Two bis-[1-(aryliminomethyleny)-2-oxy-naphthalen] nickel catalysts for the polymerization of methyl methacrylate

Yang-Jian Hu [a,b], Hua Hong Zou [a], Ming-Hua Zeng [a,*], Ng Seik Weng [c]

[a] Key Laboratory of Medicinal Chemical Resources and Molecular Engineering, Department of Chemistry and Chemical Engineering, Guangxi Normal University, 15 Yucai Rd., Guilin 541004, PR China
[b] Department of Chemistry, Huaihua College, Huaihua 418000, PR China
[c] Department of Chemistry, University of Malaya, 0603 Kuala Lumpur, Malaysia

ABSTRACT

Two bis-(1-aryliminomethylenyl-2-oxy-naphthalen) nickel complexes (aryl = 2-methylphenyl, complex **1**; aryl = 2,6-diisoproylphenyl, complex **2**) were reacted with alkylaluminium in presence of equimolar PPh$_3$ and tested as catalysts in methyl methacrylate (MMA) polymerization. The two nickel catalysts can initiate polymerization of MMA with good to high activity, the highest activity reaching 1.1×10^5 g PMMA/(mol Ni · h) by less bulky complex **1** at 0.8 mol/L of MMA, 400 of Al/Ni ratio and 0 °C. In addition, the structures of nickel complexes and polymerization conditions, such as monomer concentration, polymerization temperature and Al/Ni molar ratio on catalytic activity of polymerization have great influences on catalytic activity and product properties.

1. Introduction

Studies have been directed on the synthesis of the transition metal complexes of multifunctional ligands for catalysis [1]; in particular, the nickel complexes that are linked to ligands through N, O or N, N atoms [2,3] possess exceptional catalytic activity for the polymerization of MMA (methyl methacrylate), such as, Ni(II) [4,5], and Pd(II) complexes containing N,O-chelate atoms [6–10] served as catalysts for copolymerization. Some of the features are necessary for the manifestation of such behavior include, for example, high electrophilicity, a positive charge on the metal center itself, and sterically-bulky N,O- and/or N,N-chelating ligands. A number of reports have documented the last-mentioned feature [11]. Ni(acac)$_2$/MAO (acac = diacetate; MAO = methylaluminoxane) is a common system for the polymerization of MMA [12]. However, the nickel compounds that are particularly useful are the β-ketoamino type, and mixed-ligands compounds are excellent catalysts for the production of highly syndiotactic PMMA [13].

Recently Carlini used bis(salicylideneiminato)nickel(II) complex as catalyst precursor activated by MAO for polymerizing MMA to a prevailing syndiotactic polymer, exhibiting high catalytic activity, and are able also to give copolymers of MMA with ethylene. These systems were obtained by oxidative addition of salicylaldimine li-

gands to [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) and subsequent activation with MAO [14,15]. The systems of some naphtocyimine-nickel complexes/MAO were reported that can catalyze norbornene to polymerization with high catalytic activity [16,17], but there are little reports that these catalyst systems are utilized for polymerization of MMA. Other systems are known [18] but generally, activation by MAO is necessary. Unfortunately, MAO is an expensive chemical and is not easy to prepare. We have engaged in investigations on an alkylaluminium in place of MAO as activator [19], this is the main difference from aforementioned catalyst systems. Moreover, our catalyst system can give low molecular weight PMMA, which favor the serialization and differentiation of product. To assist in an understanding of the polymerization of MMA by the late transition metal catalysts, we have chosen to study the nickel system instead and have examined catalytic behavior from the angle of the bulkiness of substituents in the ortho aryl position (Scheme 1) and the influence of reaction conditions on catalytic activity and properties of polymers obtained by these nickel complexes.

The present study reports two bis(1-aryliminomethylenyl-naphthalen-2-oxy)nickel complexes and their abilities to catalyze MMA. All nickel complexes were characterized by their IR, NMR spectra and elemental analyses. In addition, X-ray structure analyses were performed for complex **2**. After being activated with alkylaluminium, these nickel(II) complexes can be used as catalysts for the polymerization of methyl methacrylate (MMA) to produce

* Corresponding author. Fax: +86 773 5812 383.
E-mail address: zmh@mailbox.gxnu.edu.cn (M.-H. Zeng).
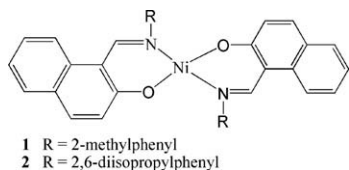
Scheme 1. The nickel complexes with different substituents in the ortho aryl position.

1 R = 2-methylphenyl
2 R = 2,6-diisopropylphenyl

syndiotactic-rich PMMA. Catalytic activities and the degree of syndiotacticity of PMMA have been investigated for various reaction conditions.

2. Experiment

The synthesis was performed under nitrogen in Schlenk-type vessels, and water- and oxygen-free reagents and solvents were used throughout. ^{1}H NMR spectra were recorded on a Bruker-300 spectrometer. The ^{13}C NMR spectra of PMMA were obtained in CDCl$_3$ on Varian INOVA-500 NMR spectrometer. Gel permeation chromatography (GPC) analyses of the molecular weight and molecular weight distribution of the polymers were performed on a Waters 150C instrument, and standard polystyrene was the reference and with chloroform as the eluent. Diethylaluminum chloride (AlEt$_2$Cl), triethyl aluminum (AlEt$_3$) and triisobutyl aluminum (Al(i-Bu)$_3$) were taken as 350 g/L solutions in n-heptane, respectively. The other chemicals were commercially procedure.

2.1. Preparation of nickel complexes

The two nickel complexes were synthesized by using a modification of a reported procedure [20].

2.1.1. Bis[(N-2-methyl-phenylimino)-2-oxy-1-naphthylmethylene]nickel(II)

Nickel acetate tetrahydrate (2.48 g, 10 mmol) and 2-hydroxy-1-naphthaldehyde (1.74 g, 10 mmol) were heated in ethanol (100 mL) along with 2-methylaniline (3.21 g, 30 mmol) for 2 h. The solvent was removed to give a dark green solid; the compound **1** was purified by crystallization from n-heptane. CHN Anal. Calc. for C$_{36}$H$_{28}$N$_2$NiO$_2$: N, 4.83; C, 74.63; H, 4.87. Found: N, 4.67; C, 74.44; H, 5.06%. ^{1}H NMR (CDCl$_3$, 300 MHz): 1.20–1.26 (m, 6H), 5.58 (d, 2H), 6.78–7.65 (m, 18H), 7.95 (d, 2H) ppm. IR (KBr): 1625 cm^{-1}($\nu_{C=N}$).

2.1.2. Bis[(N-2,6-diisopropylphenylimino)-2-oxy-1-naphthylmethylene]nickel(II)

Compound **2** was similarly prepared and was also obtained as green crystals. CHN Elemental Anal. Calc. for C$_{46}$H$_{48}$N$_2$NiO$_2$: N, 3.90; C, 76.99; H, 6.46. Found: N, 3.69; C, 76.72; H, 6.62%. ^{1}H NMR (CDCl$_3$, 300 MHz): 1.23 (d, 24H), 4.27–4.34 (m, 4H), 5.69 (d, 2H), 7.13-7.67 (m, 16H), 8.15 (s, 2H) ppm. IR (KBr): 1628 cm^{-1}($\nu_{C=N}$).

2.2. General procedure for polymerization of MMA

Polymerizations were carried out in a 250 mL Schlenk flask fitted with a magnetic stir. The flask was filled with 50 mL of n-heptane; AlEt$_2$Cl dissolved in n-heptane was injected into the reaction solution. The solution of catalyst and an equimolar quantity of PPh$_3$ were then added and the reactor was heated to the polymerization temperature, after which the monomer was added. After 4 h, the polymerization was quenched by addition of ethanol. The reaction solution was poured into an excess of 10% HCl–EtOH to afford

Table 1
Structure parameters of the complex **2**.

Empirical formula	C$_{46}$H$_{48}$N$_2$O$_2$Ni
Formula weight	719.55
Crystal system	Triclinic
Space group	$P\bar{1}$ (No. 2)
a (Å)	9.397(3)
b (Å)	9.721(3)
c (Å)	11.454(4)
α (°)	80.710(5)
β (°)	72.356(5)
γ (°)	82.996(5)
V (Å^3)	981.0(6)
Z	1
Temperature (K)	293
$F(000)$	382
$D_{calcd.}$ (g cm^{-3})	1.218
Goodness-of-fit (GOF) on F^2	1.05
Theta range (°)	1.9, 26.0
F_{max}/F_{min} (e Å^{-3})	0.28, −0.18,
μ (mm^{-1})	0.533
Total reflections	7765
Unique reflections	3813
Observed data [$I > 2.0\sigma(I)$]	3463
[$R_{(int)}$]	0.016
R_1 [$I \geqslant 2\sigma(I)$]	0.0368
wR_2 (all data)	0.0971

PMMA as a precipitate. The polymer was filtered and washed with water–ethanol several times, and dried in vacuum at 50 °C for 12 h.

2.3. X-ray crystallography measurement

Suitable crystals of complex **2** for X-ray diffraction were obtained by slow evaporation of the compound from n-heptane. The X-ray diffraction measurements were carried out at on a Bruker SMART 1000 CCD diffractometer fitted with graphite monochromatic Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods, and refined by full-matrix least-squares on F^2. Hydrogen atoms were placed in calculated positions, and were refined using a riding model. All nonhydrogen atoms were refined anisotropically. Relevant crystal data are summarized in Table 1.

3. Results and discussion

3.1. Characterization of complexes

The ready solubility of the two compounds implicates a monomeric nature for both. Element analysis revealed that the polycrystalline compound **1** is structurally similar to compound **2**, only the latter is suitable for single-crystal X-ray diffraction analysis, so that the structure of **2** is described here. For the complex **2**, the crystal
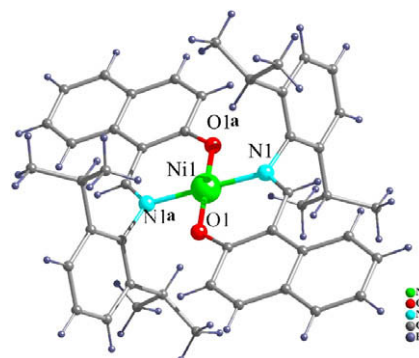

Fig. 1. The coordination environment of Ni^{II} in compound **2**.

Table 2
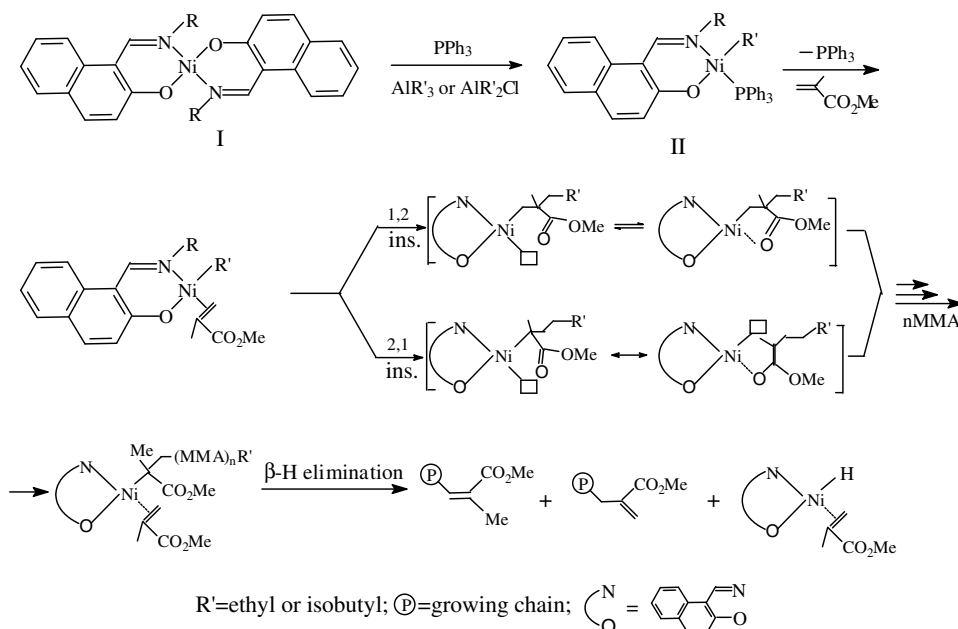Selected bond distances (Å) and bond angle (°) for complex **2**.

Bond distances			
Ni(1)–O(1)	1.814(1)	C(2)–C(7)	1.407(3)
Ni(1)–N(1)	1.892(1)	C(3)–C(4)	1.370(4)
O(1)–C(10)	1.296(3)	C(4)–C(5)	1.371(3)
N(1)–C(11)	1.301(2)	C(5)–C(6)	1.344(4)
N(1)–C(12)	1.450(2)	C(6)–C(7)	1.407(3)
C(1)–C(2)	1.452(3)	C(7)–C(8)	1.417(3)
C(1)–C(10)	1.392(3)	C(8)–C(9)	1.343(4)
C(1)–C(11)	1.417(2)	C(9)–C(10)	1.431(3)
C(2)–C(3)	1.395(3)	C(12)–C(13)	1.391(3)
Bond angles			
O(1)–Ni(1)–N(1)	92.40(6)	Ni(1)–O(1)–C(10)	131.1(1)
O(1)–Ni(1)–O(1a)	180.00	Ni(1)–N(1)–C(11)	125.3(1)
O(1)–Ni(1)–N(1a)	87.60(6)	Ni(1)–N(1)–C(12)	119.2(1)
O(1a)–Ni(1)–N(1)	87.60(6)	C(11)–N(1)–C(12)	115.4(1)
N(1)–Ni(1)–N(1a)	180.00	O(1)–C(10)–C(1)	124.3(2)
O(1a)–Ni(1)–N(1a)	92.40(6)	O(1)–C(10)–C(9)	116.1(2)

Table 3
Polymerization of MMA by the catalytic system of complexes **1** and **2**.

Run	Cat.	Al/Ni	T (°C)	Cocat.	Yield[a]/%	Activity[b]	M_n	M_w	M_n/M_w[c]
1	1	400	30	AlEt₂Cl	69	8.3	1572	1967	1.25
2	1	400	30	AlEt₃	71	8.2	1783	2349	1.31
3	1	400	30	Al(i-Bu)₃	62	6.6	1812	2669	1.47
4	1	200	30	AlEt₃	41	3.8	1876	2685	1.43
5	1	600	30	AlEt₃	70	8.1	1774	2461	1.38
6	1	800	30	AlEt₃	72	7.8	1712	2338	1.36
7	2	400	30	AlEt₂Cl	67	7.6	2349	3508	1.49
8	2	400	30	AlEt₃	68	6.9	3491	5419	1.55
9	2	400	30	Al(i-Bu)₃	61	6.2	3556	6255	1.75
10	1	400	0	AlEt₃	72	11.0	2937	5036	1.71
11	1	400	50	AlEt₃	62	4.8	1653	2037	1.23
12	1	400	70	AlEt₃	61	4.2	1511	1897	1.25

Conditions: [MMA] = 0.8 mol/L; [Ni] = 0.0003–0.0004 mol/L, time = 4 h; solvent: *n*-heptane.
[a] Yield is defined as the mass of dry polymer recovered/mass of monomer used.
[b] 10^4 g PMMA/mol Ni · h.
[c] Determined by means of GPC.

structure shows the nickel atom at a center-of-inversion in a *trans*-N₂O₂Ni square-planar geometry (Fig. 1 and Table 2). On the basis of the crystal structure, the complex **2** is also assigned a square-planar geometry at Ni(II) ion. The chelate ring with Ni(II) ion is planar, and is co-planar with the naphthalene fused-ring. The reason for the four-coordinate geometry is evident from the 2,4,6-trimethylphenyl substituents as they block any attempt by other Lewis-basic sites to interact with Ni. Such a geometry has also been noted in, for example, the bis-[*N*-(substituted methyl)-salicylideneiminato] nickel [21]. The Ni–O and Ni–N bond lengths are 1.814(2), 1.892(2) Å, respectively, which are essentially the same as in the complexes of tetrahedral Ni^{II}, showing that coordination of the N, O chelating function. The adjacent molecules are stacked with respect to each other only by van der Waals interactions. It is mainly raised by the sterically hindered ligands which impose the geometry on the isolate molecules.

3.2. Polymerization of MMA

3.2.1. Catalyst

The two complexes function as excellent as initiators in presence of alkylaluminium for the polymerization of MMA to PMMA; they are highly active and syndiotactic for the reaction in heptane (Table 3). In fact, their activities exceed that of nickel α-diimine catalysts (6.9×10^3 g PMMA/mol Ni · h) [3a] and about equal to that of the bis(α-ketoamino)nickel(II)/MAO system [13]. Compared with phenoxyimine/Ni(cod)₂/MAO systems, despite their good catalytic activity (up to 1.5×10^5 g PMMA/mol Ni · h) [15a], Ni(cod)₂ is known to be very expensive and extremely sensitive to air, humidity and protic impurities. The somewhat higher activity of complex **1** (Table 3) can be rationalized in terms of the bulkiness of the substituents. The complex **1** has the less bulky methyl substituent whereas the complex **2** has the more bulky diisopropyl substituent. Accumulated studies [3,20,22] have shown that the Ni center should be able to expand its coordination number, at least in the transition state, something the first compound can do better than the second. However, despite the decreased activity, the average molecular weight of PMMA for the bulkier Ni compound is higher, which suggests that steric bulk protruding into the 'axial' sites above and below the square plane retards the

R'=ethyl or isobutyl; Ⓟ=growing chain;

Scheme 2. Proposed mechanism of MMA polymerization.

termination of progapation chain. Before the onset of polymerization added PPh₃ then serves as promoter for formation of activity centers [20a] that accelerate the polymerization process. To check if the addition of PPh₃ should be requisite, we performed the contrast experiment with complex **1** and **2**/AlEt₃ in the absence of PPh₃ under the same conditions adopted for the polymerization experiments of MMA under dry nitrogen. The results showed that two catalytic systems had very low catalytic activity and only traces of product were found independently. Therefore, this indicates that PPh₃ can serve as ancillary ligand to stabilize the activity centers. This result also confirms that in the presence of an alkylating agent one of the two imine-naphtholato ligands is released, with the formation of an alkylnickel species, which is stabilized by the coordination of the phosphine to give rise to the species II (Scheme 2). In order to confirm the formation of the above species II, we have investigated the interaction of the equimolar complex **2**/PPh₃ mixture with Et₃Al (1:1:50) in heptane solution under nitrogen atmosphere, and then detect if the species II ($C_{43}H_{44}NOPNi$, molecular weight is 679) has formed in the reaction by ESI-MS (LCQ DECA XP, mobile phase is *n*-hexane and THF of 9:1). The result showed that the species II existed in catalyst system (Fig. 2, the peaks at about 679 contain nickel and its isotope complexes). The addition to the catalyst of an equimolar amount of PPh₃ (Table 3) allowed to conclude that the activity remained extremely high (1.1×10^5 g/mol Ni · h) (entry 10), thus indicating that the phosphine, in the presence of an excess of alkylaluminum, does not behave as a poison for the nickel sites, the alkylaluminum Lewis acidity probably weakening the coordinative interaction of the phosphine to the metal.

So the proposed mechanism is as follows.

3.2.2. Cocatalyst

Unlike other reported catalytic nickel complexes with O,N-containing ligands [13,14], the present two nickel complexes require
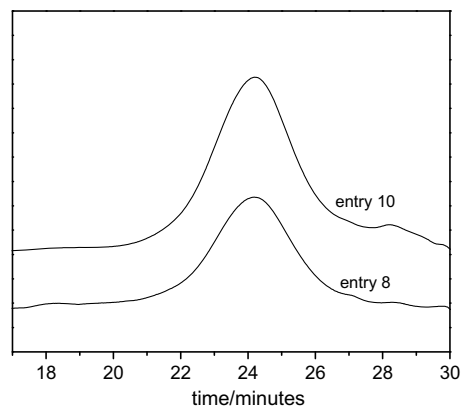

Fig. 3. The GPC elution curves of entry 8 and 10.

merely either AlEt₃ or Al(*i*-Bu)₃ and AlEt₂Cl as cocatalysts for the polymerization of MMA. Polymerization to produce PMMA and the effect of three cocatalysts on MMA polymerization with an Al/Ni ratio 400 and at 30 °C furnishes results (Table 3) that prove that the three alkylaluminiums can initiate the reaction. The catalytic activity of two catalysts with Al(*i*-Bu)₃ is lowest, a possible reason being a trialkylaluminum being bulkier and therefore hinders access of the monomer to the site of activity.

3.2.3. Al/Ni ratio

Catalytic activity increased with the increasing Al/Ni molar ratios, reaching highest at 400 (Table 3). For complex **1**, the activity increases to a maximum of 8.3×10^4 g PMMA/mol Ni · h at a ratio at an Al/Ni 400, possibly arising from that the effect this ratio has on the active site. Most likely, too little aluminum reagent cannot completely balance the polarity of the nickel complex, which is necessary for the formation of the active nickel species. Any further
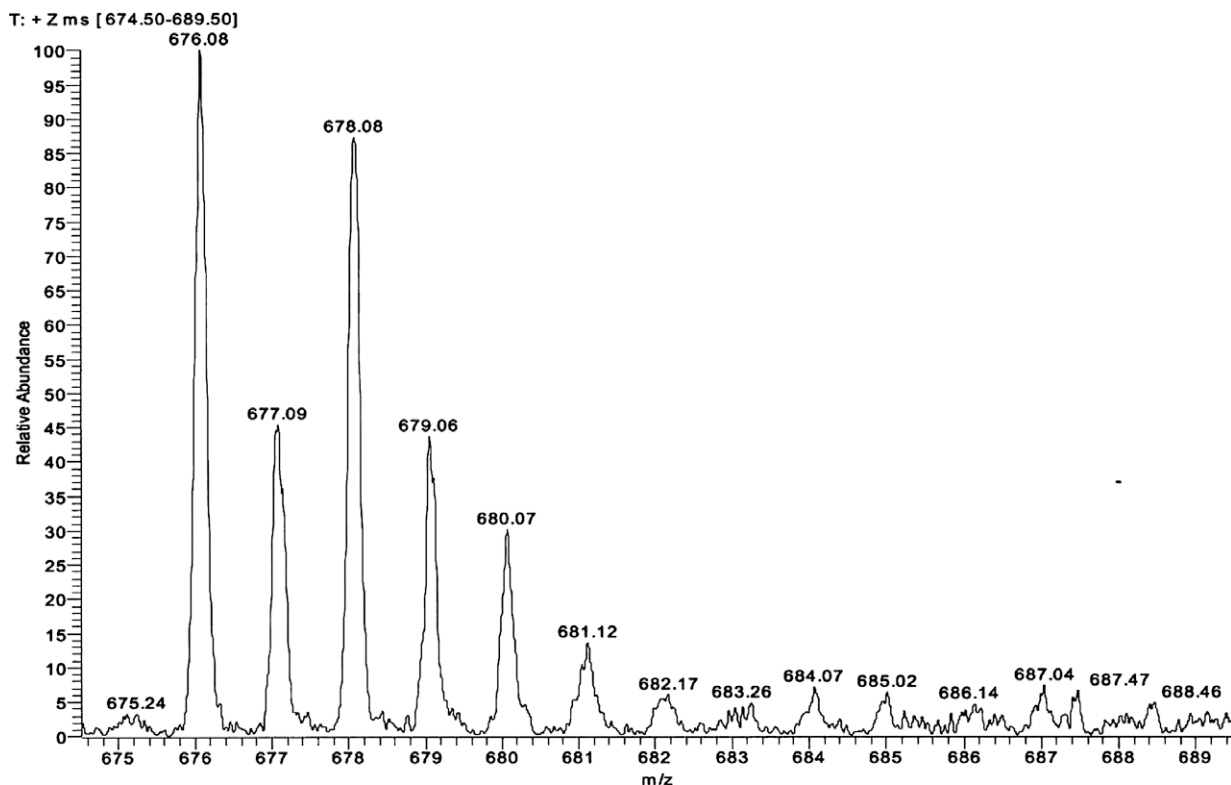

Fig. 2. ESI mass spectrum of products of reaction.

increase in the quantity of the aluminum reagent will hasten chain transfer on alkylaluminium, thereby decreasing the catalytic activity.

3.2.4. Polymerization temperature (T_p)

The highest activity for complex **1** was observed at 0 °C, at nearly 1.10×10^5 g PMMA/mol Ni · h (Table 3). Catalytic activity decreased with an increase of the temperate of polymerization. At around 70 °C, the yield of PMMA is low, being only 4.2×10^4 g PMMA/molNi·h. Obviously, with increasing temperature, the rate of polymerizatiom quickly decreases. These results suggests that higher polymerization temperature may influence the number of active sites formed *in situ* for the polymerization or that the alkylaluminium strongly interacts with the active site.
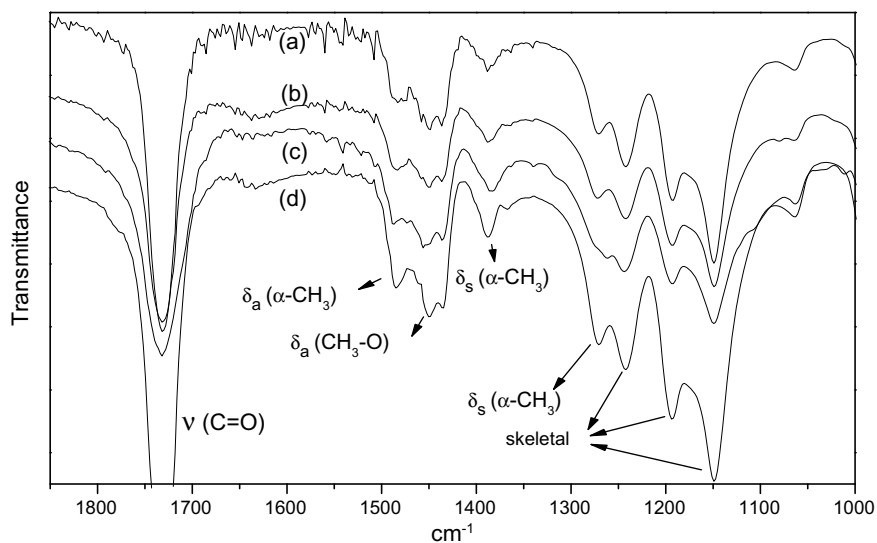

Fig. 4. IR spectra of PMMA produced by 1/AlEt$_3$ catalyst at T_p (a) 0 °C, (b) 30 °C, (c) 50 °C, (d) 70 °C. Polymerization conditions are given in Table 1.
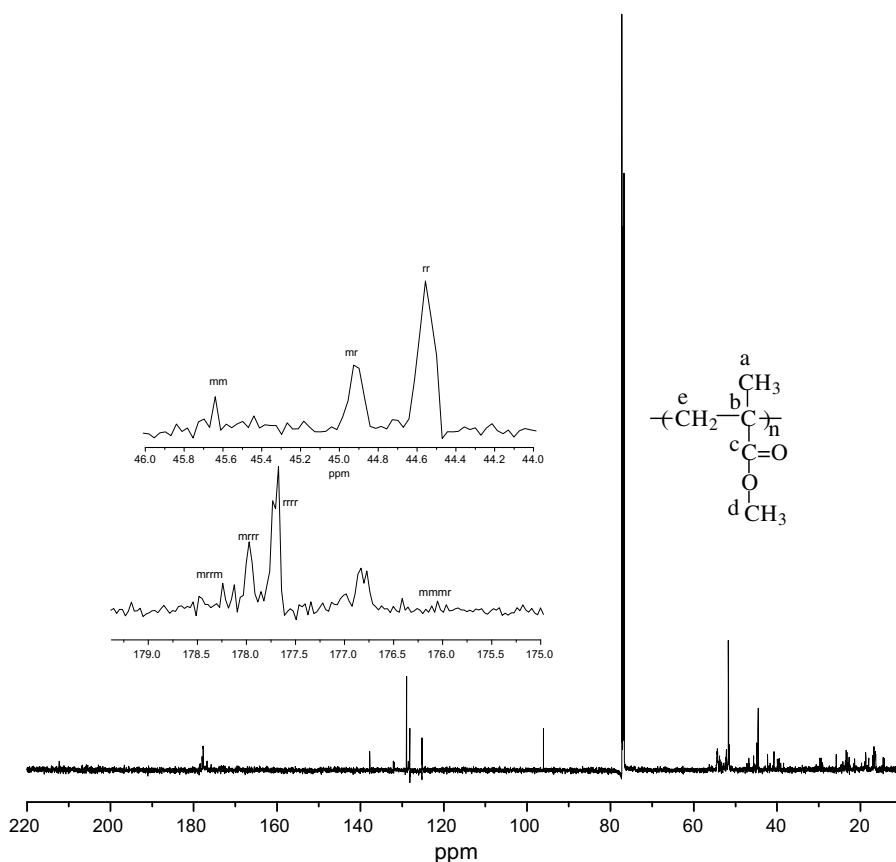

Fig. 5. ^{13}C NMR spectrum of entree 8.

Table 4
Triad and pendant fractions of PMMA obtained with complexes **1** and **2**.

Entry[a]	Triad fractions(%)[b]			Penendant fractions(%)[c]					
	mm	*mr*	*rr*	*rmmr*	*rmrr + mmrr*	*mmrm + rmrm*	*rrrr*	*rrrm*	*mrrm*
2	10.9	23.0	66.1	0.6	20.2	5.8	49.1	20.2	4.1
8	8.7	21.1	70.2	1.2	19.5	5.2	51.3	19.3	3.5
10	8.5	18.2	73.3	1.5	19.2	4.6	52.4	18.5	3.9
11	8.1	28.4	63.5	0.9	20.8	5.4	47.5	21.1	4.3
12	7.3	31.3	61.4	1.1	21.3	6.2	45.4	21.6	4.4

[a] Entry numbers are common to Table 3.
[b] Observed in ^{13}C NMR spectra of quaternary carbon resonance; from low to high field in the spectra (=47.3–43.5 ppm) [22].
[c] Observed in ^{13}C NMR spectra of quaternary carbon resonance; from low to high field in the spectra (=178.3–176.1 ppm) [22].

3.3. Microstructure of PMMA

The average molecular weight (M_w) of products as determined by GPC ranged from 1967 to 6255 (Fig. 3), which are lower than those reported in the literature [13,14]. It also decreased with increasing of temperature (Table 3). Possibly, chain transfer in the catalytic systems is faster than chain propagation so that only low molecular weight polymers are formed.

The complex **1** with the methyl substituent gave PMMA of broad polydispersity whereas the diisopropyl substituent analog gave PMMAs with of a narrow polydispersity at all T_ps. On the average, the polydispersities obtained of both types of PMMA were narrower than those resulting from other late transition metal catalysts such as Ni(acac)$_2$/MAO [12], phenoxyimine-nickel/MAO, as well as neutral Pd(II) and Ni(II) acetylide [13–15].

The infrared spectra of PMMA by the complex **1** (Fig. 4) are sensitive to tacticity [23,24] and although the polymers showed the bands characteristic of syndiotactic PMMA, the detailed microstructure could not, unfortunately, be differentiated. The microstructure of PMMA was, however, eluciated from the ^{13}C NMR spectra of PMMA [25–28]. All the above catalyst systems produced PMMAs with similar microstructures. Fig. 5 is the ^{13}C NMR spectrum of entry 8. It shows the characteristic chemical-shift signals of the carbon types in MMA units. The chemical-shift signals appearing around 176.10–178.3 ppm (c), 18.25–22.24 ppm (a), 52.97–54.92 ppm (e), 50.64–52.86 ppm (d) and 43.51–47.31 ppm (b) can be assigned to the resonances of ester carbonyl (C=O), α-methyl (α-CH$_3$), methoxy (–OCH$_3$), methenes (–CH$_2$–) and quaternary carbons in MMA units, respectively. The chemical-shift signal at about 14.20 ppm can be assigned to γ-methyl(γ-CH$_3$), which is one end of PMMA chain from the Et$_3$Al when chain initiating (Scheme 2). The signals of 127.12–131.22 can be assigned to another chain end in which a double bond can be contained from chain termination by β-H elimination.

The triad and pendant content tests of the PMMA samples (Table 4) show that the two nickel complexes furnish syndiotactic-rich PMMA, and structural variations of the catalyst and polymerization temperature should have some degree of influence on the microstructure of PMMA. On the basis of the racemic triad values, the more crowded catalyst yielded PMMA of a higher syndiotacticity at the same T_p. For example, the *rr* triad content in PMMA of entry 2 reached 73% relative 66% of entry 8. Such a difference is again attributed to the steric environment around the metal center. With increasing temperature, the *rr* triad content decreases although the antactic content in PMMA increases. The complex **2** shows stereoregularity in from 0 °C to 70 °C, the *rr* triad content reaching 73%. The complex **1** shows relatively low selectivity as it generates syndio-rich or atactic PMMA at normal temperature. The polydispersity of the PMMA is relatively narrow (ranging from 1.232 to 1.759). The similarity in polymer microstructures suggests that chain initiation and chain growth most likely proceed along similar pathways for all bis(naphtocyimine) nickel(II)/alkylaluminum catalyst systems used in this study.

4. Conclusions

In summary, common alkylaluminums such as AlEt$_3$, Al(i-Bu)$_3$ and AlEt$_2$Cl are efficient cocatalysts to activate bis(1-arylimino-methylenyl-naphthalen-2-oxy)nickel complexes for MMA polymerization without MAO. The complexes **1, 2** that were activated with general alkylaluminium in presence of equimolar PPh$_3$ showed high catalytic activities for the polymerizations of MMA, producing PMMA with lower molecular weight. The polymerization temperature and the Al/Ni molar ratio were found also to be the main factors that influence catalyst efficiency. Determinated by GPC, the average molecular weight (M_w) of products range from 1967 to 6255 and dispersity index (M_w/M_n) from 1.25 to 1.75. It was found that the syndiotactic content of PMMA was predominant by ^{13}C NMR and higher polymerization temperature favourable to atactic content of PMMA.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.11.006.

References

[1] (a) L.S. Boffa, B.M. Novak, Chem. Rev. 100 (2000) 1479–1494;
(b) S.D. Ittel, L.K. Johnson, M. Brookhart, Chem. Rev. 100 (2000) 1169–1204;
(c) L.T.J. Evans, M.P. Coles, F. Geoffrey, N. Cloke, P.B. Hitchcock, Dalton Trans. (2007) 2707–2717;
(d) D.B. Liu, S.B. Wang, H.T. Wang, W. Chen, J. Mole. Catal. A: Chem. 246 (2006) 53–58;
(e) W.H. Sun, P. Hao, S. Zhang, Q.S. Shi, W.W. Zuo, X.B. Tang, X. Lu, Organometallics 26 (2007) 2720–2734;
(f) M. Zhang, P. Hao, W.W. Zuo, S.Y. Jie, W.H. Sun, J. Organomet. Chem. 693 (2008) 483–491.
[2] (a) C.N. Elia, A. Sen, A.C. Albeniz, P. Espinet, in: Proceedings of the ACS National Meeting, Washington, August 2000, pp. 20–24.;
(b) G.R. Tang, G.X. Jin, Dalton Trans. (2007) 3840–3846.
[3] (a) I. Kim, J.M. Hwang, K.L. Jin, Macromol. Rapid Commun. 24 (2003) 508–511;
(b) M. Zhang, S. Zhang, P. Hao, S.Y. Jie, W.H. Sun, P.Z. Li, X.M. Lu, Eur. J. Inorg. Chem. (2007) 3816–3826;
(c) S. Adewuyi, G. Li, S. Zhang, W.Q. Wang, P. Hao, W.H. Sun, N. Tang, J.J. Yi, J. Organomet. Chem. 692 (2007) 3532–3541.
[4] (a) G.J.P. Brltovsek, V.C. Gibson, D.M. Wass, Angew. Chem., Int. Ed. 38 (1999) 428–447;

(b) S. Meking, Coord. Chem. Rev. 203 (2000) 325–351;
(c) S. Meking, Angew. Chem., Int. Ed. 40 (2001) 534–540.

[5] (a) B.Y. Lee, G.C. Bazan, J. Vela, Z.J.A. Komon, X. Bu, J. Am. Chem. Soc. 123 (2001) 5352–5353;
(b) F.A. Hicks, M. Brookhart, Organometallics 20 (2001) 3217–3219;
(c) D. Zhang, G.X. Jin, Appl. Catal. A: Gen. 262 (2004) 13–18;
(d) S.Y. Jie, S. Zhang, W.H. Sun, Eur. J. Inorg. Chem. (2007) 5584–5598.

[6] M. Peukert, W. Keim, Organometallics 2 (1983) 594–597.

[7] B. Reuben, H.J. Wittcoff, J. Chem. Educ. 65 (1988) 605–607.

[8] C. Wang, S. Friedrich, T.R. Younkin, R.T. Li, R.H. Grubbs, D.A. Bansleben, M.W. Day, Organometallics 17 (1998) 3149–3151.

[9] H. Sun, Q. Shen, X. Peng, M. Yang, Catal. Lett. 80 (2002) 11–13.

[10] T. Younkin, E.F. Connor, J.I. Henderson, S.K. Friedrich, R.H. Grubbs, D.A. Bansleben, Science 287 (2000) 460–462.

[11] G.Q. Gui, F. Bao, H.Y. Gao, F.M. Zhu, Q. Wu, Appl. Organomet. Chem. 19 (2005) 627–632.

[12] (a) F.M.B. Coutinho, M.A.S. Costa, L.F. Monteiro, L.C. Maria, Polym. Bull. 38 (1997) 303–309;
(b) K. Endo, A. Inukai, Polym. Int. 49 (2000) 110–114.

[13] (a) X.H. He, Y.Z. Yao, X. Luo, J.K. Zhang, Y.H. Liu, L. Zhang, Q. Wu, Organometallics 22 (2003) 4952–4957;
(b) X. He, Q. Wu, Appl. Organomet. Chem. 20 (2006) 264–271.

[14] C. Carlini, V.D. Luise, M. Martinelli, A.M.R. Galletti, G. Sbrana, J. Polym. Sci. Part A: Polym. Chem. 44 (2006) 620–633.

[15] (a) C. Carlini, M. Martinelli, A.M.R. Galletti, G. Sbrana, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 2117–2124;

(b) C. Carlini, M. Martinelli, A.M.R. Galletti, G. Sbrana, J. Polym. Sci. Part A: Polym. Chem. 41 (2003) 1716–1724.

[16] F. Chang, D.H. Zhang, G.Y. Xu, H.J. Yang, J.T. Li, H.B. Song, W.H. Sun, J. Organomet. Chem. 689 (2004) 936–946.

[17] J.X. Hou, S.Y. Jie, W.J. Zhang, W.H. Sun, J. Appl. Polym. Sci. 102 (2006) 2233–2240.

[18] C. Mast, M. Krieger, K. Dehnicke, A. Greiner, Macromol. Rapid Commum. 20 (1999) 232–235.

[19] X.G. Fan, H.H. Wang, Z.H. Hu, M.P. Hu, Q.X. Zhang, Polym. Mater. Sci. Eng. 20 (2004) 94–96.

[20] (a) S. Borkar, P.K. Saxena, Polym. Bull. 44 (2000) 167–169;
(b) O.A. Osipov, V.I. Minkin, N.R. Kalnitskii, Z.A. Tumakova, Zh. Neorg. Khim. 12 (7) (1967) 1867–1876.

[21] H. Yang, W. Sun, F. Chang, Y. Li, Appl. Catal. A: Gen. 252 (2003) 261–267.

[22] R.J. Maldanis, J.S. Wood, A. Chandrasekaran, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 645 (2002) 158–167.

[23] C. Carlo, I. Mauro, L. Vincenzo, et al., Appl. Catal. A: Gen. 231 (2002) 307–320.

[24] J.M. O'Reilly, R.A. Mosher, Macromolecules 14 (1981) 602–608.

[25] T. Konishi, Y. Tamai, M. Fuji, Y. Einaga, H. Yamakawa, Polym. J. 21 (1989) 329–334.

[26] S. Collins, D.G. Ward, J. Am. Chem. Soc. 114 (1992) 5460–5462.

[27] H. Yasuda, H. Yamamoto, K. Yokota, S. Miyake, A. Nakamura, J. Am. Chem. Soc. 114 (1992) 4908–4910.

[28] H. Yasuda, H. Yamamoto, M. Yamashita, K. Yokota, A. Nakamura, S. Miyake, Y. Kai, N. Kanehisa, Macromolecules 26 (1993) 7134–7143.