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Copolymerization of Norbornene and Methyl Acrylate by β-ketoiminato Palladium Complexes / MAO

Lingyun Wang, Yongfei Li, Fangming Zhu, Qing Wu (✉)

Institute of Polymer Science, School of Chemistry and Chemical Engineering,
Zhongshan University, Guangzhou 510275, China
E-mail: ceswuq@zsu.edu.cn; Fax: +86-20-84112245

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Summary

Neutral palladium complexes bearing β-ketoiminato ligand Pd[$CH_3C(O)CHC(NAr)CH_3$](PPh_3)(Me) (**I** Ar = α-napthyl, **II** Ar = fluorenyl) were activated by MAO to give catalytic system able to polymerize methyl acrylate (MA), thus producing atactic high molecular weight poly(methyl acrylate). Both catalysts exhibited catalytic activities for the copolymerization of norbornene with MA. The polymers were characterized by ^{13}C NMR, GPC and FT-IR spectra. The analyses of the product by ^{1}H NMR and ^{13}C NMR spectra gave the verification of random vinyl addition copolymer. The composition of the copolymers was controlled by varying the monomer feed ratio.

Keywords:

palladium catalyst; copolymerization; methyl acrylate; norbornene

Introduction

The copolymerization of polar vinyl monomers with nonpolar alkenes remains an area of great interest because the functionalized polyolefins are excellent polymeric materials. In particular, copolymers of acrylates with norbornene derivatives are interesting as materials for deep ultraviolet photolithography. Polyacrylates show good adhesion and have been used extensively as photoresist materials, but suffer poor dry etch resistance. On the other hand, polynorbornenes exhibit superior etch resistance and thermal stability, but show some deficiency such as low solubility, mechanical brittleness, weak adhesive properties and poor processibility. Thus, the copolymerization of norbornene and acrylates may provide the optimum properties. However, there are very few reports on the copolymerization of acrylates with norbornene monomers because of a disparity in their polymerization mechanism. Methyl acrylate (MA) usually polymerizes by radical or anionic initiation. Norbornene, however, polymerizes cationically or by insertion mechanism, and is very difficult to polymerize radically.

Copolymerization of norbornene (NBE) and MA through radical systems such as atom transfer radical polymerization (ATRP) and nitroxide-mediated polymerization (NMP) has been reported to give a MA-enriched random copolymer [1-2]. Starmer patented the radical-initiated synthesis of acrylate/norbornene copolymers, but the maximum incorporation of norbornene in the copolymers was 5% [3]. The copolymerization of norbornen and acrylates by transition metal catalysts has also been investigated. Goodall et al. disclosed the addition copolymerization of norbornene with acrylates in the presence of a Group VIII transition metal catalyst, providing random copolymers [4]. Sen and coworkers described the copolymerization of MA and norbornene using neutral palladium complexes $(L_2)Pd(Me)(Cl)$ or (L)Pd(Me)(Cl) (L= monodentate phospines or one bidentate phosphorus ligand, respectively), producing MA-enriched copolymers [5-6]. A coordination-insertion mechanism has been proposed for these catalysts based on the fact that polymers could be produced in the presence of a “radical inhibitor” (e.g. 4-methoxyphenol). Moreover, the **c**opolymerization of NBE and *tert*-butyl methacrylate has also been reported in the presence of $[Ni(acac)_2]$/MAO catalyst system via the trigger coordination mechanism [7]. It is still a challenge to design catalysts suitable for copolymerization of acrylates with norbornene.

In view of the observed significant attenuation of polymerization activity by polar vinyl monomers for cationic palladium and nickel complexes due to the coordination of the polar functionality to the metal center, attention has turned to the development of less electrophilic, neutral complexes for polymerization of such monomers [8]. Recently, neutral β-ketoiminato nickel(II) complexes have been reported to be promising systems for the homopolymerization of MMA and copolymerization of ethylene with MMA [9-10]. Until now, reports on copolymers of norbornene with MA by using coordination-type catalysts are very few. Taking into account that palladium complex bearing β-ketoiminato ligand when combined with MAO, was found by us to activate the homopolymerization of norbornene and copolymerization of norbornene with 5-norbornene-2-yl acetate [11], herein, we report a cited catalysts, $Pd[CH_3C(O)CHC(NAr)CH_3](PPh_3)(Me)$ (**I** Ar = α-napthyl, **II** Ar = fluorenyl) /MAO catalytic systems (Scheme 1) were used to homopolymerize of MA and copolymerize of norbornene with MA .

Experimental

Materials

All manipulations involving air- and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk and vacuo-line techniques. Solvents were purified using standard procedures. Norbornene (from Aldrich) was distilled over potassium and then dissolved in dried toluene to give 0.4 g/mL solution. MA was dried over CaH_2, and then freshly distilled under vacuo prior to use. Methylaluminoxane (MAO) was prepared by partial hydrolysis trimethylaluminum (TMA) with $Al_2(SO_4)_3{\cdot}18H_2O$ in toluene at 0-60 °C as water source. The initial $[H_2O]/[TMA]$ molar ratio was 1.3. Palladium(II) complexes were synthesized according to our previous work [11].

Instruments

Elemental analyses were performed on a Vario EI microanalyzer. ^{1}H NMR and ^{13}C NMR analyses were performed on a Varian Unity 300 MHz spectrometer at room temperature. FTIR spectra were recorded as KBr pellets on a Perkin-Elmer1600 spectrometer. Gel permeation chromatography (GPC) analyses of molecular weight and molecular weight distribution of the polymers were measured on a Waters 515 instrument using standard polystyrene as the reference and with THF as the eluent at 40 °C.

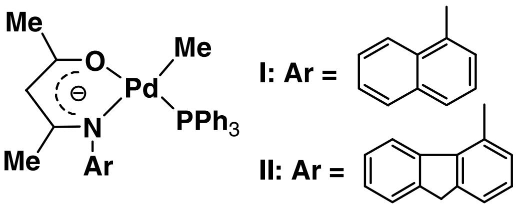
Polymerization

Polymerization was carried out in a 50 mL glass flask equipped with a magnetic stirrer under nitrogen atmosphere. Desired amounts of monomer(s), chlorobenzene, MAO and the total reaction volume were kept 20 mL. The reaction was continuously stirred for an appropriate period at polymerization temperature, which was controlled with an external oil bath. Polymerizations were terminated by addition 200mL of the acidic ethanol (ethanol-HCl, 95:5). The resulting precipitated polymers were collected and treated by filtering, washing with ethanol several times, and drying in vacuum at 60 °C to a constant weight.

Results and discussion

Homopolymerization of MA

The polymerization of MA by palladium complexes, such as neutral pyrrole-imine palladium complexes, [(COD)PdMeCl/PR$_3$] and [(PMePh$_2$)PdMe$_2$] has been described [12-15]. This urges us to investigate if Pd(II)-based β-ketoiminato complexes are capable of catalyzing MA polymerization. Unlike Novak's neutral pyrrole-imine palladium complexes which can be alone used for MA polymerization [12], polymerizations by either the palladium(II) complexes used herein or MAO alone showed no catalytic activity, demonstrating that binary components are necessary to initiate the polymerization of MA. Therefore, all the experiments were carried out in the presence of both components. Table 1 shows the results of polymerization for MA. Polymerizations were carried out using **I**/MAO system at various temperatures from 20 to 80°C with high activity (entry 1-4). The highest catalytic activity of 3.5×10^5 g/(molPd.h) was obtained at 60 °C. The activity values were comparable or even higher than those found by pyrrole-imine palladium complexes [12]. As indicated in Table 1, increasing polymerization temperature caused a substantial decrease of the molecular weight from 329 kg/mol to 103 kg/mol, which were high compared with the corresponding data using other late



Scheme 1. Structure of palladium(II) complexes

transition metal catalysts, such as α-diimine Ni(II)/MAO and Fe(II) and Co(II) pyridyl bis(imine)/MAO systems [16]. In each case, the GPC chromatogram displayed a relatively broad monomodal molecular weight distribution, the M_w/ M_n values being below 3.6. In addition, the influence of the cocatalyst concentration on the catalytic activity and the molecular weight of the obtained polymer were investigated by varying the Al/Pd ratio from 100 to 800 (Table 1, entry 2 and entries 5-7). The activity clearly increased with the Al/Pd ratio up to an optimal value (Al/Pd =500), after which it decreased with further enlarging Al/Pd ratio. The catalyst activities were in the range of 1.1×10^5 – 3.4×10^5 g/(molPd.h), and the molecular weights were in the range of 145 kg/mol – 368 kg/mol.

The atacticity degree of the poly(MA) ascertained from analysis of the methine-coupled and -decoupled ^{1}H NMR spectra in the *mr* = 54-57 % range was present in all cases.

When the **II**/MAO system was used, thus changing both electronic and steric requirement on the metal center, the activity of the catalyst decreased (compare entry 3 and entry 8, Table 1) under the same polymerization conditions. The resulting PMA revealed slightly low molecular weight (M_n = 197 kg/mol) and the same broad distribution (M_w/M_n=3.31). However, an increase in the atacticity degree of the polymer was found (*mr* = 65 %).

Table 1. Polymerizations of MA with Pd(II)/MAO [a].

Entry	Cat.	Tp °C	Al/Pd	Activity	M_n kg/mol	M_w/ M_n	Tacticity [b]		
							mm	*mr*	*rr*
1	**I**	20	300	0.19	329	3.19	0.18	0.54	0.28
2	**I**	40	300	0.28	265	3.24	0.16	0.55	0.29
3	**I**	60	300	0.35	212	3.45	0.22	0.54	0.24
4	**I**	80	300	0.31	103	3.56	0.17	0.57	0.26
5	**I**	40	100	0.11	145	3.48	n.d.	n.d.	n.d.
6	**I**	40	500	0.34	368	3.29	n.d.	n.d.	n.d.
7	**I**	40	800	0.29	287	3.47	n.d.	n.d.	n.d.
8	**II**	60	300	0.27	197	3.31	0.14	0.65	0.21

[a] [Pd] = 0.5 mmol/L, [MA] = 2.91 mol/L, time = 1h, Vtot= 20 mL, Solvent: chlorobenzene. Activity expressed as : 10^6g/(molPd.h); n.d. = not determined.

[b] Determined by means of ^{1}H NMR analysis in $CDCl_3$.

Copolymerization of norbornene and MA

Although the polymerization of MA by palladium complexes has been described [12-14], there is no report on copolymerization of norbornene with MA using these palladium catalysts. Thus, the copolymerization of norbornene with MA using Pd(II)-based β-ketoiminato complexes was tested in the presence of MAO. Taking into account that Pd(II)/MAO catalytic system displayed the best performance in the homopolymerization of MA at 60 °C, preliminary NBE/MA copolymerization experiments were carried out by adopting the above mentioned catalytic components at 60 °C. As mentioned in the introduction, the same Pd(II)-based β-ketoiminato complex in combination with MAO has shown very high activity in norbornene polymerization of up to 8.0×10^7 g/(molPd.h), giving vinyl addition polynorbornenes (PNB) insoluble in common solvents such as cyclohexane, chlorobenzene, and 1,2-dichlorobenzene, 1,2,4-trichlorobenzene [11]. On the other hand, as demonstrated above, this catalytic system also showed high activity for MA homopolymerization. Therefore, crude polymers were extracted by boiling solvents acetone and chloroform in that order. It is known that PMA is completely soluble in acetone whereas PNB is insoluble. On the other hand, chloroform would dissolve copolymeric products with a high content of norbornene co-units, but it is not able to dissolve PNB. The data for polymers obtained with different monomer feed ratios were shown in Table 2 and Table 3. The previously reported results for that obtained with other polymerization systems were also indicated to comparison (entries 16-19). As seen from Table 2, the copolymerization showed greatly reduced yields in comparison with MA homopolymerization in each case, but the crude polymer yields increased with an increase of MA concentration in the feed.

Table 2. Copolymerization of MA and norbornene by Pd(II)/MAO systems [a].

Entry	Catalyst	MA mmol	NBE mmol	MA in feed mol-%	Crude polymer g
9	**I**	9.4	37.4	20.0	1.08
10	**I**	15.4	31.4	32.9	1.28
11	**I**	23.4	23.4	50.0	1.56
12	**I**	31.4	15.4	67.1	1.99
13	**I**	39.0	7.8	83.3	2.93
14	**I**	42.1	4.7	90.0	3.25
15	**II**	23.4	23.4	50.0	1.67
16	**ATRP** [1]	11.2	11.2	50.0	0.91
17	**AIBN** [1]	11.6	10.6	52.2	0.99
18	**NMP** [2]	40.0	40.0	50.0	1.90
19	**Pd(II)** [5]	11.1	11.1	50.0	0.40

[a] Polymerization conditions: [Pd] = 1.64 mmol/L, Al/Pd = 200, Tp = 60 °C, chlorobenzene, Vtot 20mL, time = 20h.

As expected, high molecular weight PMA was completely soluble in boiling acetone (Table 3, entry 3). From Table 3, it was interesting to find that the extraction by boiling solvents of the polymeric products obtained from entries 9 to 12 allowed to obtain three fractions at ratios of MA in feed from 20.0 to 67.1 mol-%. The acetone soluble fractions of the polymers (Fraction A) resulted to contain 72.8-89.7 mol-% of MA units. Due to insolubility of PNB in both acetone and chloroform, any norbornene content measured in the Fraction A should be from the copolymer. A confirmation to the presence in the polymers of both co-units derived from ^{1}H NMR spectrum analysis. Figure 1 showed the ^{1}H NMR spectrum of the Fraction A obtained from entry 11, Table 3. Obviously, the obtained polymer included major peaks from PMA homopolymer and showed a broad singlet at 3.6 ppm for the methoxy group in the acrylate unit, as well as broad resonances between 0.8 and 2.4 ppm.

Table 3. Fraction of crude polymers obtained by Pd(II)/MAO systems for copolymerization of MA and norbornene [a].

Entry	A				B				C
	wt-%	M_n[b]	*PDI*[b]	MA units[c] mol-%	wt-%	M_n[b]	*PDI*[b]	MA units[c] mol-%	wt-%
3	100	212	3.45	100	-	-	-	-	-
9	27.1	15.4	2.54	72.8	22.5	3.3	3.04	53.7	50.4
10	35.0	27.3	2.13	79.5	26.2	4.6	2.93	62.6	38.8
11	48.4	35.8	2.17	82.5	34.8	5.4	2.85	68.9	16.8
12	53.3	42.6	1.95	89.7	38.6	6.2	3.12	74.2	8.1
13	100	-	-	100	-	-	-	-	-
14	100	-	-	100	-	-	-	-	-
15	45.7	25.6	1.98	81.8	40.5	5.1	2.57	64.4	13.8
16	-	2.4	1.2	78.0	-	-	-	-	-
17	-	45.8	2.0	76.0	-	-	-	-	-
18	-	7.0.	1.17	82.0	-	-	-	-	-
19	-	100	2.60	78.7	-	-	-	-	-

[a] Fraction A: acetone soluble; Fraction B: acetone insoluble, chloroform soluble; Fraction C: chloroform insoluble; wt-% expressed as: percentage by weight of the total crude polymer.
[b] M_n expressed as: kg/mol, PDI expressed as M_w/M_n.
[c] As determined by ^1H NMR analysis in $CDCl_3$.

The ^{13}C NMR spectrum of the same sample was used to establish the random nature of the copolymers formed, as shown in Figure 2 (b). The ^{13}C NMR spectrum of the PMA was also showed to comparison (Figure 2 (a)). Compared to the assignment of PMA (175.4 (-***C***(O)O), 52.4 (-O***C***H$_3$), 41.9(-***C***H-), 35.6(-***C***H$_2$-)), the carbonyl peak of MA (175.0 ppm) in Figure 2 (b) shifted to a higher field than pure PMA. In general, a chemical shift to a higher field implies that the carbonyl group of MA is in a diluent segment. In light of the chemical structure of PNB, the nonpolar group of PNB may act as an inert diluent segment for the carbonyl group of MA. If PNB and PMA were physically mixed, we would not expect any chemical shift of the MA carbonyl because of no specific interaction between two polymers. The peaks at δ 175.0 (-**C**(O)O), 52.1 (-O**C**H$_3$), 41.7(-**C**H-) which was the same as in homo-PMA, resulted from consecutive long MA runs. The methylene carbon of methyl acrylate was unable to be seen because it was hidden by norbornene multiplets which appeared from 33.8 to 49.9 ppm. According to literature, additional resonances (30.9-29.9, 28.8, 22.1 ppm) were assigned for the acrylate-norbornene sequence [1]. Moreover, the peak intensity of the junction part was comparable with that of MA or norbornene units, indicating random copolymer was present, in agreement with those reported for the same copolymers by radical polymerization systems [1-2].

These acetone soluble fractions of the polymers were characterized by Gel permeation chromatography (GPC), which showed relatively low molecular weights compared to PMA with unimodal distributions. As shown in Table 3, there was an increase in molecular weight of the copolymers from 15.4 to 42.6 kg/mol with increasing amounts of MA in feed. These values of molecular weight were comparable to obtained with other neutral palladium catalysts (Table 3, entry 19). And the value of M_w/M_n was below 2.5.

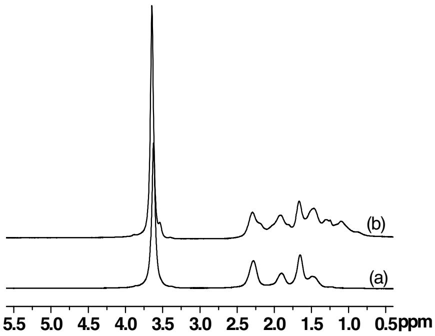


Figure 1. ^1H NMR spectra of (a) PMA in entry 3, Table 1 and (b) acetone soluble fraction of polymer (Fraction A) in entry 11, Table 3 at $CDCl_3$.

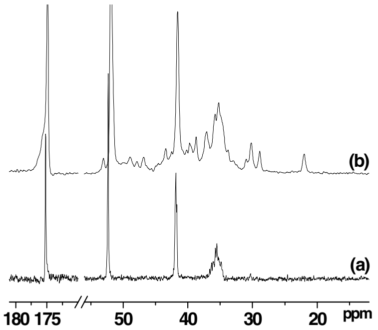


Figure 2. ^{13}C NMR spectra of (a) PMA in entry 3, Table 1 and (b) acetone soluble fraction of polymer (Fraction A) in entry 11, Table 3 at $CDCl_3$.

After extracting with boiling acetone, further extraction polymeric products obtained from entries 9 to 12 with boiling chloroform (Fraction B) yielded enriched in MA units polymers in the 53.7-74.2 mol-% range, and the incorporation of MA into the polymer increased with increasing the ratio of MA to norbornene in the feed. The GPC showed the molecular weight increased from 3.3 to 6.2 kg/mol with increasing MA ratio in feed with unimodal distributions, in good agreement with those obtained through radical polymerization systems reported by Sen and coworkers [1-2] (Table 3, entry 16, 18), but lower than the same polymer obtained with other neutral palladium catalysts and AIBN (Table 3, entry 17 and 19). However, these values appeared five-fold lower as compared with those obtained from corresponding Fraction A, attributable to higher norbornene incorporation in Fraction B.

The ^{13}C NMR spectrum of the Fraction B obtained from Table 3, entry 11 was shown in Figure 3, which closely matched those for analogous polymer prepared in Fraction A (Figure 2). However, it was clear that the relative intensity of peaks at δ 175.2 (-**C**(O)O), 52.2 (-O**C**H$_3$), 41.6(-**C**H-) as compared with norbornene multiplets in Figure 3 were less intense than that of in Figure 2 (b), which verified that higher content of norbornene incorporation in Fraction B. Moreover, as evidenced by ^{13}C NMR spectrum (Figure 2 (b) and 3), atactic copolymers were obtained from both Fraction A and Fraction B, consistent with that of PMA obtained from homopolymerization. And the characteristic peak from C=C double bond due to ROMP was absent from the spectra, which implied that the copolymerization of norbornene and MA catalyzed by Pd(II)/MAO catalyst system took place without ring opening and via an addition polymerization.

In all the chloroform insoluble fractions (Fraction C) a very low content of MA units was present through FT-IR spectrum analysis (Figure 4). The FTIR spectra revealed the band at 1740 cm^{-1}, connected with the stretching vibration of aliphatic ester groups in MA co-units was clearly present. Moreover, the absence of bands at 1680-1620 cm^{-1}, indicative of a fully saturated polymer, confirmed that the polymer was produced by vinyl polymerization. However, these polymers were insoluble in chlorobenzene, 1,2-dichlorobenzene, and 1,2,4-trichlorobenzene.

In general, the increase of MA amount in the feed provoked an increase of percentage by weight for both Fraction A and Fraction B, but a decrease for Fraction C.

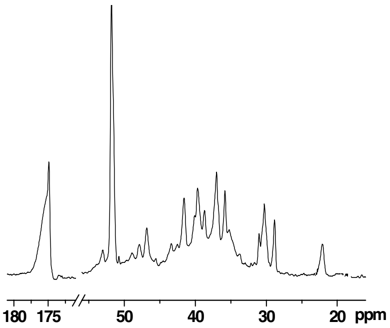


Figure 3. ^{13}C NMR spectrum of acetone insoluble, chloroform soluble fraction of polymer (Fraction B) in entry 11, Table 3 at $CDCl_3$.

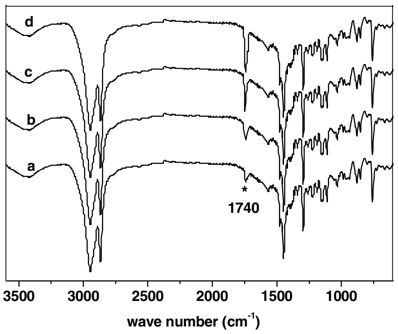


Figure 4. IR spectrum of chloroform insoluble fractions derived from (a) entry 9, (b) entry 10, (c) entry 11, (d) entry 12 in Table 3.

In addition, Fraction A displayed higher MA incorporation and higher molecular weights than that of corresponding Fraction B.

On the other hand, those deriving from entries 12 and 13 at high ratios of MA in feed (83.3 mol-% and 90.0 mol-%, respectively) resulted only PMA. The same observation occurred for the copolymerization of norbornene and MA by well-documented radical polymerization systems [1-2].

As reported in Table 3, when **II**/MAO system was used to copolymerize MA and norbornene starting from MA in feed equal to 50 mol-% (entry 15), the resulting catalyst displayed a slight improved yield. And the related crude polymeric product also obtained three fractions after extraction with boiling solvents mentioned above. Both Fraction A and Fraction B produced MA enriched polymers with the former possessing higher molecular weight (M_n = 25.7 and M_n = 5.1 kg/mol, respectively), which was slightly low as compared with the corresponding polymers obtained with **I**/MAO system (Table 3, entry 11). The composition of the resulting polymer was substantially the same as that obtained in entry 11. Fraction C possessed a low content of MA units through FT-IR spectrum analysis, but it was insoluble in common solvents. Interestingly, copolymerization of MA and norbornene catalyzed by Pd(II)/MAO systems used herein yielded three fractions with different molecular weights and different content of MA incorporation, which is different from those reported by radical systems or by other Pd(II) systems. A detailed investigation of norbornene and MA copolymerization mechanism catalyzed by Pd(II)/MAO is underway to determine and will be present in future paper.

Conclusions

The β-ketoiminato palladium(II) complexes were highly active catalyst for MA homopolymerization in the presence of MAO, producing atactic high molecular weights PMA. Likewise, norbornene and MA have been successfully copolymerized. When ratios of MA in feed ranged from 20.0 to 66.7 mol-%, three fractions were obtained. Both the acetone soluble fractions and acetone insoluble, chloroform soluble fractions gave invariably MA-enriched copolymers with the former possessing higher molecular weights. The chloroform insoluble fractions showed low content MA incorporation, but insoluble in common solvents. However, at high ratios of MA in feed (83.3 mol-% and 90.0 mol-%, respectively) only PMA was present. NMR spectrum analysis indicated random vinyl addition copolymer was formed.

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