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Studies on the Copolymerization of Norbornene with CO Catalyzed by a New Catalytic System $PdCl_2$/phen/$M(CF_3SO_3)_n$[1]

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Abstract—A new three-component catalytic system, $PdCl_2$/phen/$M(CF_3SO_3)_n$ where M = La, Y, Yb, Zn, and Cu, was studied for the copolymerization of norbornene (NBE) with CO to prepare polyketone (PK). It was found that the CF_3SO_3H catalytic system gave a low catalytic activity for the copolymerization of norbornene with CO, but when $M(CF_3SO_3)_n$ was introduced instead of CF_3SO_3H, the $PdCl_2$/phen/$M(CF_3SO_3)_n$ catalytic system exhibited much higher activity. The effects of ligands, $M(CF_3SO_3)_n$, solvents, and temperatures on the copolymerization have been discussed in detail. The results showed that with 1,10–phenanthroline (phen) and $Cu(CF_3SO_3)_2$ used as cocatalysts, the corresponding reaction rate reached 82 000 g PK $(\text{mol Pd})^{-1}$ h^{-1} when the reaction was carried out in methanol at 90°C and 3.0 MPa of CO, and the weight average molecular weight (M_w) of the resultant copolymer is 1090 g/mol. The copolymer was characterized with various techniques such as FT–IR, ^{1}HNMR, ^{13}CNMR, TGA, and DSC. The infrared spectrum of the product includes two features at 1697 and 1732 cm^{-1} for the NBE/CO copolymer in CH_3OH that are attributed to carbonyl groups in ketones (repeating unit) and esters (end group), respectively. Due to the tension of the ring of norbornene, the degree of copolymerization is not high.

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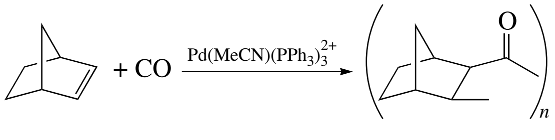
1. INTRODUCTION

Copolymerization of olefins such as ethylene, propene, and styrene with carbon monoxide is a topic of current academic and industrial interest. It is of interest for the following reasons [1]. Firstly, CO is a cheap raw material for copolymerization. Secondly, polymers containing polyketones have the potential to be photodegradable [2] or biodegradable. Thirdly, such polyketones are expected to be excellent starting materials for the synthesis of new functional polymers as the carbonyl group can easily be modified chemically [3].

For ethylene, excellent catalysts proved to be cationic palladium complexes coordinated with tertiary (especially bidentate) phosphine ligands [4]. For styrene, a somewhat different catalytic system has been employed. For example, palladium complexes with bidentate nitrogen ligands and weakly coordinated anions have been used in the presence of an oxidizing cocatalyst in an alcoholic medium [5]. Usually, the copolymerization product is polyketone. In certain cases, polymers with polyspiroketal repeating units in the backbone are observed.

Strained olefins are attractive substrates for copolymerization with CO as the resulting copolymers and cooligomers feature unique structural and chemical properties [6]. On the other hand, strained olefins have revealed themselves as useful substrates to study the mechanism of insertion of the olefin into metal–acyl bond during the chain growth process [7]. For strained olefins like norbornene and norbornadiene, palladium complexes are also active catalysts for polyketone. In 1982, Sen et al. reported the reaction of carbon monoxide with norbornadiene and norbornene under mild conditions using $[Pd(MeCN)(PPh_3)_3](BF_4)_2$ as a catalyst in noncoordinating solvents such as chloroform where norbornadiene afforded the copolymers of molecular weight 3380 and norbornene yielded the cooligomers of molecular weight 350 [4]. More recently, G.P. Belov et al. reported about the kinetics and mechanism of copolymerization of carbon monoxide with norbornene [8] and norbornadiene [9]. The overall reaction of norbornene with carbon monoxide has been depicted as follows (Scheme 1).

Drent was the first to use chelating dinitrogen ligands such as 2,2'–bipyridine (bipy) to prepare active



Scheme 1. Reaction of norbornene with carbon monoxide.

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[1] This article was submitted by the authors in English.

Table 1. Effects of $M(CF_3SO_3)_n$ on copolymerization

$M(CF_3SO_3)_n$	Potential of $M^{n+}/M(v)^b$, V	Productivity, 10^3 g PK (mol Pd)$^{-1}$ h^{-1}	M_w, 10^2 g/mol	M_w/M_n
$CF_3SO_3H^a$	–	58.0	10.9	1.6
CF_3SO_3H	–	10.6	8.36	1.6
$La(CF_3SO_3)_3$	–2.522	12.8	12.1	1.8
$Y(CF_3SO_3)_3$	–2.372	14.5	12.4	1.9
$Yb(CF_3SO_3)_3$	–2.267	26.7	12.8	2.1
$Zn(CF_3SO_3)_2$	–0.763	51.4	12.5	1.9
$Cu(CF_3SO_3)_2$	+0.337	57.3	15.4	1.6

Note: $PdCl_2$: 0.05 mmol; phen: 1.5 mmol; $M(CF_3SO_3)_n$: 1 mmol; BQ: 10 mmol; NBE: 0.05 mol; CH_3OH: 6 ml; $T = 60°C$; $P = 3.0$ MPa; $t = 2$ h; ^{a} $Pd(OAc)_2$ was used instead of $PdCl_2$; ^{b} standard redox potentials of metal ions.

Pd^{2+} catalysts for the alternating copolymerization of CO and a strained olefin [10]. The reactions with dicyclopentadiene were carried out in methanol in the presence of 1,4–benzoquinone (BQ) as an organic oxidant and yielded a polyketone with spiroketal repeating units having lactone and ester end groups of the polymer chains instead of the expected ketone repeating units [11].

In this paper, it was found that the $Pd(OAc)_2$/phen/CF_3SO_3H catalytic system gave a very high catalytic activity for the copolymerization of norbornene and CO, but if $PdCl_2$ was used instead of $Pd(OAc)_2$, the corresponding catalytic system, $PdCl_2$/phen/CF_3SO_3H, has only very low activity. It is known that the price of $Pd(OAc)_2$ is much higher than that of $PdCl_2$, so in order to improve this kind of catalytic system, $M(CF_3SO_3)_n$ was used instead of CF_3SO_3H to form a new class of three-component catalytic system, $PdCl_2$/phen/$M(CF_3SO_3)_n$, the catalytic activity of which was much higher than that of $PdCl_2$/phen/CF_3SO_3H and could be comparable with the system, $Pd(OAc)_2$/phen/CF_3SO_3H, under the same reaction conditions. To the best of our knowledge, these findings for the copolymerization of CO and NBE have not been reported yet. Herein, the studies on the copolymerization of NBE with CO catalyzed by $PdCl_2$/phen/$M(CF_3SO_3)_n$ are presented. The effects of ligands, cocatalysts, solvents, and temperatures with regard to yield and M_w are also investigated. The structure of the copolymer is determined from FT–IR, ^{1}H NMR, and ^{13}C NMR spectra, and their thermal properties are discussed.

2. EXPERIMENTAL

2.1. Reagents and Copolymerization

All the chemicals were purchased from The First Chemical Company of Shanghai (China) except for norbornene, which was purchased from Aldrich. The solvents were dried and distilled according to standard procedures. The other reagents were used directly without further purification. Copolymerization was carried out with the catalytic system consisting of $PdCl_2$, phen, $M(CF_3SO_3)_n$, and BQ. The catalysts, solvents, and NBE were charged into a 250 ml autoclave. Then the autoclave was purged with CO (≥99.9%) three times and pressurized to the desired pressure. The reactor was heated to the reaction temperature with stirring. After two hours the reaction was finished. The resultant copolymer was purified by precipitation with methanol and dried in vacuum at ambient temperature.

2.2. Characterization of the Copolymer

Molar masses were determined on Aligent 1100 HPLC (United States) gel permeation chromatograph equipped with PL gel 5 μm MIXED-C column and RI detector at 25°C in tetrahydrofuran solution at an elution rate of 1.0 ml/min against polystyrene standards. ^{1}H NMR and ^{13}C NMR were recorded on a VARIAN MERCURY VX-300 (United States) spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. The FT–IR spectrum was recorded with an EQUINOX55 (BRUKER) spectrometer by using KBr pellet. The differential scanning calorimetry (DSC) spectrum was obtained on a PERKIN DSC-7 analyzer with protection of N_2 under the condition of a 10 K/min warm-up rate. Thermogravimetric analysis (TGA) was obtained on the PERKIN TGA-7 analyzer with protection of N_2 under the condition of a 10 K/min warm-up rate.

3. RESULTS AND DISCUSSION

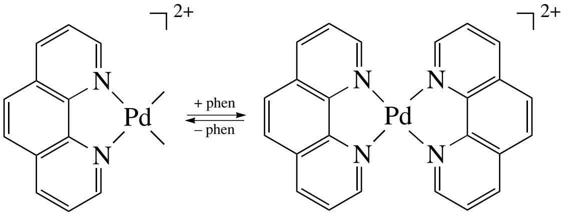
3.1. Effects of $M(CF_3SO_3)_n$ on Copolymerization

$PdCl_2$/phen/$M(CF_3SO_3)_n$ catalytic systems were studied with different $M(CF_3SO_3)_n$ components. The results are listed in Table 1. It was clearly shown that without $M(CF_3SO_3)_n$, the $PdCl_2$/phen/CF_3SO_3H catalytic system had a low catalytic activity, and the productivity was only 10600 g PK (mol Pd)$^{-1}$ h^{-1} and the M_w of the resultant copolymer was only 836 g/mol. When $M(CF_3SO_3)_n$ was introduced instead of

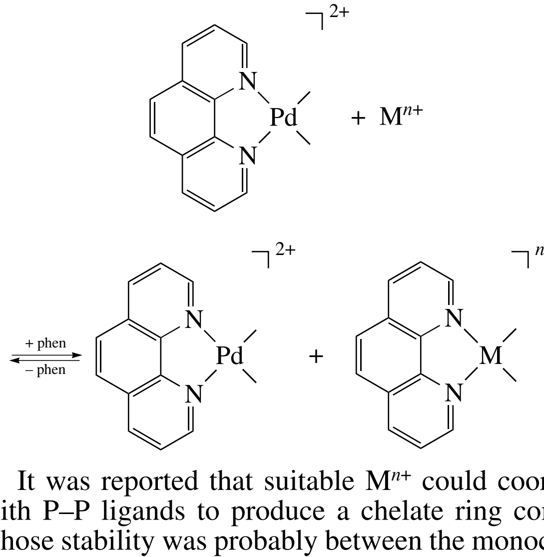
CF_3SO_3H, the $PdCl_2$/phen/$M(CF_3SO_3)_n$ catalytic system exhibited higher activity. With $La(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, $Yb(CF_3SO_3)_3$, $Zn(CF_3SO_3)_2$, and $Cu(CF_3SO_3)_2$ used, the activities of the corresponding catalytic systems were greatly increased and reached 12800, 14500, 26700, 51400, and 57300 g PK (mol Pd)$^{-1}$ h^{-1}, respectively. However, the M_w of copolymers catalyzed by different $M(CF_3SO_3)_n$ were not very much different, and that catalyzed by $Cu(CF_3SO_3)_2$ was the highest, 1540 g/mol.

Similarly to the copolymerization of CO with styrene, the active catalytic species were chelate cationic complexes of Pd^{2+} with ligands [12]. Suitable bidentate ligands, e.g., phen, had good stability on the Pd^{2+} center; suitable anions, e.g., $CF_3SO_3^-$, were easy to leave to provide the coordination vacancy of Pd^{2+}. Cl^- would be strongly coordinated with Pd^{2+} and was not easy to remove to provide the coordination vacancy [13], so the $PdCl_2$/phen/CF_3SO_3H catalytic system had only weak activity. When $M(CF_3SO_3)_n$ was introduced, the corresponding catalytic system had a high activity. The reason was probably that $CF_3SO_3^-$ was a weakly coordinating anion, and M^{n+} was probably coordinated with Cl^- more strongly than Pd^{2+} (see Eq. (I)), letting Pd^{2+} produce its coordination vacancy to comonomers to reach a high activity.

$$PdCl_2 + M^{n+} \rightleftharpoons Pd^{2+} + MCl_n, \qquad (I)$$



, (II)



(III)

It was reported that suitable M^{n+} could coordinate with P–P ligands to produce a chelate ring complex, whose stability was probably between the monochelate ring and bischelate ring complexes of Pd^{2+} [14]. Similarly, here Eq. (II) may be transformed to Eq. (III). In this way, probably more than half of the Pd^{2+} center could be made in the active monochelate ring state, so the activity of the catalytic system was improved.

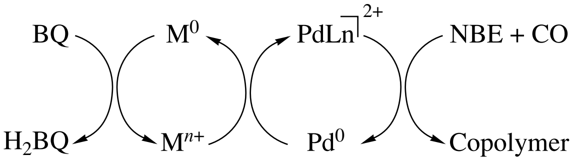
The higher the redox potential, the stronger the oxidation power of the metal ion. Under CO atmosphere, Pd^{2+} is likely to be reduced to Pd^0. As the oxidant of Pd^0, the potential of M^{n+}/M is lower than that of Pd^{2+}/Pd, which means that the oxidation power of M^{n+} is lower than that of Pd^{2+}, so the rate of the reaction of Pd^0 and M^{n+} is slow, and the corresponding catalytic activity changes with the potential of M^{n+}/M. In order to keep the concentration of Pd^{2+} constant, it is necessary to introduce an organic redox cocatalyst such as BQ [5] to oxidize M^0 to M^{n+}; thus, the circulation of Pd^{2+} is realized. As a matter of fact, our results indicated that a large excess of BQ was beneficial to the copolymerization. A proposed mechanism for the redox reactions between Pd, M, and BQ is shown in Scheme 2.

In the first step, Pd^{2+} catalyzes the reaction of NBE and CO to synthesize a copolymer with concomitant reduction of Pd^{2+} to Pd^0. Then Pd^0 is reoxidated to Pd^{2+} by M^{n+} as an inorganic redox cocatalyst under the reaction conditions. As an organic redox cocatalyst, BQ reacts with M^0 to form M^{n+} again and BQ itself is reduced to H_2BQ. Therefore, through these processes the circulation of catalysts has been realized to a certain extent.

3.2. Effects of Ligands on Copolymerization

The influence of ligands on the copolymerization of NBE with CO is shown in Table 2. Bidentate ligands, bipy, phen, 5-NO_2-phen, 5-NH_2-phen, and pyrazine-2-carboxylic acid were used. According to Table 2, the activity of nitrogen bidentate ligands in the reaction clearly exceeded that of monodentate ligand pyridine. Drent et al. [15] reported that the two nitrogen groups of a bidentate ligand are likely to bind exclusively in a *cis* configuration to a single palladium center. This effect maximizes the concentration of species for which propagation is possible.

It was found that among these ligands bipy gave the highest productivity, but the average molecular weight of the corresponding product was only 871 g/mol. Although the catalytic activity catalyzed by phen was lower than that of bipy, the M_w of the copolymer was much higher. Phen and its derivatives have larger conjugated rings in comparison with bipy; therefore, it is not very suitable to the insertion of monomers when



Scheme 2. Proposed mechanism for the copolymerization.

Table 2. Effects of ligands on copolymerization

Ligand	Productivity, 10^3 g PK (mol Pd)$^{-1}$ h^{-1}	M_w, 10^2 g/mol	M_w/M_n
Pyridine	Trace	–	–
Pyrazine-2–carboxylic acid	2.00	8.84	1.3
5-NO_2-phen	16.8	8.04	1.9
5-NH_2-phen	31.6	13.3	1.5
Phen	57.3	15.4	1.6
Bipy	80.0	8.71	1.4

Note: $PdCl_2$: 0.05 mmol; ligand: 1.5 mmol; $Cu(CF_3SO_3)_2$: 1 mmol; BQ: 10 mmol; NBE: 0.05 mol; CH_3OH: 6 ml; $T = 60°C$; $P = 3.0$ MPa; $t = 2$ h.

Table 3. Effects of solvents on copolymerization

Solvent	Productivity, 10^3 g PK (mol Pd)$^{-1}$ h^{-1}	M_w, 10^2 g/mol	M_w/M_n
Propanetriol	2.00	44.6	2.2
Ethanediol	22.3	23.5	2.5
Ethanol	29.9	16.1	1.6
Methanol	57.3	15.4	1.6

Note: $PdCl_2$: 0.05 mmol; phen: 1.5 mmol; $Cu(CF_3SO_3)_2$: 1 mmol; BQ: 10 mmol; NBE: 0.05 mol; solvent: 6 ml; $T = 60°C$; $P = 3.0$ MPa; $t = 2$ h.

they coordinate with Pd^{2+}. This kind of structure leads to a lower yield of polyketone in copolymerization.

On the other hand, the trend of the catalytic activity in the sequence of 5-NO_2-phen, bipy, phen, and 5-NH_2-phen may be related to the electron-donor properties of these ligands whose pK_a values are 3.23, 4.35, 4.86, and 5.23, respectively [16, 17]. As can be seen from Fig. 1, the productivity of copolymerization increases at first and then decreases with the increase of pK_a of the N,N–bidentate ligands. It is possible that, in the presence of less basic ligands, CO is bound too strongly to the Pd^{2+} center, thus poisoning the catalyst [18]. Comparing the reaction activity catalyzed by phen and its derivatives, we found that the productivity catalyzed by phen was the highest and that catalyzed by 5–NO_2-phen was the lowest. Besides the influence of electron-donor properties, it is also probably due to the steric hindrance of the substituted group in the 5-position of phen. So, when taking into account the pK_a values and steric effects, bipy and phen are suitable ligands for the copolymerization, about which there was a similar report [19].

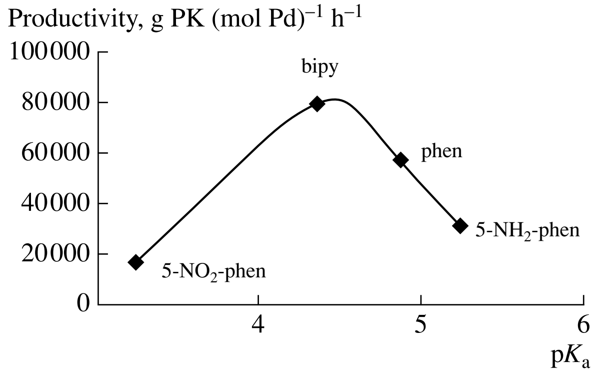


Fig. 1. Relationship between pK_a and productivity.

Pyrazine-2-carboxylic acid has little catalytic action. Due to the electron withdrawing effect of the ortho-carbonyl, the electron cloud densities of N and O in the acid are decreased to some extent. It is not beneficial to the coordination with Pd^{2+} because the stability of the corresponding Pd^{2+} complex is decreased. In fact, a lot of black palladium metal was observed after the copolymerization when using pyrazine-2-carboxylic acid as a ligand.

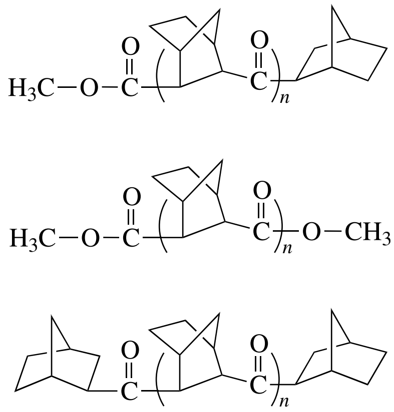
3.3. Effects of Solvents on Copolymerization

Table 3 shows that the productivity of polyketone is critically influenced by the solvents. The solvent plays important roles in the copolymerization [20]. The solvent coordinates with Pd^{2+} to produce the active center, and it is the precipitator of the copolymer. From the results in Table 3, we can see that no copolymer can be produced without any solvent.

Table 3 shows that the yield of copolymerization in a protonic solvent is very high. A protonic solvent serves as both coinitiator and chain-transfer agent in its reaction with the palladium complex, which forms palladium methoxy species (Eq. (IV)) [15]. The higher selectivity to the esters is attributed to oxidation by an oxidant (BQ) of the proposed palladium species (Eq. (V)).

$$[L_2PdX_2] + MeOH \longrightarrow [L_2Pd(OMe)X] + HX, \quad (IV)$$

$$[L_2Pd{-}H] + BQ + MeOH \longrightarrow [L_2PdOMe] + H_2BQ. \quad (V)$$



Scheme 3. Proposed structures of the copolymer of NBE and CO.

Table 4. Effects of temperatures on copolymerization

Temperature	Productivity, 10^3 g PK (mol Pd)$^{-1}$ h^{-1}	M_w, 10^2 g/mol	M_w/M_n
40	15.7	13.5	1.9
60	57.3	15.4	1.6
90	82.0	10.9	1.6
110	65.8	9.87	1.8

Note: $PdCl_2$: 0.05 mmol; phen: 1.5 mmol; $Cu(CF_3SO_3)_2$: 1 mmol; BQ: 10 mmol; NBE: 0.05 mol; CH_3OH: 6 ml; $P = 3.0$ MPa; $t = 2$ h.

Among these solvents, methanol gave the highest reaction rate, but at the same time, it gave the lowest M_w. This occurrence is probably the case because the size of the methanol molecular is smaller than that of the others, so during the propagation of the polymer chain, it is beneficial to insertion and shifting with the comonomers. However, as the end group of the copolymer, the molecular weight of methanol is lower than that of the others, which led to the M_w of the corresponding product being the lowest; and it is reasonable that the M_w of the copolymer using propanetriol was the highest, reaching 4460 g/mol.

3.4. *Effects of Temperatures on Copolymerization*

Reaction temperature has important effects both on the activity of the system and on the quality of copolymers produced as reported in the literature [21]. The data of copolymerization yield and molar mass for various temperatures are listed in Table 4. As can be seen from Table 4, both the yield and M_w increased initially and then decreased. This may be due to two competing effects [22]. Increasing temperature increases the rate constant but decreases the solubility of the monomer. However, maximum M_w is at $T = 60$°C, compared to the maximum yield at $T = 90$°C. This difference reflects the contribution of the activation energy to chain-transfer processes |23]. This may result from partial cross-linking of the N BE/CO copolymer at high temperature.

It is found that at lower temperatures the copolymerization is controlled kinetically, while at higher temperatures, the solubility of CO in liquid decreases and the thermal decomposition of the catalyst becomes the main factor affecting the reaction, which is similar to the copolymerization of styrene with CO [22]. At the same time, the copolymer is subject to decomposition at higher temperatures, which results in the decrease of M_w of the product. In fact, at 110°C the polymer produced was gray. This color is probably due to the serious decomposition of the palladium complex.

3.5. *Copolymerization of CO with Different Olefins*

The results of copolymerization of CO and various olefins with catalytic system $PdCl_2/phen/Cu(CF_3SO_3)_2$ are shown in Table 5. As indicated, $PdCl_2/phen/Cu(CF_3SO_3)_2$ is an effective catalytic system for copolymerization of olefins with carbon monoxide. The IR spectrum of the copolymer of styrene and CO shows a strong absorption band near 1698 cm^{-1}, which is the characteristic absorption band of the symmetric expanding vibration of C=O. In the IR spectrum of the copolymer of CO and dicyclopentadiene, there is a strong absorption band near 1781 cm^{-1}, which is the characteristic absorption band of the symmetric expanding vibration of C=O of lactone, while the strong band near 1736 cm^{-1} is attributed to the C=O of the ester end group. The infrared spectrum of the product includes two features at 1697 and 1732 cm^{-1} for the NBE/CO copolymer in CH_3OH, which are attributed to carbonyl groups in ketones (repeating unit) and esters (end group), respectively. As described previously, the formation of polyketoester RO–(–CO–NBE–)$_n$–COOR (in which R = CH_3) is considered to result from copolymerization in the polymer end with an alcohol as solvent [24].

3.6. *Characterization of the NBE/CO Copolymer*

Many model studies aimed at elucidating the elementary steps of CO/olefin copolymerizations have been carried out successfully with the use of strained olefins. Indeed, the products resulting from the insertion of strained olefins such as norbornene do not contain β-hydrogens that are accessible to the metal center. This makes the inserted product quite stable [7]. According to the different end groups, it is proposed that there are three kinds of structure of the NBE/CO copolymer as follows (Scheme 3) [25].

Table 5. Copolymerization of CO with different olefins

Olefin monomer	Productivity, 10^3 g PK (mol Pd)$^{-1}$ h^{-1}	M_w, 10^2 g/mol	M_w/M_n	ν(C=O), cm^{-1}
Styrene	11.0	47.9	2.9	1698
Dicyclopentadiene	49.0	11.8	2.1	1781, 1736
Norbornene	57.3	15.4	1.6	1697, 1732

Note: $PdCl_2$: 0.05 mmol; phen: 1.5 mmol; $Cu(CF_3SO_3)_2$: 1 mmol; BQ: 10 mmol; Olefin monomer: 0.05 mol; CH_3OH: 6 ml; $T = 60$°C; $P = 3.0$ MPa; $t = 2$ h.

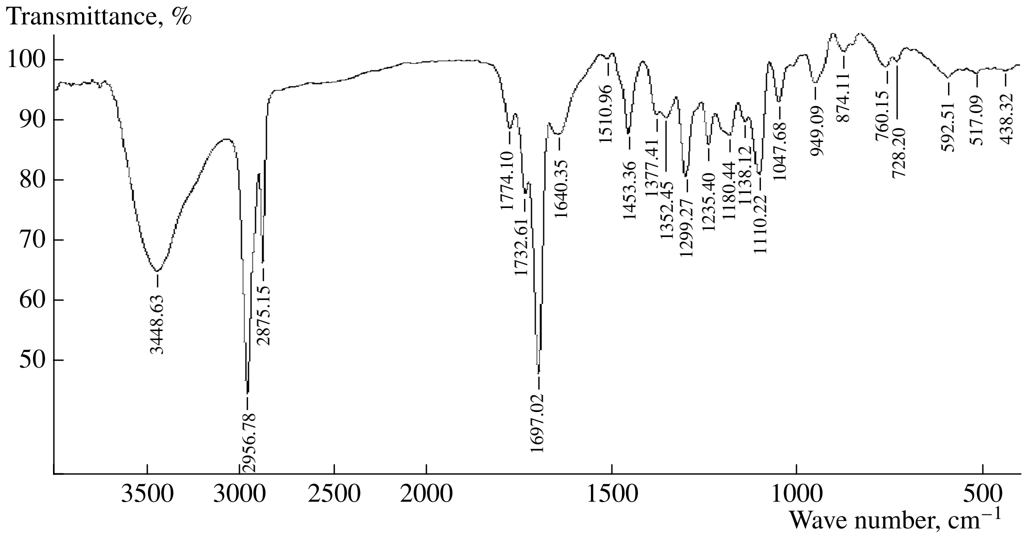


Fig. 2. FT–IR spectrum of copolymer of NBE and CO.

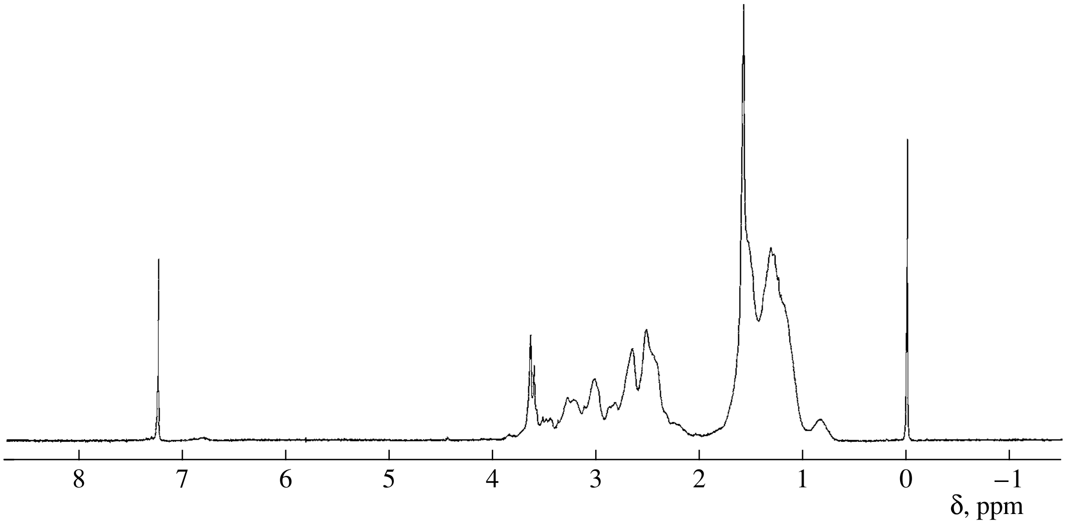


Fig. 3. ^{1}HNMR spectrum of the copolymer of NBE and CO.

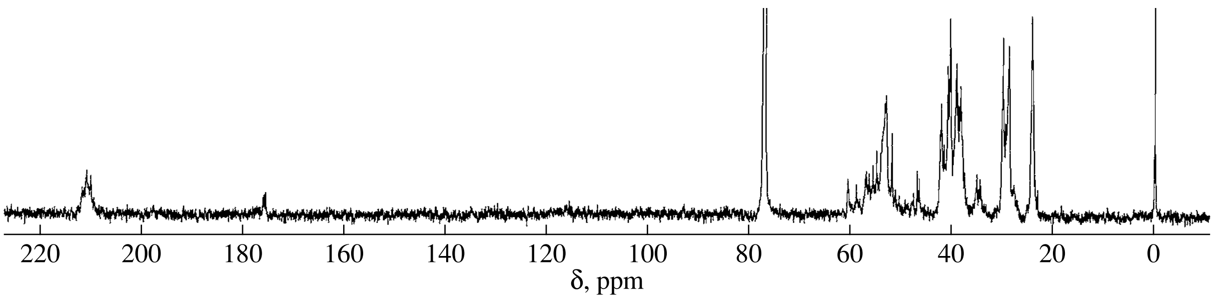


Fig. 4. ^{13}CNMR spectrum of the copolymer of NBE and CO.

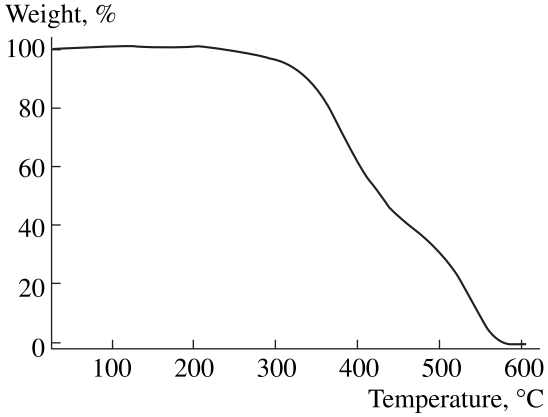


Fig. 5. TGA curve of the copolymer.

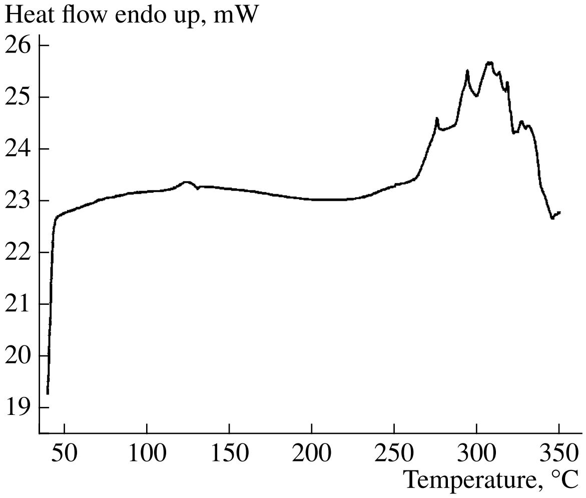


Fig. 6. DSC curve of the copolymer.

3.6.1. FT–IR. The IR spectrum of the NBE/CO copolymer catalyzed by the $PdCl_2$/phen/$Cu(CF_3SO_3)_2$ catalytic system is shown in Fig. 2. As can be seen from it, there is a strong IR absorption peak near 1697 cm^{-1}, which is the characteristic absorption band of the symmetric expanding vibration of ketonic carbonyl groups. There is a weak IR absorption peak near 1774 cm^{-1}, which is the characteristic absorption band of the symmetric expanding vibration of C=O of lactone structure. The absorption at 1732 cm^{-1} indicating the presence of vinyl ether structures is also very weak. The strong peak of 2956 cm^{-1} is attributed to the resonance of the saturated C–H of the NBE backbone.

3.6.2. ^{1}H NMR. The ^{1}H NMR spectrum of the copolymer is shown in Fig. 3. As can be seen from it, the absorption peak that corresponds to the resonance of H on CH_3O– of the ester end group appears at 3.40–3.65 ppm. The resonances of H on the saturated C of NBE backbone appear at 1.17–2.38 ppm. The peak at 7.23 ppm is probably the absorption of residual solvent.

3.6.3. ^{13}C NMR. Figure 4 shows the ^{13}C NMR spectrum of such a polymer. According to Fig. 4, the signal at 209.9 ppm is ascribed to the carbonyl carbon. The low-intensity resonance at 175.2 ppm is due to the carbonyl group (CH_3–O–(C=O)–) at the end of the copolymer chain. The multiple peaks in the range of 30–55 ppm are assigned to the resonances of saturated C of the NBE backbone supporting that NBE/CO copolymer, which contains ring structures. The signal of the methyl group at the end of the copolymer chain overlaps with the ring structure of NBE/CO copolymer at 52 ppm. This further proves that CO is indeed copolymerized with norbornene. The peaks near 76–77 ppm are the resonance of the solvent.

3.6.4. TGA and DSC. The TGA curve of the copolymer of norbornene and CO appears in Fig. 5 with a 10 K/min heating rate in nitrogen. Weight loss occurred at about 280°C. The main thermal degradation takes place around 280–550°C. The sample loses most weight very quickly. During this process the rate of weight loss changes a little near 450°C. After the main thermal degradation, the rate of weight loss slows; the temperature of complete weight loss is about 600°C.

Figure 6 shows the curve of DSC. Because different states of polyketone have different specific heat capacities, the curve of DSC shows the peaks of the melting state and the decomposition state. It has been reported that the NBE/CO polyketone is partially crystalline, but the approximation of the melting point and glass-transition temperature may make the crystalline exothermal peak unclear [24]. As can be seen from Fig. 6, the melting point of the prepared polyketone catalyzed by the $PdCl_2$/phen/$Cu(CF_3SO_3)_2$ catalytic system is about 130°C and the decomposition temperature is about 280°C.

4. CONCLUSIONS

The work reported here demonstrates the possibility of $PdCl_2$/phen/$M(CF_3SO_3)_n$ as a new catalytic system in the copolymerization of norbornene with CO. This one-pot reaction can take place under mild conditions, and the corresponding productivity of the copolymer is reasonably high under optimal reaction conditions. The copolymer of CO and norbornene is demonstrated to be the polyketone structure characterized by ^{1}H NMR, ^{13}C NMR, and FT–IR, and the thermal properties of the copolymer are analyzed by TGA and DSC.

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