

Studies on new palladium(II) catalyst system for copolymerization of CO with ethylene

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Abstract

In this paper, a new class of four-membered catalyst system, PdCl₂/MA_n/DPPP¹/CF₃COOH, was firstly studied for copolymerization of CO with ethylene to prepare linear alternating polyketone, in which MA_n component was mainly studied. The experimental results showed that this kind of new catalyst system exhibited highly efficient activity; especially when Cd(OAc)₂·2H₂O, Zn(OAc)₂·4H₂O, Fe(ClO₄)₃·9H₂O, Pb(OAc)₂·3H₂O and Cu(OAc)₂·H₂O were used as MA_n component, the corresponding catalyst system had very highly efficient activity of 8100, 7100, 6000, 6000 and 5800 g polyketone/(g Pd h), respectively, under conditions of 6.5 MPa and 110°C. The effects of MA_n component were also investigated; the results showed that suitable MA_n was probably a metal compound of weakly coordinating anions; Mⁿ⁺ probably coordinated with Cl⁻ more strongly than palladium(II); the stability of chelate complex (c) of Mⁿ⁺ with DPPP was probably between mono-chelate ring and bis-chelate ring complexes of palladium(II) with DPPP. This new highly efficient catalyst system had the advantages of having high stability and low cost. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium(II) catalyst; Polyketone; Carbon monoxide; Ethylene; Copolymerization

1. Introduction

The copolymerization of CO with ethylene to prepare polyketone has attracted much interest both in academic studies and industrial applications in the past 20 years [1–4], and has developed very quickly. Up to now, it has been reported that SHELL has been building industrial devices of several 10,000 tons/year, used to produce linear alternating polyketones. Aliphatic polyketone belongs to high-grade functional material. When compared with traditional polyethylene, in terms of comonomers, 50% ethylene was used instead of cheap CO directly to prepare

fine chemical products with high attached value; by this way, petroleum resources were saved, and coal resources and CO from other chemical processes obtained as a by-product were utilized finely and reasonably. Therefore, this is an important route to utilize coal resources finely. In terms of product performances, besides good mechanical properties, good solvent resistance and unpoisonous property, polyketones have excellent photodegradable ability, with which “white pollution” could be avoided; therefore, polyketones are friendly to the environment. In terms of application, polyketone could be used widely, e.g., to manufacture film for agricultural use, spare parts of automobile, long effect and slow-releasing fertilizer, etc. In addition, polyketone could be transferred to other functional polymers by chemical reactions

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¹ 1,3-Bis(diphenylphosphino)propane.

of carbonyl groups in the backbone. It was reported that polyketone could be transferred to more than 20 kinds of functional polymers, such as polyalcohol and polyammonia, etc., showing good developing prospects.

Linear alternating polyketone was prepared with transition-metal-catalyzed copolymerization of CO with ethylene. In the 1940s, Reppe and Margin [5] firstly prepared alternating polyketone with $K_2[Ni(CN)_4]$ as catalyst. In the 1970s, many researchers were attracted to study transition metal catalysts for alternative copolymerization of CO with ethylene. Iwashita et al. [6] and Iwashita and Sakuraba [7] used $Rh_4(CO)_{12}$ as catalyst. Fenton [8,9] used $Pd(CN)_2$ and $Pd(CN)_2/RCOOH$ ($R=CHCl_2$, CH_2Cl , CF_3) as catalysts. Nozaki [10,11] used $PdCl_2/PPh_3$, $Pd(PPh_3)_2Cl_2$, $HPd(CN)_3/PPh_3$, and $Pd(PPh_3)_4$ as catalysts. Shryne and Holler [12] used $Ni(CN)_2$ as catalyst, etc. The abovementioned catalysts usually had very low activity, and the obtained polyketones were usually oligomers with low molecular weight, and therefore had little application significance.

In the early 1980s, Drent [13,14] of SHELL successfully developed the $Pd(OAc)_2/DPPP/CF_3COOH$ catalyst system [15]. The application of bidentate ligands, DPPP, has made a breakthrough improvement in catalysts studies. Both the catalytic activity and molecular weight were increased significantly, making the commercial utilization of polyketone possible. After that, SHELL researched on various bidentate ligands extensively, e.g., with 1,3-bis(bis(2-methoxyphenyl)phosphino)propane instead of DPPP, and the activity of the corresponding catalyst system was increased evidently [16,17]; with tetraphosphine ligands instead of DPPP, the corresponding catalyst system was increased greatly, meanwhile the problem of polymer blocking in reactor was avoided [18]. Recently, Drent [19] studied $Ni(OAc)_2/1,2$ -bis(bis(2-methoxyphenyl)phosphino)ethane/ CF_3COOH , but the activity was much lower than the corresponding palladium(II) catalyst system. Besides SHELL, many other companies also made great efforts on developing catalysts for preparing polyketone. BP mainly studied the cocatalyst or anions [20–23], or used P–O/Pd(II) chelate complex as catalysts [24]. Akzo Nobel synthesized chelate complexes [$Pd(DPPP)$

$(CH_3CN)_2][Tos]_2$ [25] and [$Pd(DPPP)(CH_3CN)_2][B(C_6F_5)_4]_2$, [$Pd(DPPP)(CH_3CN)_2][BPh_4]_2$ [26] as catalyst precursor. Enichem synthesized [$Pd(chel)(chel')][A]_2$ as catalyst precursor [27], or used $Cu(OAc)_2/DPPP/CF_3COOH$ as catalyst system having very weak activity [28,29]. In conclusion, it is the focus to improve the catalyst by researching for more suitable metal center, bidentate ligand and anion cocatalyst, etc.

$Pd(OAc)_2/DPPP/CF_3COOH$ catalyst system has very high catalytic activity. But when $PdCl_2$ was used instead of $Pd(OAc)_2$, the corresponding catalyst system, $PdCl_2/DPPP/CF_3COOH$, only had very weak activity [15]. $Pd(OAc)_2$ was usually prepared from $PdCl_2$ via two steps. Therefore, its price was much higher than that of $PdCl_2$. In order to improve this kind of catalyst system, here a second metal compound (MA_n) was introduced into the $PdCl_2/DPPP/CF_3COOH$ catalyst system to form a new class of four-membered catalyst system, $PdCl_2/MA_n/DPPP/CF_3COOH$, the catalytic activity of which could be increased by over 100 times, and could be comparable with the catalyst system, $Pd(OAc)_2/DPPP/CF_3COOH$, at similar conditions. Moreover, this new four-membered catalyst system had more stability and lower cost. When $Cd(OAc)_2 \cdot 2H_2O$, $Zn(OAc)_2 \cdot 4H_2O$, $Fe(ClO_4)_3 \cdot 9H_2O$, $Pd(OAc)_2 \cdot 3H_2O$, and $Cu(OAc)_2 \cdot H_2O$ were used as MA_n component, the corresponding catalyst systems reached high activity of 8100, 7100, 6000, 6000 and 5800 g polyketone/(g Pd h). In this paper, the studies on this new catalyst system were presented.

2. Experimental

2.1. General considerations

Carbon monoxide is the product of Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences. Ethylene is the product of polymer grade of 303 plant of Lanzhou Petroleum Chemical. $Pd(OAc)_2$ was prepared by myself. Other reagents were of commercial grade.

The nuclear magnetic resonance (NMR) spectra of polyketones were recorded on a Bruker AM400 spectrometer.

2.2. General procedure for CO/ethylene copolymerization

The device used for CO/ethylene copolymerization has been reported elsewhere [30]. Copolymerization was carried out in a 200 ml stainless steel autoclave. First, solid catalyst components, including PdCl₂, DPPP and MA_n, were weighed accurately and added into the autoclave directly immediately, the autoclave was sealed and was purged with ethylene at least three times, then the solvent containing needed CF₃COOH was introduced and ethylene was charged to chosen pressure. After the autoclave was heated to chosen temperature in 30 min, equimolar CO was introduced and total pressure was controlled at about 6.5 MPa during the copolymerization by introducing equimolar CO and ethylene. After reaction for 1 or 2h, the autoclave was rapidly cooled, and the unreacted gases were vented. The product slurry was filtered off, washed with fresh methanol, and dried in the air to give snow white powder. The average catalytic activity was calculated from copolymer weight as unit of gram polyketone/(g Pd h).

3. Results

3.1. Studies on various MA_n components under conditions of Pd(II)/DPPP=1:1.5 and Pd²⁺:Mⁿ⁺=1:5

PdCl₂/MA_n/DPPP/CF₃COOH catalyst system was studied with 14 different MA_n components under conditions of Pd(II)/DPPP=1:1.5 and Pd²⁺:Mⁿ⁺=1:5. The results are listed in Table 1.

Table 1 shows clearly that, without MA_n component, PdCl₂/DPPP/CF₃COOH catalyst system had very weakly catalytic activity, and only trace product was obtained. When MA_n was introduced, PdCl₂/MA_n/DPPP/CF₃COOH catalyst system exhibited high activity. When Cd(OAc)₂·2H₂O, Zn(OAc)₂·4H₂O, Fe(ClO₄)₃·9H₂O, Pd(OAc)₂·3H₂O, and Cu(OAc)₂·H₂O were used as MA_n, the activities of the corresponding catalyst systems were increased greatly and reached 8100, 7100, 6000, 6000 and 5800 g polyketone/(g Pd h), respectively. When Al(O-*iso*-Pr)₃, Ni(OAc)₂·4H₂O, Co(OAc)₂·4H₂O, Mn(OAc)₂·4H₂O, Cr(OAc)₃, Mg(ClO₄)₂,

Table 1

Studies on PdCl₂/MA_n/DPPP/CF₃COOH catalyst system with various MA_n under Pd(II)/DPPP=1:1.5. General conditions: copolymerization was carried out in 200 ml autoclave. PdCl₂/DPPP=1:1.5, PdCl₂/MA_n=1:5, DPPP 12.6 mg, CF₃COOH 0.08 ml, CH₃OH 50 ml, total pressure 6.5 MPa, CO:ethylene=1:1, under 110°C and reaction for 60 min

PdCl ₂ (mg)	MA _n (mg)	Yield (g)	Rate (g/(g Pd h))
3.6	Cd(OAc) ₂ ·2H ₂ O, 26.2	17.4	8100
3.4	Zn(OAc) ₂ ·4H ₂ O, 22.3	14.4	7100
3.7	Fe(ClO ₄) ₃ ·9H ₂ O, 53.7	13.3	6000
3.8	Pb(OAc) ₂ ·3H ₂ O, 38.9	13.6	6000
3.5	Cu(OAc) ₂ ·H ₂ O, 20.9	12.2	5800
3.6	Al(<i>o-iso</i> -Pr) ₃ , 20.4	5.8	2700
3.4	Ni(OAc) ₂ ·4H ₂ O, 25.1	4.0	2000
3.8	Co(OAc) ₂ ·4H ₂ O, 24.6	4.5	2000
3.9	Mn(OAc) ₂ ·4H ₂ O, 25.4	7.5	3200
3.7	Cr(OAc) ₃ , 23.2	4.8	2200
3.5	Mg(ClO ₄) ₂ , 23.8	5.8	2800
3.7	La(OAc) ₂ ·1.5H ₂ O, 34.8	4.8	2200
3.8	LiClO ₄ ·3H ₂ O, 33.0	5.8	2550
3.7	Hg(OAc) ₂ , 32.8	1.0	450
3.6	no	trace	for comparison

La(OAc)₂·1.5 H₂O and LiClO₄·3H₂O were used as MA_n, the activities of corresponding catalyst systems were increased significantly and reached 2700, 2000, 2000, 3200, 2200, 2800, 2200 and 2550 g polyketone/(g Pd h), respectively. When Hg(OAc)₂ was used as MA_n, the activity of corresponding catalyst system was increased evidently, and reached 450 g polyketone/(g Pd h).

3.2. Studies on different MA_n under conditions of Pd(II)/DPPP=1:6, Pd²⁺/Mⁿ⁺=1:1.5 and (Pd²⁺+Mⁿ⁺)/DPPP=1:1

PdCl₂/MA_n/DPPP/CF₃COOH catalyst system was studied with four different MA_n components, under conditions of Pd(II)/DPPP=1:6, Pd²⁺/Mⁿ⁺=1:1.5 and (Pd²⁺+Mⁿ⁺)/DPPP=1:1. The results are listed in Table 2.

Table 2 shows clearly that, at high DPPP/Pd(II) mole ratio, without MA_n, the catalyst system, PdCl₂/DPPP/CF₃COOH, had no activity. But when MA_n was introduced, the four-membered catalyst system showed high activity. When Ag(OAc) was used as MA_n, the activity of corresponding catalyst system was increased significantly, and reached

Table 2

Studies on PdCl₂/MA_n/DPPP/CF₃COOH catalyst system with different MA_n under Pd(II)/DPPP=1:6. General conditions: copolymerization was carried out in 200 ml autoclave, using 50 ml CH₃OH as solvent and reaction for 60 min. CO:Ethylene=1:1, PdCl₂/DPPP=1:6, Pd²⁺/Mⁿ⁺=1:5, (Pd²⁺+Mⁿ⁺)/DPPP=1:1

PdCl ₂ (mg)	MA _n (mg)	DPPP (mg)	CF ₃ COOH (ml)	Temperature (°C)	Pressure (MPa)	Yield (g)	Rate (g/(g Pd h))
3.6	Ag(OAc), 10.2	13.1	0.1	90	7.0	6.9	3200
3.6	Cu(OAc) ₂ ·H ₂ O, 20.6	49.6	0.16	90	6.5	4.0	1860
3.7	Al(<i>o-iso-Pr</i>) ₃ , 20.0	49.9	0.16	115	7.0	1.7	770
3.6	Hg(OAc) ₂ , 32.8	50.0	0.16	111	7.4	0.2	90
3.6	no	50.0	0.16	111	7.4	0	for comparison

Table 3

Studies on PdCl₂/Cu(OAc)₂·H₂O/DPPP/CF₃COOH catalyst system. General conditions: copolymerization was carried out in 200 ml autoclave under 6.5 MPa and reaction for 60 min, CO:ethylene=1:1, (Pd²⁺+Cu²⁺)/DPPP=1:1

PdCl ₂ (mg)	Cu(OAc) ₂ ·H ₂ O (mg)	DPPP/Pd (mole ratio)	Cu/Pd (mole ratio)	CF ₃ COOH (ml)	CH ₃ OH (ml)	Temperature (°C)	Yield (g)	Rate (g/(g Pd h))
4.2	20.3	5.1	4.3	0.16	50	112	16.5	6600
Filtrate of the above experiment						111	7.2	2860
2.1	40.7	18.5	17.2	0.32	100	115	13.8	11,000
2.2 ^a	40.3	21.4	20.6	0.32	50	95	10.4	10,000
1.9	40.0	19.9	18.7	0.32	100	116	21.8	9600 ^b
2.1	no	22		0.32	100	116	0	for comparison
2.2 ^a	no	21.4		0.32	100	116	0	

^aPd(OAc)₂ was used here.

^bReaction for 2 h.

3200 g polyketone/(g Pd h) when Cu(OAc)₂·H₂O, Al(*o-iso-Pr*)₃ and Hg(OAc)₂ were used as MA_n, and the activities of corresponding catalyst systems reached 1860, 770 and 90 g polyketone/(g Pd h), respectively.

3.3. Studies on PdCl₂/Cu(OAc)₂·H₂O/DPPP/CF₃COOH catalyst system

The results of studies on PdCl₂/Cu(OAc)₂·H₂O/DPPP/CF₃COOH catalyst system under different DPPP/Pd(II) mole ratios are listed in Table 3. From Table 3, it could be concluded that under high DPPP/Pd(II) mole ratio, without Cu(OAc)₂·H₂O, the corresponding catalyst system had no activity, but when Cu(OAc)₂·H₂O was introduced, and (Pd²⁺+Cu²⁺)/DPPP=1:1, under high DPPP/Pd(II) mole ratio, such as 5.1, 18.5, 19.9, the corresponding catalyst system reached high activity of 6600, 11000, 9600 g polyketone/(g Pd h), respectively. For catalyst system Pd(OAc)₂/DPPP/CF₃COOH,

under DPPP/Pd(II)=21.4, it showed no activity. But when Cu(OAc)₂·H₂O was introduced and (Pd²⁺+Cu²⁺)/DPPP=1:1, the corresponding catalyst system, Pd(OAc)₂/Cu(OAc)₂·H₂O/DPPP/CF₃COOH, reached high activity of 10,000 g polyketone/(g Pd h). With the filtrate as catalyst solution for catalyst system, PdCl₂/Cu(OAc)₂·H₂O/DPPP/CF₃COOH, the catalytic activity was still very high and reached 2860 g polyketone/(g Pd h) calculated as the initial palladium loading.

4. Discussion

4.1. Effects of MA_n

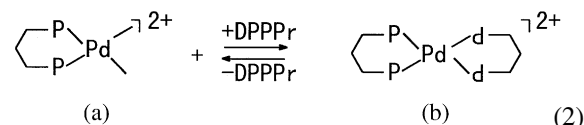
The three-membered catalyst system, PdCl₂/DPPP/CF₃COOH, had very weak activity for copolymerization of CO with ethylene. When MA_n was introduced, a new four-membered catalyst system, PdCl₂/MA_n/DPPP/CF₃COOH, showed high activity,

indicating that MA_n was an essential component for this highly efficient catalyst system. In order to improve $Pd(OAc)_2/DPPP/CF_3COOH$ catalyst system or research for new catalyst system for copolymerization of CO with ethylene, many researchers studied the catalytic mechanism deeply and extensively [2,3,15,31–40], and suggested that the active catalytic species were chelate cationic complexes of palladium(II) with DPPP; suitable bidentate ligand, e.g., DPPP, had good stability on palladium(II) center; suitable anions, e.g., CF_3COO^- , was easy to leave away to provide the coordinate vacant of palladium(II). Cl^- could be coordinated with palladium(II) strongly and was not easy to leave away to provide the coordinate vacant [40,41]; therefore $PdCl_2/DPPP/CF_3COOH$ catalyst system only had very weak activity. When MA_n was introduced, the corresponding catalyst system, $PdCl_2/MA_n/DPPP/CF_3COOH$, had high activity; the reason was probably that A^- in MA_n was weakly coordinating anions, and M^{n+} was probably coordinated with Cl^- more strongly than palladium(II) (see Eq. 1), letting palladium(II) leave out its coordinate vacant to comonomers to reach high activity. Therefore, suitable MA_n was probably metal compound of weakly coordinating anions, and M^{n+} could coordinate with Cl^- more strongly than palladium(II). Table 1 shows that $Cd(OAc)_2 \cdot 2H_2O$, $Zn(OAc)_2 \cdot 4H_2O$, $Fe(ClO_4)_3 \cdot 9H_2O$, $Pd(OAc)_2 \cdot 3H_2O$, and $Cu(OAc)_2 \cdot H_2O$ may have this function:



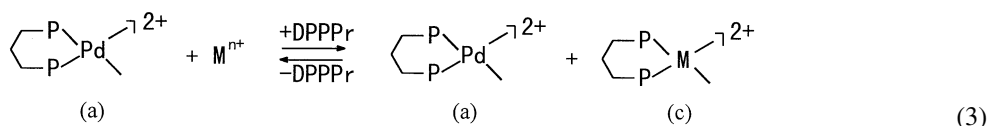
In order to investigate the coordination of palladium(II) with DPPP, our group has even studied catalyst system, $Pd(OAc)_2/DPPP/CF_3COOH$, with high pressure in situ ^{31}P NMR techniques [40,42]. For $Pd(OAc)_2/DPPP/CF_3COOH$ catalyst system, the highest efficient catalytic activity was reached at $DPPP/Pd(II)=1.5$. In situ ^{31}P NMR studies showed that when $DPPP/Pd(II)$ was 1.5, two equimolar

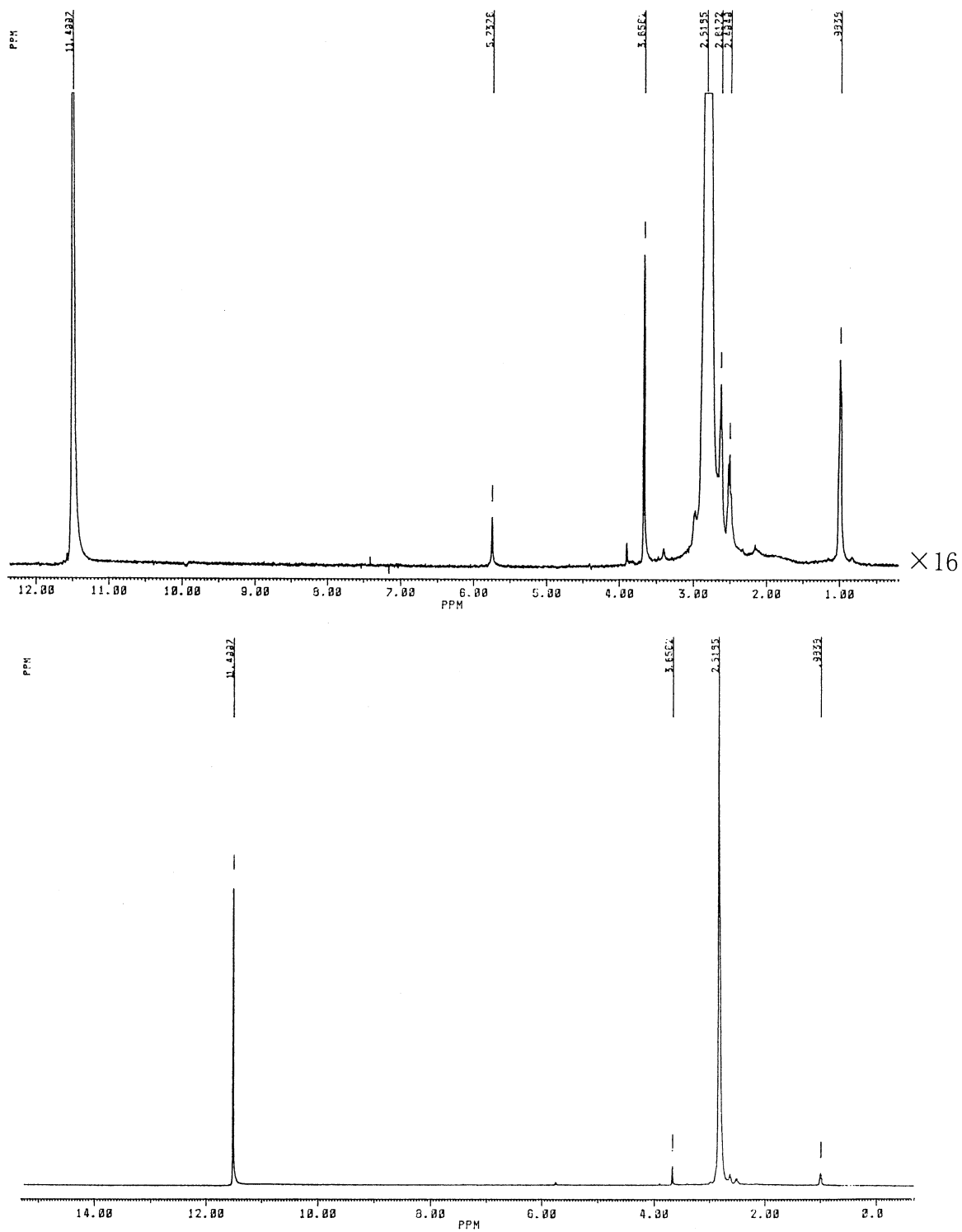
complexes of mono-chelate ring complex (a) and bis-chelate ring complex (b) were produced, and they had interconversion relationship (see Eq. 2):



Only mono-chelate ring complex (a) had catalytic activity, indicating that only half of the Pd(II) center in the system had catalytic activity. Although bis-chelate ring complex (b) had no activity, when the diphosphine ligand in mono-chelate ring complex (a) was decomposed, bis-chelate ring complex (b) could provide a ligand to keep the active state of Pd(II).

In order to investigate the coordination of DPPP with Pd(II) and M^{n+} in four-membered catalyst system, in this paper, copolymerization was carried out under different DPPP/Pd(II) mole ratios and $(Pd^{2+} + M^{n+})/DPPP=1:1$. In Table 1, DPPP/Pd(II) was 1.5, in Table 2, DPPP/Pd(II) mole ratio was 6, in Table 3, the highest DPPP/Pd(II) mole ratio reached 22. Experimental results showed that, under different DPPP/Pd(II) mole ratios, catalyst system, $PdCl_2/MA_n/DPPP/CF_3COOH$, and catalyst system, $Pd(OAc)_2/Cu(OAc)_2 \cdot H_2O/DPPP/CF_3COOH$, all showed highly efficient activity. The studies on catalyst system $Pd(OAc)_2/DPPP/CF_3COOH$ showed that when DPPP/Pd(II) mole ratio was above 2.5, the catalyst system deactivated completely [30,40]. The above statement probably suggested that MA_n coordinated with DPPP and produced chelate complex (c); the stability of chelate complex (c) may be between mono-chelate ring and bis-chelate ring complexes of Pd(II) with DPPP; therefore, Eq. 2 may be transferred to Eq. 3. By this way, probably more than half of the Pd(II) center could be made in active mono-chelate ring state, so the catalyst system was improved. In conclusion, suitable MA_n could coordinate with DPPP to produce chelate ring complex (c), whose stability was probably between the mono-chelate ring and bis-chelate ring complexes of Pd(II). From Tables 2 and 3, $Cu(OAc)_2 \cdot H_2O$ may have this effect.



Fig. 1. ^1H NMR of polyketone prepared with new four-membered catalyst system.

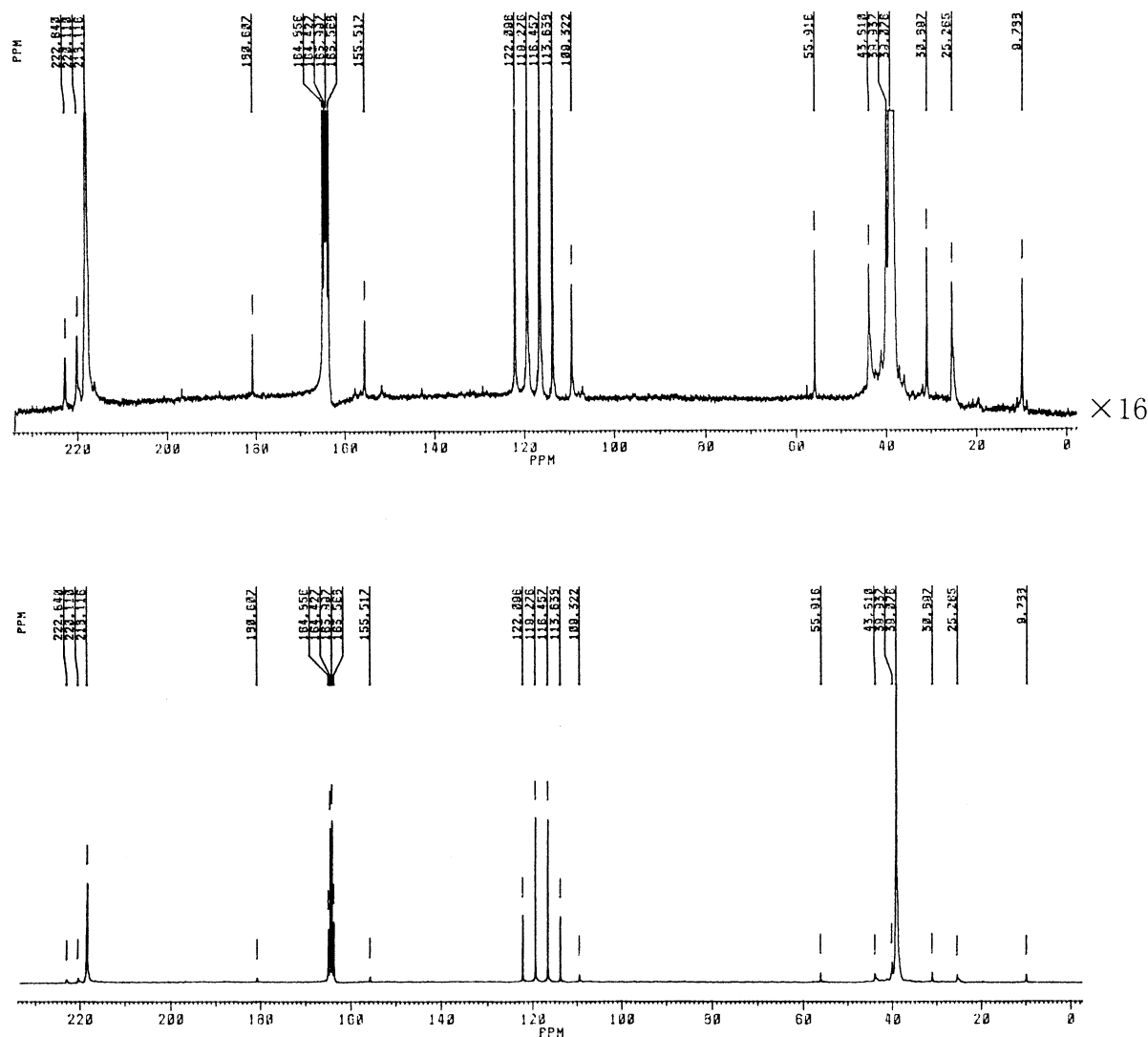
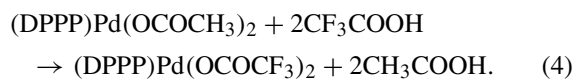


Fig. 2. ^{13}C NMR of polyketone prepared with new four-membered catalyst system.

In conclusion, the four-membered catalyst system, $\text{PdCl}_2/\text{MA}_n/\text{DPPP}/\text{CF}_3\text{COOH}$, generated an active catalyst in the form of $(\text{DPPP})\text{Pd}(\text{OCO}-\text{CF}_3)_2$ for copolymerization of CO with ethylene (see Eq. 4):



4.2. The stability of new four-membered catalyst system

Although chelate complex (c) had no catalytic activity, its participation could probably make more than half of the Pd(II) center in active mono-chelate ring state (a). Moreover, when the diphosphine of mono-chelate ring complex (a) is decomposed, com-

plex (c) could provide diphosphine to keep Pd(II) in active state (a). Therefore, complex (c) could increase the catalytic activity, make the catalytic species more stable, and prolong the catalyst life. Table 3 shows that the filtrate after the copolymerization still had high activity, and that clearly, the new four-membered catalyst system was very stable, and could be used again without further activation. Moreover, no palladium(0) black was observed on the inner wall with new four-membered catalyst system, but palladium(0) black was usually observed on the inner wall with traditional Pd(OAc)₂/DPPP/CF₃COOH catalyst system under similar conditions, showing the decomposition of catalytic palladium(II) species. The above statement showed that the new four-membered catalyst system was more stable and had significance in industrial application for producing polyketone.

4.3. The cost of the new four-membered catalyst system

The cost of highly efficient PdCl₂/MA_n/DPPP/CF₃COOH catalyst system was reduced by using PdCl₂ instead of Pd(OAc)₂. The added MA_n component was rich metal compound and very cheap. The new four-membered catalyst system was also cheap. Therefore, new four-membered catalyst system was cheaper than traditional Pd(OAc)₂/DPPP/CF₃COOH catalyst system, and had competitive superiority in industrial application.

5. Characterization of polyketones

In order to prove that the product produced with the new four-membered catalyst system was linear alternating polyketone, here the ¹H NMR and ¹³C NMR spectra of polyketones prepared with new four-membered catalyst systems of Cd(OAc)₂·2H₂O, Zn(OAc)₂·4H₂O, Fe(ClO₄)₃·9H₂O, Pd(OAc)₂·3H₂O and Cu(OAc)₂·H₂O were recorded on high-resolution NMR spectrometer.

The ¹H NMR and ¹³C NMR spectra are shown in Figs. 1 and 2, and their attributions are listed in Tables 4 and 5. The results showed that polyketones prepared with new four-membered catalyst systems had strictly linear alternating structure; in the backbone,

Table 4

Attributions of ¹H NMR of polyketone prepared with new catalyst system

Chemical shift	Attributions
0.98	CH ₃ CH ₂ CO-
2.49	CH ₃ CH ₂ CO-
2.82 (main)	-(CH ₂ CH ₂ CO) _n -
3.66	-COOCH ₃
5.74	furan ring ^a

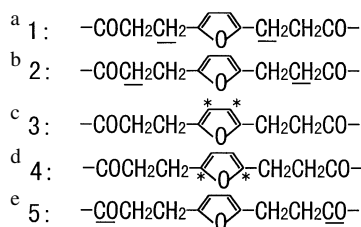
^aFormed by intramolecular condensation of part of the 1,4-diketone unit of the polyketone backbone.

Table 5

Attributions of ¹³C NMR of polyketone prepared with new catalyst system*

Chemical shift		Attributions
Experimental	Calculated	
9.79	9.41	-COCH ₂ CH ₃
25.27	24.90	^a
30.90	30.41	-CH ₂ CH ₂ COOCH ₃
39.08 (main)	39.41	-(CH ₂ CH ₂ CO) _n -
39.94	39.41	-CH ₂ CH ₂ COOCH ₃
43.81	41.1	^b
55.92	51.4	-COOCH ₃
109.32	104.6	^c
155.52	154.2	^d
180.61		-COOCH ₃
218.12 (main)		-(CH ₂ CH ₂ CO) _n -
220.11		^e
222.64		-COCH ₂ CH ₃

*Note: furan ring was formed by intramolecular condensation of part of the 1,4-diketone unit of the polyketone backbone.



only trace segment of furan ring was observed, whose quantity was comparable with end groups.

6. Conclusions

(1) A new class of four-membered catalyst system, PdCl₂/MA_n/DPPP/CF₃COOH, was studied, and the results showed that when Cd(OAc)₂·2H₂O,

Zn(OAc)₂·4H₂O, Fe(ClO₄)₃·9H₂O, Pd(OAc)₂·3H₂O and Cu(OAc)₂·H₂O were used as MA_n, the corresponding catalyst systems had very highly catalytic activity for copolymerization of CO with ethylene.

(2) The effects of MA_n were investigated, and showed that suitable MA_n was probably metal compound of weakly coordinating anions; Mⁿ⁺ could probably coordinate with Cl⁻ more strongly than Pd(II); the stability of chelate complex (c) of Mⁿ⁺ with DPPP was probably situated between mono-chelate ring and bis-chelate ring complexes of Pd(II).

(3) Compared with traditional Pd(OAc)₂/DPPP/CF₃COOH catalyst system, the new four-membered catalyst system had the advantages of having more stability and lower cost, and therefore had significance in industrial application.

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