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ORIGINAL PAPER

Copolymerization of norbornene and *n*-butyl methacrylate catalyzed by bis-(*β*-ketoamino)nickel(II)/$B(C_6F_5)_3$ catalytic system

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Abstract Copolymerization of norbornene with *n*-butyl methacrylate (*n*-BMA) was carried out with catalytic systems of bis-(*β*-ketoamino)nickel(II) complexes Ni{RC(O)CHC[N(naphthyl)]CH_3}$_2$ (R = CH_3, CF_3) and $B(C_6F_5)_3$ in toluene and exhibited high activity for both catalytic systems. Influence of the catalyst structure and comonomer feed content on the polymerization activity as well as on the incorporation rates were investigated. The catalysis was proposed to involve the insertion mechanism of norbornene and *n*-BMA catalyzed by bis-(*β*-ketoamino)nickel(II)/$B(C_6F_5)_3$ catalytic systems, and the decreasing polymerization activity with an increasing content of *n*-BMA in the feedstock composition could be attributed to the competition of carbonyl group coordination onto the Ni(II) active center instead of the olefin double bond. The reactivity ratios were determined to be $r_{n\text{-BMA}} = 0.095$ and $r_{\text{norbornene}} = 12.626$ by the Kelen–TÜdÕs method. The copolymer films prepared show good transparency in the visible region.

Keywords Late transition metal · Catalytic polymerization ·
n-Butyl methacrylate · Norbornene

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Introduction

Interest in polymers of cyclic olefins such as norbornene has increased dramatically over the past decade due to their high chemical resistance, good UV resistance, high glass-transition temperature, low dielectric constant, excellent transparency, large refractive index, and low birefringence [1–7]. The vinyl polynorbornene, however, also exhibits some negative properties. For example, they are normally brittle at room temperature and have poor solubility in common organic solvents. In addition, the materials exhibit poor processability because of high T_g values [8]. In order to improve their properties, a series of copolymers of norbornene with ethylene [9, 10], propylene [11, 12], norbornene derivatives [13–15], polar group terminal olefin monomer [16], higher 1-alkene have been also studied [17, 18]. However, copolymerizations of α-olefin with polar group terminal olefin monomers using common homogeneous metallocene catalyst systems have their limitations due to the high Lewis acidity of the catalyst center which is deactivated by the coordination of the polar group [19–22]. Late transition metal-based nickel and palladium complexes have been reported as an efficient catalyst for the polymerization of α-olefin and polar olefins due to their low Lewis acidity [14, 15]. The development of new mixed-ligand nickel(II) complexes is important for the discovery of new late transition metal catalysts for α-olefin and polar olefin.

A little variation of the ligand structure may lead to a profound changing in the catalytic reactivity. In this paper, we reported the synthesis of two nickel(II) complexes with *β*-ketoamino chelate ligands and their copolymerization behavior toward norbornene and *n*-butyl methacrylate (*n*-BMA) after activation with $B(C_6F_5)_3$. The influence of the catalyst structure and comonomer feed content on the polymerization activity as well as on the incorporation rates were also investigated in detail. The catalysis was proposed to involve the insertion mechanism of norbornene and *n*-BMA catalyzed by bis-(*β*-ketoamino)nickel(II)/$B(C_6F_5)_3$ catalytic systems, and the lower activity could be attributed to the competition of carbonyl group coordination onto the Ni(II) active center instead of the olefin double bond. The reactivity ratios were determined by the Kelen–TÜdÕs method. New copolymer films were obtained and they show good transparency in UV–Vis region.

Experimental

Materials

All manipulations involving air- and moisture-sensitive compounds were performed under a dried and purified argon atmosphere standard glove box and Schlenk techniques. Toluene was dried over sodium/benzophenone and distilled under argon. Norbornene (bicyclo-[2.2.1]hept-2-ene) was purified by distillation over sodium and used as a solution (4.25 mol/L) in toluene. *n*-Butyl methacrylate (*n*-BMA) was purchased from Shanghai reagent factory and purified by washing twice with aqueous sodium hydroxide(5.0 wt%) and twice with water for removing inhibitors, followed by drying over anhydrous $CaCl_2$ and distillation over CaH_2 under argon atmosphere at reduced pressure. Other commercially available reagents were purchased and used without purification.

Preparation of bis-(β-ketoamino)nickel(II) complexes

Bis-(β-ketoamino)nickel(II) complexes, Ni{RC(O)CHC[N(naphthyl)]CH_3}$_2$ (R = CH_3, CF_3), were synthesized according to the method reported in our previous work [23].

{CF_3C(O)CHC[HN(naphthyl)]CH_3}

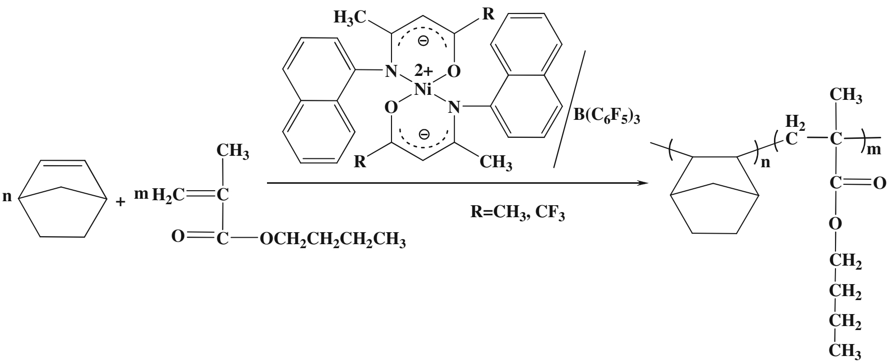
1,1,1-Trifluoro-2,4-pentanedione (5 mL, 0.041 mol), 1-naphthylamine (5.871 g, 0.041 mol), and a catalytic amount of *p*-toluenesulfonic acid in toluene (150 mL) were combined and refluxed for 2–3 h. Water was removed as a toluene azeotrope at 125–130 °C using a water separator. Volatile substance was removed in vacuo and recrystallization from hexane gave {CF_3C(O)CHC[HN(naphthyl)]CH_3} (6.2 g, 54%). Mp: 73 °C. ^{1}H NMR ($CDCl_3$), δ (ppm): 12.83 (s, 1H, O–H); 7.33–7.94 (m, 7H, naphthyl-H); 5.68(s, 1H, C–$H_{backbone}$); 2.01(s, 3H, –CH_3).

Ni{CF_3C(O)CHC[N(naphthyl)]CH_3}$_2$

Potassium (0.4 g, 0.01 mol) was added to 25 mL of dried ^{t}BuOH. After the potassium had dissolved, the solution was heated to 50 °C and of {CF_3C(O)CHC [HN(naphthyl)]CH_3} (1.40 g, 0.005 mol) was added. The solution changed to yellow-orange as {CF_3C(O)CHC[HN(naphthyl)]CH_3} completely reacted with ^{t}BuOK. The reaction mixture was stirred for another 20 min. The solution was then slowly cooled to room temperature, and of $[Et_4N]_2[NiBr_4]$ (1.586 g, 0.0025 mol) was introduced; the reacting mixture immediately formed a dark-green precipitate. After stirring vigorously for several hours at room temperature, the excess ^{t}BuOH was removed in vacuo. The reacting slurry was extracted successively with hot toluene, and the mixture was filtrated quickly. The filtrate was allowed to crystallize by cooling slowly overnight. The product was isolated and dried under reduced pressure. Additional recrystallization from *n*-hexane/toluene mixture solution gave blocks of dark-blue crystals. Yield: 0.511 g, 33%. ^{1}H NMR ($CDCl_3$), δ (ppm): 7.21–8.00 (m, 14H, naphthyl-H); 6.21(s, 2H, C–$H_{backbone}$); 0.75–1.40 (m, 6H, –CH_3).

Polymerization

All procedures were carried out under purified nitrogen atmosphere. A typical copolymerization procedure is as follow: a toluene solution of norbornene and *n*-BMA was added via a syringe into a 100 mL two necked round bottom flask containing a magnetic stirrer, the Ni(II)l complex solution was then introduced followed by $B(C_6F_5)_3$ solution. The total volume was kept constant at 10 mL. The polymerization reaction was performed for an appropriate time at a controlled temperature. The reaction was terminated by addition of acidic ethanol (90:10



Scheme 1 Copolymerization of norbornene and *n*-BMA catalyzed by bis-(β-ketoamino)nickel(II)/$B(C_6F_5)_3$ catalytic systems

ethanol/HCl). The resulting precipitated polymers were collected by filtration and washed with ethanol several times, and were dried under vacuum at 60 °C. Cyclohexane solutions of the different copolymers were used to prepare the copolymer films on glass slide. The transparent films that were obtained had thickness of about 100 μm (the copolymerization procedure and the structure of the catalyst are shown in Scheme 1).

Characterization

The molecular weight and molecular weight distribution (MWD) of the copolymers were measured by gel permeation chromatography (GPC) using a Breeze Waters system equipped with a Rheodyne injector, a 1515 Isocratic pump and a Waters 2414 differential refractometer using polystyrenes as the standard and chloroform as the eluent at a flow rate of 1.0 mL/min and 40 °C through a Styragel column set, Styragel HT3 and HT4 (19 mm × 300 mm, 10^2+10^3 nm) to separate molecular weight (MW) ranging from 10^2 to 10^6.

The polymer samples were processed into KBr thin films for IR measurement. FTIR spectra were recorded on a Shimadazu IRPrestige-21 FTIR spectrometer.

^{1}H NMR spectra of polymers were obtained on a Bruker ARX 400 NMR spectrometer at room temperature using chloroform-*d* as solvent and tetramethylsilane (TMS, $\delta = 0$) as internal reference. Thermogravimetric analysis (TGA) data were measured with a Perkin–Elmer Thermogravimetric Analyzer TGA 7 thermal analysis system instrument under a nitrogen atmosphere for up to 650 °C at a heating rate of 10 °C/min.

The glass transition temperatures of the copolymers were determined by differential scanning calorimetry (DSC) with a Shimadazu DSC 60 at a heating rate of 10 °C/min.

The UV–Vis transmittance spectra of the copolymer films were recorded with a Hitachi UV-2300 UV–Vis spectrophotometer. Digital images were obtained by using a Canon powershot A520 camera.

Results and discussion

In the present work, two different bis-(β-ketoamino)nickel(II) complexes, which contain various steric and electronic ligands, were used to investigate the influence of the catalyst framework on the polymerization activity as well as on the incorporation rates. The results of copolymerization of norbornene and *n*-BMA with various bis-(β-ketoamino)nickel(II)/$B(C_6F_5)_3$ catalytic systems and comonomer feed contents are summarized in Tables 1 and 2.

The results show a decreasing polymerization activity with an increasing content of *n*-BMA in the feedstock composition. Moreover, the weight average molecular weights of the copolymers are dependent on the *n*-BMA feed content, this suggests a reversible interaction of the ester group on *n*-BMA and the Ni(II) active center which may inhibit the coordination of double bond [24].

The deactivation effect with an increasing *n*-BMA content in the feedstock composition is that *n*-BMA blocks the free coordination site at the Ni(II) active center by forming a "bond" between its oxygen and the nickel atom (**3** in Scheme 2, reaction K_1). However, the steric interaction between the catalyst and the *n*-BMA also increase, favoring the back reaction (K_{-1}) and shifting the equilibrium toward

Table 1 The effects on yield and activity of copolymerizations of norbornene and *n*-BMA catalyzed by $Ni\{RC(O)CHC[N(naphthyl)]CH_3\}_2/B(C_6F_5)_3$ systems

Run		NB/*n*-BMA (mol/mol)	Yield (%)		Activity ($g_{polymer}$/mol Ni h)	
R = CH_3	R = CF_3		R = CH_3	R = CF_3	R = CH_3	R = CF_3
1	2	100/0	100	100	3.20×10^4	3.20×10^4
3	4	90/10	37.17	43.17	1.23×10^4	1.42×10^4
5	6	70/30	16.54	19.95	0.60×10^4	0.72×10^4
7	8	50/50	7.64	11.47	0.30×10^4	0.45×10^4
9	10	0/100	0	6.00	0	0.28×10^4

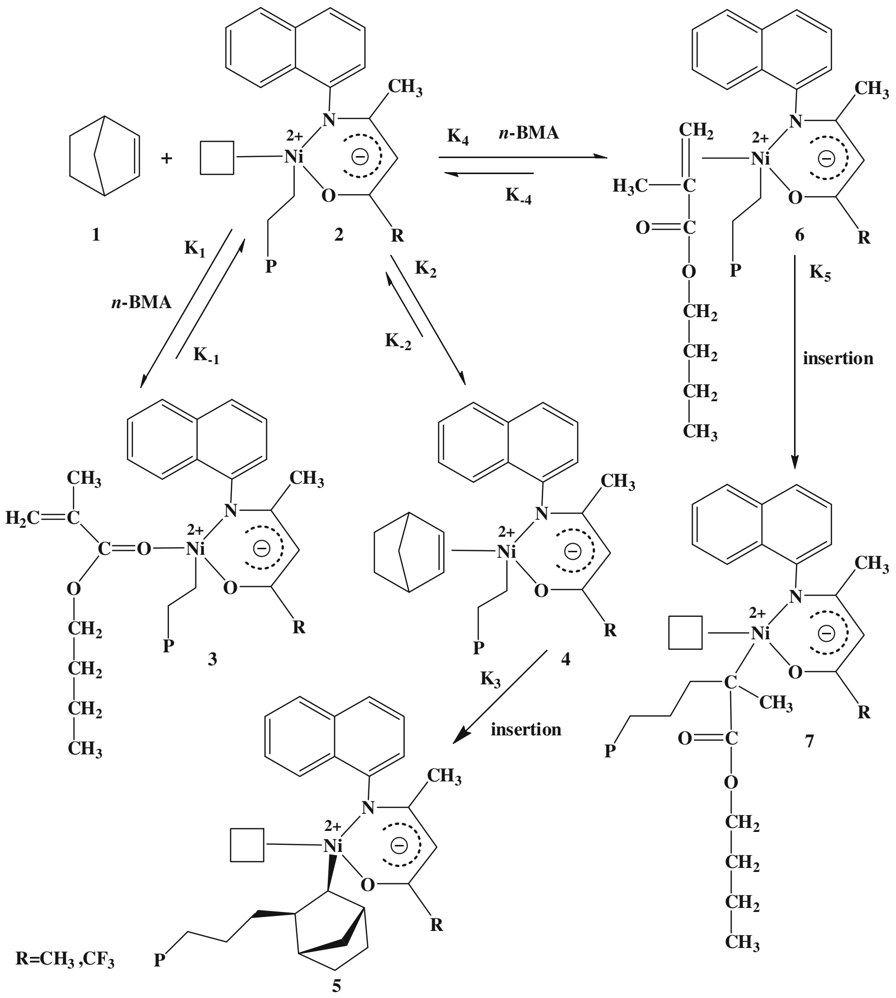
Conditions: c[Cat.] = 5.0×10^{-4} mol/L; n[NB] + n[n-BMA] = 0.01 mol; n[B]/n[Ni] = 20/1; t_p = 6 h; T_p = 60 °C; solvent: toluene; V_p = 10 mL

Table 2 The effects of comonomer feed ratios on M_w, MWD and the *n*-BMA (mol %) of the copolymerization catalyzed by $Ni\{RC(O)CHC[N(naphthyl)]CH_3\}_2/B(C_6F_5)_3$ systems

NB/*n*-BMA (mol/mol)	$M_n \times 10^{-4}$(g/mol)		$M_w \times 10^{-4}$(g/mol)		MWD		*n*-BMA (mol%)[a]	
	R = CH_3	R = CF_3	R = CH_3	R = CF_3	R = CH_3	R = CF_3	R = CH_3	R = CF_3
90/10	14.5	23.7	20.8	28.9	1.43	1.22	3.65	3.54
70/30	5.7	6.3	9.7	9.9	1.70	1.57	3.66	4.76
50/50	2.7	2.9	5.2	5.9	1.93	2.03	4.35	7.29

Conditions: c[Cat.] = 5.0×10^{-4} mol/L; n[NB] + n[n-BMA] = 0.01 mol; n[B]/n[Ni] = 20/1; t_p = 6 h; T_p = 60 °C; solvent: toluene; V_p = 10 mL

[a] Determined from ^{1}H-NMR spectra. *n*-BMA (mol%) = $I_{CH3}/(I_{CH3} + 3Ic_2/c_3)$ (where I_{CH3} represents the area of the methyl in the *n*-BMA region and Ic_2/c_3 represents the area of the position C_2 and C_3 methine in the norbornene, see Fig. 4)



Scheme 2 Insertion mechanism including deactivation reaction on copolymerization of norbornene and *n*-BMA catalyzed by bis-(*β*-ketoamino)nickel(II)/B(C_6F_5)$_3$ catalytic systems

the free cationic catalyst. The olefinic coordination (**4**, reaction K_2) is capable of competing with the deactivation (K_{-1}) since the steric interaction in **4** should be much weaker than in **3**. By inserting into the copolymer chain (K_3), the *n*-BMA is removed from the equilibrium K_{-1}/K_1 again and this shifts the equilibrium toward the free cationic catalyst. At the same time, the C=C of *n*-BMA also has the chance to coordinate to the free cationic catalyst and form another olefinic complex (**6**, reaction K_4). The equilibrium will shift to the free cationic catalyst (**2**, reaction K_{-4}) or the copolymer (**7**, reaction K_5) due to the steric hindrance of the olefinic coordination (**6**), [24].

The use of catalysts with differently substituted ligands has an effect on the polymerization activity due to the various steric and electronic interactions between ligand and polar *n*-BMA. The activities detected in copolymerization of norbornene and *n*-BMA using Ni{$CH_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/$B(C_6F_5)_3$ system were somewhat lower in comparison with the activities observed by using Ni{$CF_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/$B(C_6F_5)_3$. Similar result was reported in the literature [25] and indicated that the CF_3 group with a strong electron-withdrawing effect is beneficial to the catalytic activity toward the copolymerization.

In order to determine the monomer reactivity ratios ($r_{n\text{-BMA}}$ and $r_{\text{norbornene}}$), a series of experiments were performed with different initial comonomer feed concentrations and stopped at a low yield by control of the polymerization time and the results are shown in Table 3. The reactivity ratios, determined by the Kelen–TÜdÕs method [26] (Fig. 1), are $r_{n\text{-BMA}} = 0.095$, and $r_{\text{norbornene}} = 12.626$, illustrating the reactivity of norbornene is higher than that of *n*-BMA.

Table 3 Copolymerization results of norbornene and *n*-BMA catalyzed by Ni{$CH_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/$B(C_6F_5)_3$ system

n-BMA in the feed (mol%)	*n*-BMA incorporated (mol%)	Yield (%)	Polymerization time
10	–[a]	32.31	1 min
20	–[a]	20.83	2 min
30	2.84	11.94	5 min
40	4.29	8.33	15 min
50	5.11	6.31	20 min
60	5.52	3.90	25 min
70	10.18	1.22	2 h
80	–[a]	0.91	3 h

Conditions: c[Cat.] $= 5.0 \times 10^{-4}$ mol/L; $n[\text{NB}] + n[n\text{-BMA}] = 0.01$ mol; $n[\text{B}]/n[\text{Ni}] = 20/1$; $T_p = 60$ °C; solvent: toluene; $V_p = 10$ mL

[a] Not detected

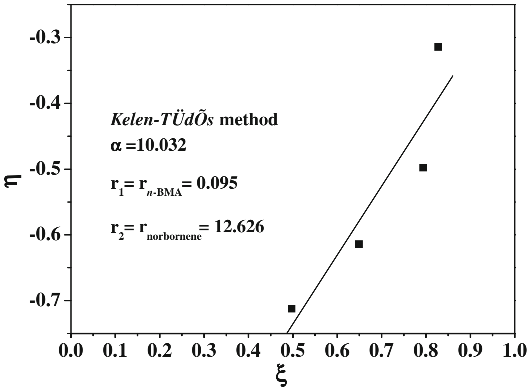


Fig. 1 Linear fitting of the norbornene/*n*-BMA copolymers system according to Kelen–TÜdÕs method: $\eta = (r_1 + \frac{r_2}{\alpha})\xi - \frac{r_2}{\alpha}$, $\eta = \frac{G}{\alpha+F}$, $\xi = \frac{F}{\alpha+F}$, $G = \frac{x(y-1)}{y}$, $F = \frac{x^2}{y}$, $\alpha = \sqrt{F_{\min} * F_{\max}}$, $F_{\min} = \text{minimum}(F)$, $F_{\max} = \text{maximum}(F)$, $x = \frac{[n\text{−BMA}]}{[\text{NB}]}$, $y = \frac{\text{d}[n\text{−BMA}]}{\text{d}[\text{NB}]}$

GPC curve of copolymer

The MWDs are close to 2.0 and appear as a single modal in the GPC chromatogram (Fig. 2), which indicate copolymerizations occur at the single active site and the products are the true copolymers instead of blends of the homopolymers [27]. Polynorbornene (PNB) prepared by the bis-(β-ketoamino)nickel(II)/$B(C_6F_5)_3$ catalytic system is soluble in cyclohexane while the poly(*n*-BMA) is soluble in acetone. Moreover, the copolymerization products were found to be dissolved completely in either cyclohexane or chloroform whereas both of homopolymers are not dissolved in chloroform. These results give an impression of the high influence of *n*-BMA on copolymerization product and prove that the products are the true NB/*n*-BMA copolymers instead of blends of homopolymers. The poor solubility of copolymer in acetone can be ascribed to the low content of *n*-BMA in the copolymers.

FTIR spectrum of copolymer

FTIR spectra of the copolymers and monomer are shown in Fig. 3. The characteristic absorption of vinyl-type addition polynorbornene at 941 cm^{-1} could be attributed to the bicyclo[2.2.1] heptane ring as Kennedy and Makowski [3] noted. The absence of absorption band at 1620–1680 cm^{-1} and at 960 cm^{-1}, are characteristic for the *trans* form of ROMP structure of polynorbornenes [28]. The carbonyl group of *n*-BMA is observed at about 1726 cm^{-1} in Poly(NB-*co*-*n*-BMA). The disappearance of the absorption band at 1715 cm^{-1} in both PNB and Poly(NB-*co*-*n*-BMA) indicate that the polymerization products are the true copolymers. The spectra of the Poly(NB-*co*-*n*-BMA) generated by both of catalytic systems are similar indicating that variation to the catalytic system have insignificant effect on

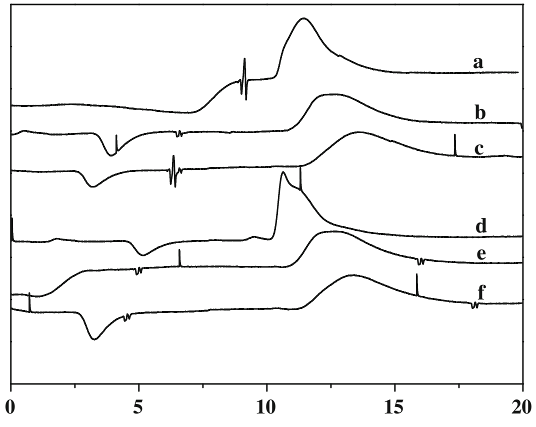


Fig. 2 GPC curves of NB/*n*-BMA copolymers with different *n*-BMA molar ratios: (*a*) 3.65%, (*b*) 3.66%, (*c*) 4.35% obtained by $Ni\{CH_3C(O)CHC[N(naphthyl)]CH_3\}_2/B(C_6F_5)_3$ system, and (*d*) 3.54%, (*e*) 4.76% and (*f*) 7.29% obtained by $Ni\{CF_3C(O)CHC[N(naphthyl)]CH_3\}_2/B(C_6F_5)_3$ system

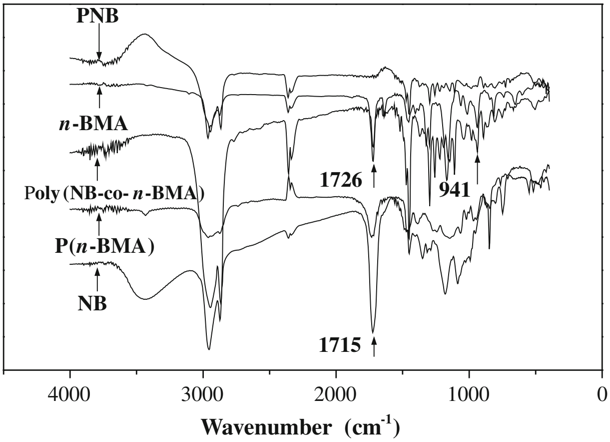


Fig. 3 FTIR spectra of *n*-BMA, NB and PNB, Poly(NB-*co*-*n*-BMA), P(*n*-BMA) obtained by Ni{$CF_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ system

the polymerization mechanism. All copolymers obtained by above catalytic systems were confirmed to undergo vinyl-type addition polymerization mechanism rather than ROMP mechanism.

^{1}H NMR spectra of copolymer

Figure 4 shows the ^{1}H NMR spectra of the poly(*n*-BMA) and copolymers obtained by bis-(*β*-ketoamino)nickel(II) complex/B(C_6F_5)$_3$ catalytic system. As shown in Fig. 4a, three groups of resonance peaks that appear between 0.8 and 4.0 ppm in the ^{1}H NMR spectrum of poly(*n*-butyl methacrylate). The peak at 0.8–1.0 ppm could be attributed to the methyl hydrogen corresponding to 2′/6′, and peak at 1.1–2.0 ppm could be attributed to methane hydrogen corresponding to 1′/4′/5′, 3.9 ppm could be attributed to methane hydrogen corresponding to 3′ that connect with ester group of *n*-BMA segment, respectively. As shown in Fig. 4b, however, four group resonance peaks appear between 0.8 and 4.0 ppm in the ^{1}H NMR spectrum of poly(norbornene-*co*-*n*-butyl methacrylate). The peak at 0.8–1.0 ppm could be attributed to the methyl hydrogen corresponding to 2′/6′, at 1.1–1.7 ppm could be attributed to methene hydrogen corresponding to 7/5/6/1′/4′/5′, at 1.7–2.0 ppm could be attributed to methine hydrogen corresponding to 1/4, at 2.0–2.5 ppm could be attributed to methine hydrogen corresponding to 2/3, at 3.8–3.9 ppm could be attributed to methene hydrogen corresponding to 3′, and a new peak at 3.4 ppm could be attributed to methene hydrogen connecting with ester group of *n*-BMA segment, respectively. In addition, the absence of resonance at 5.0–6.0 ppm indicate no double bonds, which are typical for metathesis-type polynorbornene [29]. Copolymer compositions have been calculated using ^{1}H NMR spectra. It could be noted that incorporations of polar monomer lies approximately between 3.0 and 8.0 mol% by using 10–50 mol% *n*-BMA in the feedstock composition. The peak of methyl hydrogen corresponding to 2′/6′ (at 0.8–1.0 ppm) and the peak area of methyene hydrogen corresponding to 3′/the new peak are relatively enhanced with the increase of *n*-BMA content in

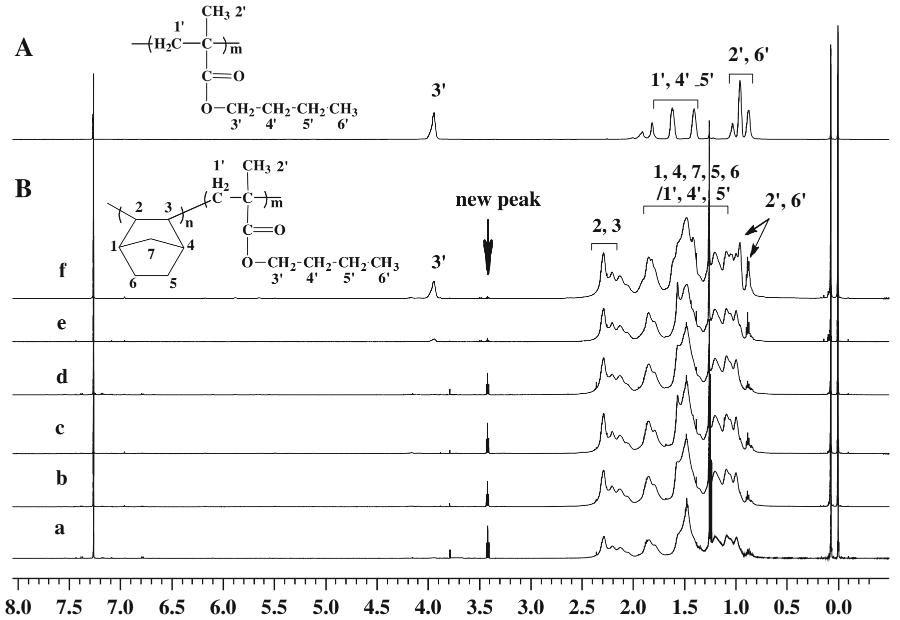


Fig. 4 ^{1}H-NMR spectra of poly(*n*-butyl methacrylate) (**a**) and of NB/*n*-BMA copolymers with different *n*-BMA molar ratios (**b**): (*a*) 3.65%, (*b*) 3.66%, (*c*) 4.35% obtained by Ni{$CH_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ system, and (*d*) 3.54%, (*e*) 4.76% and (*f*) 7.29% obtained by Ni{$CF_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ system

copolymers whereas the peak area of 3′ is relatively increased and the new peak is relatively decreased with the increase of *n*-BMA content in the feed. These mean that when increasing *n*-BMA content in the feed the probability of forming *n*-BMA connecting with *n*-BMA sequence increases comparing to *n*-BMA connecting with norbornene sequence.

Thermogravimetric analyses of copolymers

TGA curves of poly(norbornene-*co*-*n*-butyl methacrylate) with different *n*-BMA content prepared by Ni{$CF_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ are shown in Fig. 5. The thermal stabilities of all copolymers are similar and decompositions occur at high temperatures from 370 to 450 °C. The glass transition temperatures (T_g) of the copolymers were investigated by DSC analyses. However, all the efforts to observe T_g over 300 °C failed. These results indicate that the copolymers obtained by bis-(β-ketoamino)nickel(II)/B(C_6F_5)$_3$ catalytic systems exhibit good thermostability under nitrogen.

UV–vis measurement of copolymers

The UV–vis measurements for these copolymer films indicate that the transparency of the copolymers in the visible region decrease with an increasing content of

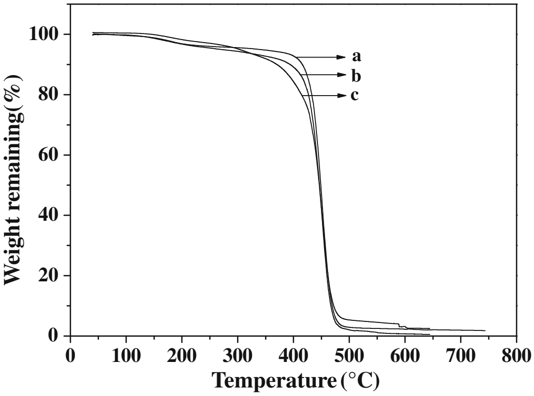


Fig. 5 TGA curves of poly(norbornene-*co*-*n*-butyl methacrylate) with (*a*) 3.54%, (*b*) 4.76% and (*c*) 7.29% of *n*-BMA molar ratio obtained by Ni{$CF_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ system

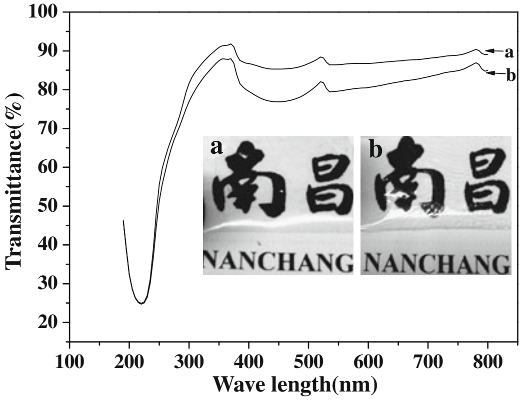


Fig. 6 Transmission of the films prepared by NB/*n*-BMA copolymers with (*a*) 3.54% and (*b*) 4.76% of *n*-BMA molar ratio obtained by Ni{$CF_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ systems

n-BMA; the transmittance of the poly(NB-*co*-*n*-BMA) decrease from ca. 90% to ca. 80%, suggesting that the addition of *n*-BMA has a negative effect on the transparency of the polymers. The strong absorption of the ester groups in *n*-BMA results in a decrease up to 25% in the ultraviolet region (Fig. 6).

Conclusions

The copolymerizations of norbornene with *n*-BMA are catalyzed by Ni{RC(O)CHC [N(naphthyl)]CH_3}$_2$ (R = CH_3, CF_3)/B(C_6F_5)$_3$; it was shown that an increase in the initial *n*-BMA feed content leads to an increase in the incorporated *n*-BMA content of the resulting copolymer. The Ni{$CF_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ system was found to exhibit higher catalytic activity than the Ni{$CH_3C(O)CHC[N(naphthyl)]CH_3$}$_2$/B($C_6F_5$)$_3$ system. The copolymer sequences were influenced by the feed ratio of the comonomer. The insertion mechanism including deactivation reaction on copolymerization of norbornene and *n*-BMA catalyzed by bis-(β-ketoamino) nickel(II)/$B(C_6F_5)_3$ catalytic system was proposed. The reactivity ratios were determined by the Kelen–TÜdÕs method and $r_{n\text{-BMA}}$ is 0.095 while $r_{\text{norbornene}}$ is 12.626. The analyses of copolymers' structures and properties indicate that the copolymerization of norbornene and *n*-BMA occurs via vinyl-polymerization mode. The copolymers show good thermostability (T_{dec} >400 °C). The prepared films with Poly(NB-*co*-*n*-BMA) exhibit good transparency in the visible region.

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References

1. Janiak C, Lassahn PG (2001) Metal catalysts for the vinyl polymerization of norbornene. J Mol Catal A 166:193–209
2. Janiak C, Lassahn PG (2001) The vinyl homopolymerization of norbornene. Macromol Rapid Commun 22:479–493
3. Kennedy JP, Makowski HS (1967) Carbonium ion polymerization of norbornene and its derivatives. Macromol Sci Chem A1:345–370
4. Gaylord NG, Deshpande AB (1976) Structure of "vinyl-type" polynorbornenes prepared with Ziegler-natta catalysts. J Polym Sci Polym Lett Ed 14:613–617
5. Maezawa H, Matsumoto J, Ajura H, Asahi S (1991) Norbornene-based polymer, process for production of said polymer, film of said polymer, and process for production of said film. EP Pat 445:755
6. Goodall BL, Benedikt GM, McIntosh III LH, Barnes DA (1995) Process for making polymers containing a norbornene repeating unit by addition polymerization using an organo(nickel or palladium) complex. U. S. Patent 5, 468, 819
7. Goodall BL, Risse W, Mathew JP (1996) Addition polymers of polycycloolefins containing functional substituents. U.S. Patent 5, 705, 503
8. Barnes DA, Benedikt GM, Goodall BL, Huang SS, Kalamarides HA, Lenhard S, Mclntosh LH III, Selvy KT, Shick RA, Rhodes LF (2003) Addition polymerization of norbornene-type monomers using neutral nickel complexes containing fluorinated aryl ligands. Macromolecules 36:2623–2632
9. Nishizawa O, Misaka H, Sakai R, Kakuchi T, Satoh T (2008) Copolymerization of ethylene and norbornene using cyclopentadienylzirconium trichloride activated by isobutyl-modified methylaluminoxane. J Polym Sci A 46:7411–7418
10. Skupov KM, Marella PR, Hobbs JL, McIntosh LH, Goodall BL, Claverie JP (2006) Catalytic copolymerization of ethylene and norbornene in emulsion. Macromolecules 39:4279–4281
11. Cai ZG, Nakayama Y, Shiono T (2006) Living random copolymerization of propylene and norbornene with *ansa*-fluorenylamidodimethyltitanium complex: synthesis of novel syndiotactic polypropylene-*b*-poly(propylene-*ran*-norbornene). Macromolecules 39:2031–2033
12. Boggioni L, Zatnpa C, Ravasio A (2008) Propene–norbornene copolymers by C_2-symmetric metallocene *rac*-$Et(Ind)_2ZrCl_2$: influence of reaction conditions on reactivity and copolymer properties. Macromolecules 41:5107–5115
13. Kaita S, Matsushita K, Tobita M, Maruyama Y, Wakatsuki Y (2006) Cyclopentadienyl nickel and palladium complexes/activator system for the vinyl-type copolymerization of norbornene with norbornene carboxylic acid esters: control of polymer solubility and glass transition temperature. Macromol Rapid Commun 27:1752–1756
14. Yamashita M, Takamiya I, Jin K, Nozaki K (2006) Syntheses and structures of bulky monophosphine-ligated methylpalladium complexes: application to homo- and copolymerization of norbornene and/or methoxycarbonylnorbornene. Organometallics 25:4588–4595

15. Takamiya I, Yamashita M, Murotani E, Morizawa Y, Nozaki K (2008) Polymerization of norbornene with a pendent sulfonyl fluoride group catalyzed by palladium complex bearing (BU3P)-B-t ligand. J Polym Sci A 46:5133–5141
16. Huang CF, Wang SK, Kuo SW, Huang WJ, Chang FC (2004) Homopolymerization and copolymerization of *tert*-butyl methacrylate and norbornene with nickel-based methylaluminoxane catalysts. J Appl Polym Sci 92:1824–1833
17. Jung HY, Hong SD, Jung MW, Lee H, Park YW (2005) Norbornene copolymerization with α-olefins using methylene-bridged *ansa*-zirconocene. Polyhedron 24:1269–1273
18. Shiono T, Sugimoto M, Hasan T, Cai ZG, Ikeda T (2008) Random copolymerization of norbornene with higher 1-alkene with *ansa*-fluorenylamidodimethyltitanium catalyst. Macromolecules 41:8292–8294
19. Deng H, Soga K (1996) Isotactic polymerization of *tert*-butyl acrylate with chiral zirconocene. Macromolecules 29:1847–1848
20. Cheng TC, Rhubright D (1993) Kinetic aspects of the copolymerization between α-olefins and borane monomer in Ziegler-Natta catalyst. Macromolecules 26:3019–3025
21. Aaltonen P, Lofgren B (1995) Synthesis of functional polyethylenes with soluble metallocene/methylaluminoxane catalyst. Macromolecules 28:5353–5357
22. Yasuda H, Ihara E (1995) Rare earth metal initiated polymerizations of polar and nonpolar monomers to give high molecular weight polymers with extremely narrow molecular weight distribution. Macromol Chem Phys 196:2417–2441
23. He XH, Yao YZ, Luo X, Zhang JK, Liu YH, Zhang L, Wu Q (2003) Nickel(II) complexes bearing N, O-chelate ligands: synthesis, solid-structure characterization, and reactivity toward the polymerization of polar monomer. Organometallice 22:4952–4957
24. Wendt RA, Angermund K, Jensen V, Thiel W, Fink G (2004) Ethene copolymerization with trialkylsilyl protected polar norbornene derivates. Macromol Chem Phys 205:308–318
25. Zhu YZ, Liu JY, Li YS, Tong YJ (2004) Synthesis, structure and norbornene polymerization behavior of nickel complexes bearing two beta-ketoiminato chelate ligands. J Organomet Chem 689:1295–1303
26. Kelen T, TüdÕs F (1975) Analysis of the linear methods for determining copolymerization reactivity ratios. I. A new improved linear graphic method. J Macromol Sci Pure Appl Chem 9:1–27
27. Gao HY, Chen Y, Zhu FM, Wu Q (2006) Copolymerization of norbornene and styrene catalyzed by a novel anilido-imino nickel complex/methylaluminoxane system. J Polym Sci A 44:5237–5246
28. Tsujino T, Saeguss T, Furukawa J (1965) Polymerization of norbornene by modified Ziegler-catalysts. Makromol Chem 85:71–79
29. Sacchi MC, Sonzogni M, Losio S, Forlin F, Locatelli P, Tritto I, Licchelli M (2001) Vinylic polymerization of norbornene by late transition metal-based catalysis. Macromol Chem Phys 202:2052–2058