedral angle is 38.7° between two coordination planes, which is larger than those of other [N,O]copper(II) complexes.^{28–31} The bond lengths of Cu(1)—O (1.8919(13) Å) and Cu(1)—N (1.9700(15) Å) are similar to those of bis(salicylaldiminato)copper(II) complex and other [N,O]copper(II) complexes. And the presence of *N*-2,6-diisopropylphenyl group has caused an increase in the length of the Cu—N bond than that of the Cu—O bond. The angle of *N*—Cu—O is $93.71(6)^\circ$, which is slightly larger than those of bis(salicylaldiminato)copper(II) complex.²⁸

MA Homopolymerization

In the presence of MAO, copper complexes **1** and **2** were investigated for MA homopolymerization. The results are listed in Table 1. Two copper complexes **1** and **2** exhibited moderate activity for MA homopolymerization. Steric hindrance of the copper complexes on aryl substituents influences their activities and the molecular weight of the produced polymer: **1** with *N*-2,6-dimethylphenyl group showed higher activity for MA polymerization than **2** with *N*-2,6-

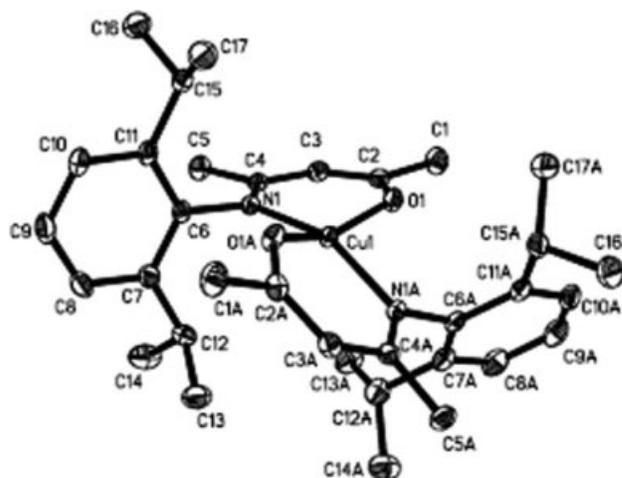


FIGURE 1 Molecular structure of **2**. The hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)—N(1) 1.9700(15), Cu(1)—N(1)#1 1.9700(15), Cu(1)—O(1)#1 1.8919(13), Cu(1)—O(1) 1.8919(13), O(1)—Cu(1)—N(1) $93.71(6)$, O(1)#1—Cu(1)—N(1)#1 $93.71(6)$, O(1)#1—Cu(1)—O(1) $153.53(9)$, N(1)—Cu(1)—N(1)#1 $153.59(9)$.

TABLE 1 Results of MA Homopolymerization with **1** and **2**/MAO

Run	Complex	T (°C)	Al/Cu ratio (mol/mol)	Conversion (%)	Activity ^a	M_w^b (10^4 g/mol)	MWD ^b (M_w/M_n)
1	1	25	100	40.5	19.4	2.34	1.97
2	1	45	100	49.1	23.5	3.62	1.79
3	1	65	100	72.6	34.8	4.87	1.64
4	1	65	50	trace	–	– ^c	–
5	1	65	200	67.3	32.2	2.09	1.42
6	1	65	400	6.9	3.30	1.13	1.89
7	2	25	200	45.8	21.9	3.57	1.68
8	2	45	200	48.1	22.8	4.62	1.81
9	2	65	200	54.1	25.7	5.40	1.72
10	2	65	50	trace	–	–	–
11	2	65	100	0.6	0.4	–	–
12	2	65	400	3.0	1.4	–	–

General Condition: 20 μ mol Cu complex; MA monomer: 5 mL; reaction time, $t = 5$ h; solvent, toluene; total volume 20 mL.

^a In units of kg/(mol Cu h).

^b Determined by GPC relative to polystyrene standards.

^c Not determined.

diisopropylphenyl group on the same polymerization condition (run 3 vs. run 11, run 5 vs. run 9, and run 6 vs. run 12). In contrast, the molecular weight of the obtained PMA obtained by **1**/MAO is obviously lower than those of the obtained PMA obtained by **2**/MAO. These results strongly suggest that the ligand plays an important role in polymerization.

The influence of temperature was also investigated. With an increase in the reaction temperature from 25 to 65 °C, the activities increased gradually. Though both complexes showed the highest activity for MA polymerization at 65 °C, copper complex **1** is more sensitive than **2** to the influence of reaction temperature on the activity. Besides, raising temperature also causes an increase in molecular weight of PMA. Similar result was reported for Cu(DMOX)Cl₂/MAO system by Sen and coworkers.²⁵

The activities are also sensitive to Al/Cu mole ratio. When Al/Cu ratio was 50, only trace of polymer was obtained for **1** and **2** systems. With an increase in Al/Ni ratio, the activities for MA polymerization increased, and then decreased markedly. An optimum Al/Ni ratio was 100 for **1** and 200 for **2**. Note that Al/Cu ratio should be among very narrow range (100–200) to achieve the high activity, which strongly

suggests that MAO has a very important influence on active center.

¹H NMR and ¹³C NMR spectra confirmed the obtained PMAs are atactic. The tacticity of the PMA can be calculated from ¹H NMR integration of methylene resonances.^{36,37} Calculation results in Table 2 indicate the obtained polymers are *syndio*-rich atactic PMA. Similar result was observed by Sen²⁵ and coworkers for well documented radical polymerization systems.^{38,39}

All of the obtained PMAs present about 60% of syndiotactic triads (rr), and the number average lengths of syndiotactic sequences ($L(r)$) is 2–3 times of the number average lengths of isotactic sequences ($L(m)$) (see Table 2). The microstructure is affected by polymerization temperature but hardly affected by steric hindrance of copper complexes. The syndiotactic triad of the produced polymers decreases when temperature increases. On the basis of first-order Markov model, it is noted that the persistence ratios (ρ) are near to B^{-1} (inverse of Bernoullian parameter). This result suggests that the control of monomer insertion is due to the stereochemistry of growing chain ends.⁴⁰

Both copper complexes were also investigated as the precursors for 1-hexene homopolymerization. It was found that

TABLE 2 Methylene Tacticity of PMAs with **1,2**/MAO

Run	Systems	Diads		Triads			B^{-1}	$L(m)$	$L(r)$	ρ
		m	r	mm	mr	rr				
5	1 /65 °C	0.29	0.71	0.15	0.28	0.57	1.47	2.07	5.07	1.47
7	2 /25 °C	0.22	0.78	0.11	0.21	0.67	1.60	2.05	7.38	1.63
9	2 /65 °C	0.31	0.69	0.15	0.32	0.53	1.34	1.94	4.31	1.34

$$B = \frac{[mr]}{2[mm] + [mr]} + \frac{[mr]}{2[rr] + [mr]}$$

$$\rho = 2[m][r]/[mr]$$

$$L(r) = 1 + 2[rr]/[mr]$$

$$L(m) = 1 + 2[mm]/[mr]$$

TABLE 3 Copolymerizations of MA and Hexene with **1,2**/MAO

Run	Complex	MA/Hexene in Feed (mol/mol)	Yield (g)	Activity ^a	MA ^b Incorporation s(mol%)	M_w^c (10 ⁴ g/mol)	MWD ^c (M_w/M_n)
13	1	20.0/80.0	0.76	3.17	80.4	2.77	1.78
14	1	44.4/55.6	2.39	9.94	87.0	5.87	1.98
15	1	58.2/41.8	3.14	13.1	90.9	6.89	2.18
16	1	80.0/20.0	3.75	15.6	94.3	12.4	2.61
17	2	20.0/80.0	0.24	0.99	83.3	3.58	2.05
18	2	44.4/55.6	1.62	6.76	88.7	6.70	1.98
19	2	58.2/41.8	2.60	10.8	92.0	9.99	2.58
20	2	80.0/20.0	3.47	14.5	95.2	18.4	2.60

General condition: 20 μ mol Cu complex; monomer total addition (MA + hexene): 95.6 mmol; temperature: 45 °C; Al/Cu = 200; reaction time, t = 12 h; solvent: toluene; total volume: 20 mL.

^a In units of kg/(mol Cu h).

^b Determined by integration of ¹H NMR.

^c Determined by GPC relative to polystyrene standards.

complexes **1** and **2** were inactive for 1-hexene homopolymerization in the presence of MAO, and no polyhexene, oligomers, or isomer of hexene (determined by GC-MS) were obtained under the similar polymerization condition with 1-hexene instead of MA monomer.

Copolymerizations of MA and 1-Hexene

Bis(β -ketoamino)copper complexes activated with MAO were found to be able to efficiently copolymerize MA and 1-hexene. Copolymerizations of MA and hexene were carried out with **1** and **2** activated with MAO at moderate reaction condition (T = 45 °C, and Al/Cu = 200) with various comonomer feed contents. All results of copolymerizations are listed in Table 3.

As shown in Table 3, the complex **1** shows higher copolymerization activity than **2**. This suggests that the structure of the copper complexes influences their copolymerization activities. The introduction of bulky steric hindrance decreases the copolymerization activities, but increases the molecular weights of MA-hexene copolymers. This result is identical to that of MA homopolymerization, indicating that homopolymerization active species is same to copolymerization active species.

Copolymerization activities and the molecular weights of the copolymers are also affected by the hexene feed content. An increase in the initial hexene feed content leads to a gradual decrease in the activity with respect to MA homopolymerization. Besides, it is noteworthy that increasing the hexene feed content up to 55.6 mol % decreased copolymerization activity, but obviously increased molecular weight of copolymers with respect to MA homopolymerization. This result indicates that 1-hexene plays an important role in the chain termination reaction, and hexene can prohibit effectively chain transfer or termination reaction. Sen and coworkers also reported similar MA-ethylene or propylene copolymerization results.²⁵ Higher hexene feed content leads to decrease in molecular weight of copolymer when compared with PMA, which can be reasonably explained from the kinetic aspect.⁴¹

As the hexene feed content increases, both the activity and the molecular weight of the product decreases. Although increasing the hexene feed contents raises the hexene incorporation into the copolymer, the hexene content incorporated into the copolymer is always lower than the hexene content in the monomer feed. The molecular weight distributions (MWDs) are close to 2 and appear as a unimodal in the GPC chromatogram (see Fig. 2) suggesting that copolymerizations occur at the single active site and that the polymerization products are the true copolymers and not mixtures of the homopolymers.

To determine the monomer reactivity ratios, a series of experiments were performed with **2**/MAO system and stopped at the short time to achieve the low conversions (<10%). The copolymer compositions were determined by ¹H NMR integration of the methoxy protons versus methyl protons. The reactivity ratios $r(\text{MA}) = 8.47$ and $r(\text{hexene}) = 0.14$ determined by a Fineman-Ross method illustrates the much higher reactivity of MA. These are in good agreement with those reported in the literature for radical copolymerization of the two monomers.⁴² Besides, $r(\text{hexene})$ is near to 0, indicating that there is no hexene self-propagation.

The structure of MA-hexene copolymers was also analyzed by NMR spectroscopy. Comparing ¹H NMR spectrum (Fig. 3) of MA-hexene copolymer with those of MA homopolymer, the methoxyl peak at 3.67 ppm, the MA methine proton at 2.34 ppm, and the methyl of hexene peak at 0.90 are easily distinguished suggesting hexene is effectively incorporated.

The ¹³C NMR spectrum is much more definitive, as shown in Figure 4. The peak at 175.0 ppm, which is the same as in homopolymer of MA, is assigned to the carbonyl carbon in long consecutive MA runs. The peaks for the methoxyl carbon (51.8 ppm), methylene carbon (41.3 ppm), and methine carbon (35.0 ppm) in MA unit are assigned on the basis of the ¹³C NMR spectrum of PMA. In addition, two peaks (14.1, and 23.0 ppm) can be assigned to the methyl carbon and methylene carbon in the side chain of hexene (butyl group of hexene). On the other hand, the presence of MA-hexene dyads is signaled by the resonances at 37.8 ppm. At same

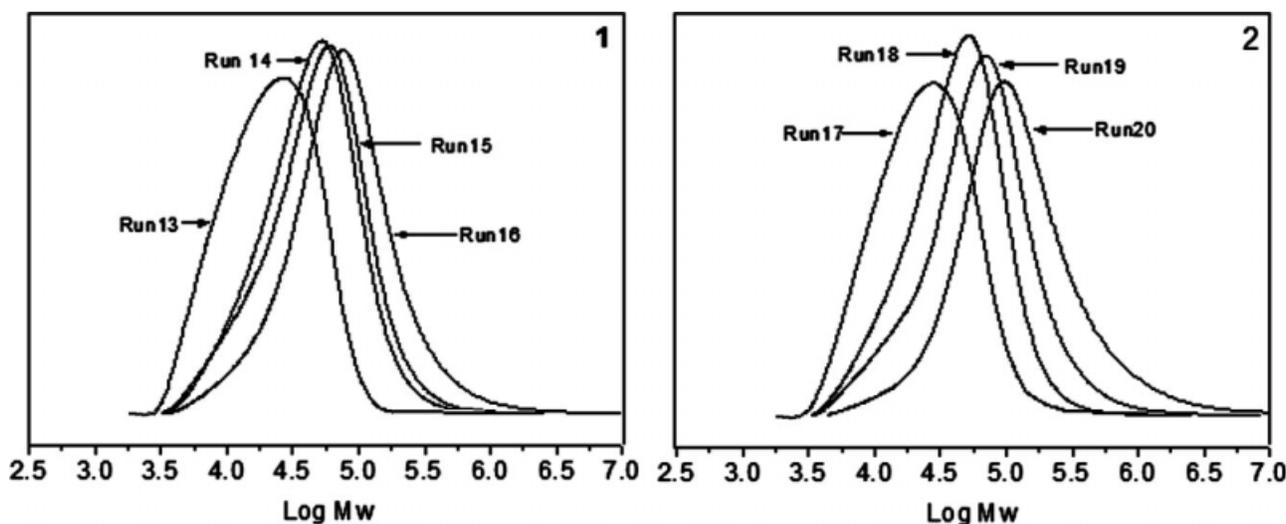


FIGURE 2 GPC curves of MA-hexene copolymers using 1, 2/MAO.

time, the resonance from hexene-hexene dyads at 43.0 ppm is not observed, indicating that hexene is randomly distributed in the copolymer chains. This result is in good agreement with reactivity ratios result ($r(\text{hexene}) \approx 0$). Therefore, it is concluded that the polymer produced in copolymerization of MA, and hexene is a copolymer with long MA sequences and isolated hexenes in the backbone.

Mechanistic Consideration

Two possible mechanisms for the copper-mediated homo- and copolymerization of acrylates with alkenes are radical and insertion. Some authors have already studied polymerization mechanism for acrylates and alkenes with copper(II)/MAO system. Stibrany et al. postulated a coordination/insertion mechanism for bis(benzimidazole)copper/MAO systems.²² Shibayama thought that the active species for MMA polymerization with Cu(II) amidinate/MAO system is a Cu(I) complex.⁴³ Carlini et al. also suggested that homo- and copolymerization MMA with ethylene proceeded through a Cu(I)-mediated polymerization mechanism, but the author did not completely exclude that radical species may also participate in the polymerization.¹⁰ Sen and coworkers pointed out that the use of radical traps, such as galinoxyl, DPPH, and TEMPO as probes for a radical mechanism in the copper complex, such as Cu(DMOX)Cl₂ using MAO can lead to the wrong conclusion.²⁵ The radical traps may fail to intercept radical reactions that proceed in the presence of MAO. Foley and coworkers recently presented that salicylaldimine or α -diimine copper species cannot be an active catalyst for ethylene polymerization because of ligand transfer to aluminum.²⁶

Our observations consistent with a radical mechanism are as follows. The tacticity of mm, mr, and rr stereotriads of the obtained atactic PMA is very similar to those of PMA with a free radical initiator, such as AIBN. Besides, control experiments involving the polymerization of MA in the presence of

1-hexene using bis(β -ketoamino)copper/MAO systems reveal the incorporation of 1-hexene in copolymer at levels comparable to those observed with radical initiator system.⁴² The calculated reactivity ratios, $r(\text{MA}) = 8.47$ and $r(\text{hexene}) = 0.14$, also support a radical mechanism.⁴⁴ 1-Hexene cannot be polymerized or oligomerized with bis(β -ketoamino)copper/MAO system, and the hexene units are isolated in the backbone of the copolymer, which are in sharp contrast with typical insertion/coordination polymerization.

To probe the polymerization mechanism of this system, several experiments were designed and carried out. First, when only MAO was introduced into solution of MA in toluene without copper complex, no polymer was obtained. This result suggests that MAO alone cannot initiate the polymerization of MA under the adopted reaction conditions. Second, mixing MAO or trimethylaluminum (TMA) with β -ketoamino ligand in solution of MA in toluene also results in no polymer suggesting that chains grow on aluminum center for MA

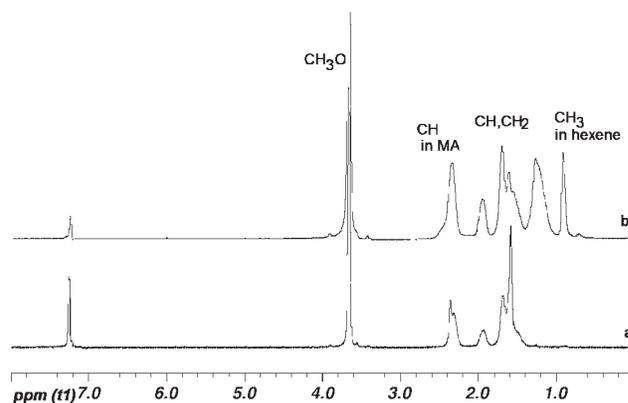


FIGURE 3 ¹H NMR spectra of PMA and MA-hexene copolymer. a: PMA (run 8); b: Copolymer (run 17).

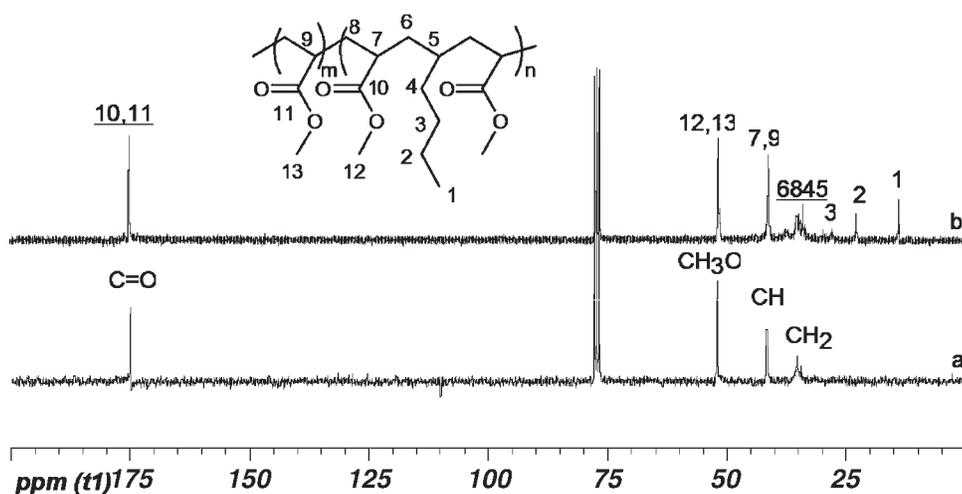


FIGURE 4 ^{13}C NMR spectra of PMA and MA-hexene copolymer. a: PMA (run 8); b: Copolymer (run 17).

polymerization can be ruled out.²⁶ In addition, bis(β -ketoamino)copper complex cannot polymerize MA without MAO. Therefore, it is concluded that bis(β -ketoamino)copper(II) complex and MAO cooperate in MA polymerization process.

In addition, it was found that β -ketoamino ligands and CuBr can *in situ* polymerize MA in the presence of MAO with similar activity (conditions: 20 μmol CuBr, 20 μmol L2, 200 equiv MAO, 5 mL MA, 5 h, toluene, 20 mL). This result clearly indicates that Cu(I) is true active species. Therefore, it is deduced that MAO as a reducing agent reduces copper(II) to copper(I). Besides, our experimental results of influence of Al/Ni ratio and previous reports also show that MAO can stabilize active species (e.g., MAO can remove radical traps),²⁵ and may promote polymerization rate and increase activity as Lewis acid.⁴²

A possible insertion-triggered mechanism that reconciles our observations was proposed. Mixing MAO and copper(II) complex leads to a copper(I) complex by the reduction of the precursor, which is consistent with our and other group's result determined by EPR.^{10,22} The next step involves the interaction of MA and copper(I) complex, thereby producing a copper(I)-carbon bond. Then the homolysis of this copper(I)-carbon bond happens, thus, producing radical initiator. The bond homolysis step is reversible and the concentration of radical is low at any given time. This explains our inability to detect the radical by EPR. Similar pathway for radical generation has been observed in cobalt-mediated radical polymerization⁴⁵ and palladium-mediated radical polymerization.^{11,39,46-49} The actual polymerization occurs by successive addition of acrylate monomer to the alkyl radical. Chain termination majorly occurs by recombination with copper metal radical and growing radical chain, and then undergoing β -H elimination. Radical disproportionation and bimolecular coupling terminations may also be termination pathways. However, the stability of acrylate radicals and control of diffusion of macromolecule radical make these two pathways less favorable than other radical species.^{47,50}

For copolymerization of MA and 1-hexene, 1-hexene is isolated in backbone because $r(\text{hexene})$ is near to zero. When 1-hexene monomer is added into the growing chain, macromolecule radical with the new added 1-hexene is disfavored for chain termination and chain propagation. Therefore, it is found that an increase in the hexene feed content decreased the activity, but obviously increased molecular weight of copolymers with respect to MA homopolymerization. Besides, bulky steric hindrance of the ligand leads to a great barrier of the interaction between MA and Cu(I) complex, thus decreases the concentration of the initial radical initiator. And bulky steric hindrance of the ligand can also stabilize copper metal radical, and prohibit chain termination between copper metal radical and macromolecules radical. These can explain why the ligand plays a very important role on the activity and molecular weight of the obtained polymers. For copper(II)/MAO system, a reasonable explain for no activity toward other traditional radical monomers, such as styrene, is that there is no interaction between monomer and copper(I) complex or homolysis cannot happen, thus no radical species can produce in the system.

Radical mechanism of the palladium-based system for acrylate monomer polymerization has been proved.⁴⁶⁻⁴⁹ Albeniz and coworkers monitored the insertion of MA into the Pd-C₆F₅ bond and homolytic cleavage of the new Pd-C bond with NMR. Authors presented that homopolymerization of MA and copolymerization of MA and 1-hexene proceed by the insertion-triggered radical polymerization.^{48,49} Microstructures of PMA and MA-hexene copolymer produced by palladium-based system^{11,39,46-49} are very similar to those produced by bis(β -ketoamino)copper(II)/MAO system. Therefore, it is believable that homopolymerization and copolymerization of MA with 1-hexene proceed through insertion-triggered radical mechanism. According to our proposed mechanism, all of observations can be reasonably explained, although a direct evidence for metal-carbon bond homolysis is lack and hard to be determined.

EXPERIMENTAL

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen with standard vacuum-line, Schlenk, or glovebox techniques.

Materials

Toluene was dried over sodium metal and distilled under nitrogen. 1-Hexene (Acros) was purified by distillation over potassium. MA (Guangzhou Chemical) was dried over CaH₂ and then freshly distilled in vacuum before use. MAO was prepared by partial hydrolysis of TMA in toluene at 0–60 °C with Al₂(SO₄)₃·18H₂O as water source. The initial [H₂O]/[TMA] molar ratio was 1.3. Other commercially available reagents were purchased and used without purification.

Polymerization

In a typical procedure, the appropriate MAO solid was introduced into the round-bottom glass flask, and then the solution of monomer in toluene (1-hexene and/or MA) was added via a syringe. Toluene and the solution of copper complex were syringed into the well-stirred solution in order, and the total reaction volume was kept at 20 mL. The polymerization reaction was continuously stirred for an appropriate period at the polymerization temperature, which was controlled with an external oil bath. The polymerization was terminated by the addition of 200 mL of acidic ethanol (95:5 ethanol/HCl). The resulting precipitated polymers were collected and treated by filtration, washing with ethanol several times, and drying in vacuum at 40 °C to a constant weight.

Characterization

Elemental analyses were performed on a Vario EL microanalyzer. Mass spectra were measured on a VG ZAB-HS instrument using fast atom bombardment (FAB). ¹H NMR and ¹³C NMR spectra were carried out on a Varian Mercury-Plus 500 MHz instrument at room temperature in chloroform-*d* solutions. GPC analyses of the molecular weight and MWD of the polymers were performed on a Waters 150C instrument with standard polystyrene as the reference and with THF as the eluent at 40 °C. FTIR spectra were recorded on a Nicolet Nexus 670 FTIR spectrometer. Analysis of hexene homopolymerization product was performed by GC-MS on a Finnigan Voyager GC-8000 TOP gas chromatograph-mass spectrometer with DB-5MS GC column.

Crystal Structure Determination

Crystal data obtained with the ω -2 θ scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71, 073 \text{ \AA}$) at 293 K. The structure was solved using direct methods, whereas further refinements with full-matrix least squares on F^2 were obtained with the SHELXTL program package. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms.

Synthesis of Ligands

Acetylacetone (15.0 mL, 0.146 mol), 2,6-dimethylaniline (18.0 mL, 0.146 mol) or 2,6-diisopropylaniline (27.5 mL,

0.146 mol), and catalytic amount of *p*-toluenesulfonic acid in toluene (150 mL) were combined and heated to reflux 5 h, whereas water was removed as a toluene azeotrope under 130 °C using a water separator. The ligands **L1** and **L2** were collected by vacuum distillation and recrystallization from hexane.

L1, yield: 76%. Anal. Calc. For C₁₃H₁₇NO: C, 76.81; H, 8.43; N, 6.89. Found: C, 76.54; H, 8.42; N, 6.93. FAB-MS (m/z): 204, 188, 160, 146, 105. ¹H NMR (CDCl₃, 500 MHz), δ (ppm): 11.9 (1H, —NH), 7.07–7.13(3H, —C₆H₃), 5.21(1H, CH=), 2.20(3H, —CH₃), 2.11 (3H, —CH₃), 1.63 (6H, —(CH₃)₂). ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 195.9, 162.8, 136.5, 136.1, 128.1, 127.4, 96.1, 29.0, 18.8, 18.2.

L2, yield: 65%. Anal. Calc. For C₁₇H₂₅NO: C, 78.72; H, 9.71; N, 5.40. Found: C, 79.01; H, 9.60; N, 5.26. FAB-MS (m/z): 260, 244, 202. ¹H NMR (CDCl₃, 500 MHz), δ (ppm): 12.06(1H, —NH), 7.16–7.31(3H, —C₆H₃), 5.21(1H, CH=), 3.00–3.06(2H, —CH(CH₃)₂), 2.13(3H, CH₃C(O)—), 1.64(3H, —CH₃), 1.22(6H, CH(CH₃)₂), 1.16(6H, CH(CH₃)₂). ¹³C NMR (CDCl₃, 125 MHz), δ (ppm): 195.8, 163.3, 146.2, 133.5, 128.2, 123.5, 95.5, 29.0, 28.4, 24.5, 22.6, 19.1.

Synthesis of Copper Complexes

Ligand **L1** (2.424 g, 11.92 mmol) was allowed to react with Cu(OAc)₂·H₂O (0.905 g, 4.55 mmol) in 150 mL methanol at the refluxing temperature for 2 h. After cooling, the solid was collected by removing solvent in vacuum and recrystallized from the toluene/methanol solution to give copper complex **1** as black crystals in 85% yield. The copper complex **2** as brown crystals was prepared by the same procedure in 89% yield.

Complex **1**: Anal. Calc. For C₂₆H₃₂N₂O₂Cu: C, 66.71; H, 6.89; N, 5.98. Found: C, 66.58; H, 7.15; N, 5.86. FTIR (KBr, cm⁻¹): 3418(w), 2911(w), 1575(s), 1514(s), 1404(s), 1279(w), 1186(w), 1020(w), 847(w), 762(m).

Complex **2**: Anal. Calc. For C₃₄H₄₈N₂O₂Cu: C, 70.37; H, 8.34; N, 4.83. Found: C, 70.01; H, 8.37; N, 4.82. FTIR (KBr, cm⁻¹): 3433(m), 2960(s), 2869(w), 1582(s), 1515(s), 1445(s), 1414(s), 1322(w), 1271(w), 1181(w), 1016(w), 940(w), 800(w), 765(m).

CONCLUSIONS

We have discovered new bis(β -ketoamino)copper(II)/MAO systems for the homopolymerization of MA and their copolymerization with 1-hexene. Copper complexes activated with MAO can polymerize MA to produce the *syndio*-rich atactic PMA, but cannot polymerize 1-hexene. With an increase in the polymerization temperature, the activity and molecular weight of the produced PMAs increased. The bulky steric hindrance of the copper complex leads to low activity and high molecular weight of the produced PMA. Copolymerizations of MA with 1-hexene with **1,2**/MAO produce acrylate-enriched copolymers (MA > 80%) with isolated hexenes in the backbone. As the hexene feed content increases, both the activity and the copolymer molecular weight decreases, but the incorporation of hexene in the copolymer increases. The

reactivity ratios $r(\text{MA})$ is 8.47, and $r(\text{hexene})$ is close to 0. An insertion-triggered radical mechanism has been proposed, and radical initiator is produced by homolysis of Cu(I)—carbon bond.

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