A new catalytic system for copolymerization of styrene with CO:PdCl$_2$/bipy/M(CF$_3$SO$_3$)$_n$

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Abstract

A new three-component catalytic system, PdCl$_2$/bipy/M(CF$_3$SO$_3$)$_n$, was studied for copolymerization of styrene with CO to prepare alternating polyketone (PK). It is found that the PdCl$_2$/bipy/CF$_3$SO$_3$H catalytic system had a very low catalytic activity for copolymerization of CO with styrene, but when M(CF$_3$SO$_3$)$_n$ was introduced instead of CF$_3$SO$_3$H, the PdCl$_2$/bipy/M(CF$_3$SO$_3$)$_n$ catalytic system exhibited high activity. The copolymer was characterized by elemental analysis, FTIR, ^{1}H NMR, DSC and TGA. The results indicated that the copolymer is a linear alternating copolymer of carbon monoxide and styrene with glass transition temperature, melting point, and decomposition temperature of 275, 350, and 400 °C, respectively. The effects of M(CF$_3$SO$_3$)$_n$, ligands, *p*-benzoquinone/PdCl$_2$ ratio, solvents, and reaction temperatures on the reaction have been discussed in detail. The results showed that this novel catalytic system exhibited high activity, especially when Cu(CF$_3$SO$_3$)$_2$ was used. The corresponding productivity was 20,000 gPK/molPd h when the reaction was carried out at 338 K for 4 h under 3.0 MPa of CO.

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1. Introduction

Polyketones (PK), obtained by alternation copolymerization of carbon monoxide with olefinically unsaturated monomers such as styrene, is a class of low-cost innovative thermoplastics. The synthesis, properties and applications of PK are still the object of intense fundamental and applied research [1–3]. The investigation of catalysts for the synthesis is a key step in these reactions. The catalytic systems on the perfectly alternating copolymerization of styrene with CO to give syndiotactic polyketone are typically composed of a palladium(II) salt, either acetate or trifluofoacetate, and of a chelating dinitrogen ligand such as 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen). The reactions are generally carried out in the presence of strong oxidants such as *p*-benzoquinone (BQ) in excess of palladium, and of a suitable Bronsted acid, e.g. *p*-toluene sulphonic acid, as cocatalyst [4].

It has been reported that the Pd(OAc)$_2$/bipy/CF$_3$SO$_3$H catalytic system has a very high catalytic activity [5], but if PdCl$_2$ was used instead of Pd(OAc)$_2$, the corresponding catalytic system, PdCl$_2$/bipy/CF$_3$SO$_3$H, has very low activity. Similar results were also observed for the copolymerization of CO with ethylene [6]. It is known that the price of Pd(OAc)$_2$ is much higher than that of PdCl$_2$. In order to improve the activity of this catalytic system, M(CF$_3$SO$_3$)$_n$ was used instead of CF$_3$SO$_3$H to form a new class of three-component catalytic system, PdCl$_2$/bipy/M(CF$_3$SO$_3$)$_n$, the catalytic activity of which was much higher and could be comparable with the catalytic system, Pd(OAc)$_2$/bipy/CF$_3$SO$_3$H, under the same reaction conditions. These findings for the copolymerization of CO and styrene have not been reported yet. Herein, the studies on this new catalytic system are presented.

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2. Experimental

All the chemicals were purchased from The First Chemical Company of Shanghai. Methanol and styrene were dried and distilled according to the standard procedures. The copolymerization was carried out in a 100 ml autoclave. In a typical experiment, the catalysts consisting of $PdCl_2$, bipy, $M(CF_3SO_3)_n$ and BQ, methanol, and styrene were charged into the reactor. Then CO ($\geq$99.9%) was charged and purged three times and pressurized to a desired pressure. The reactor was heated to the polymerization temperature. After the reaction, the copolymer was purified by precipitation with methanol and dried in vacuum at ambient temperature.

The elemental analysis was carried out on a Vario EL III elemental analyzer. Fourier transform infrared spectroscopy (FTIR) spectrum was recorded with an Equinox55 (Bruker) spectrometer by using KBr peller. ^{1}H NMR spectrum was obtained on a Varian Mercury-VX300 spectrometer in $CDCl_3$ with tetramethylsilane as the internal standard. Differential scanning calorimetry (DSC) spectrum was obtained on Perkin DSC-7 analyzer. Thermogravimetry (TGA) analysis was obtained on Perkin TGA-7 analyzer under N_2 at a heating rate of $10\,^\circ C/min$.

3. Results and discussion

3.1. Characterization of copolymer

The copolymerization of styrene and CO was carried out in the $PdCl_2$/bipy/$M(CF_3SO_3)_n$ catalytic system. The IR spectrum of the resultant copolymer is shown in Fig. 1. There is a strong absorption peak near $1698\,cm^{-1}$, which is the characteristic absorption band of symmetric expanding vibration of C=O. The four weak equal-interval peaks among $1350–1500\,cm^{-1}$ are the characteristic absorption bands of mono-substituted benzene. The strong peak near $697\,cm^{-1}$ is the absorption band of outer-face bending vibration of the five H on the mono-substituted benzene. The peak near $751\,cm^{-1}$

Table 1
Elemental analysis of polyketone

Sample	Mass fraction (%)		
	C	H	O
Polyketone	81.89	6.02	12.09
Alternating copolymer[a]	81.82	6.06	12.12

[a] Calculated values.

is the absorption band of outer-face bending vibration of aromatic nucleus. These results indicate that the structure of the copolymer has the components of CO and styrene, which coincides with that in the literature [7].

The results of elemental analysis are shown in Table 1. It can be seen that the components of C, H, O of the prepared copolymer are consistent with the calculated values of the linear alternating copolymer of CO and styrene. So it can be confirmed that the prepared polyketone is the linear alternating copolymer of styrene and CO.

The ^{1}H NMR spectrum of the copolymer is shown in Fig. 2. The resonances at 3.7 and 4.8 ppm are assigned to backbone methylene and methyne, respectively, of the repeating molecular unit $-CH_2CHphCO-$. The aromatic hydrogen resonances are located at 6.6–7.2 ppm. In copolymers of sufficiently low molecular weight the end groups are also visible. Easter ($-CHphCH_2COOCH_3$) groups which appear at 3.3 ppm and ketone ($-CHphCOCH=CHph$) groups which appear at 3.5 ppm, are usually observed in ratios close to 1. The resonances at 1.2 ppm are probably attributed to the active hydrogen of the residual solvent methanol. Thus, the ^{1}H NMR analysis confirms chemoselectivity to a perfectly alternation copolymer of carbon monoxide and styrene, as has been reported [2].

Fig. 3 shows the curve of DSC. Because different states of polyketone have different specific heat capacity, the curve of DSC shows the peaks of glass state, melting state and decomposition state. It has been reported that polyketone is a crystalline copolymer, but the approximation of melting point and glass-transition temperature may make the crystalline exothermal peak unobvious [5]. As can be seen
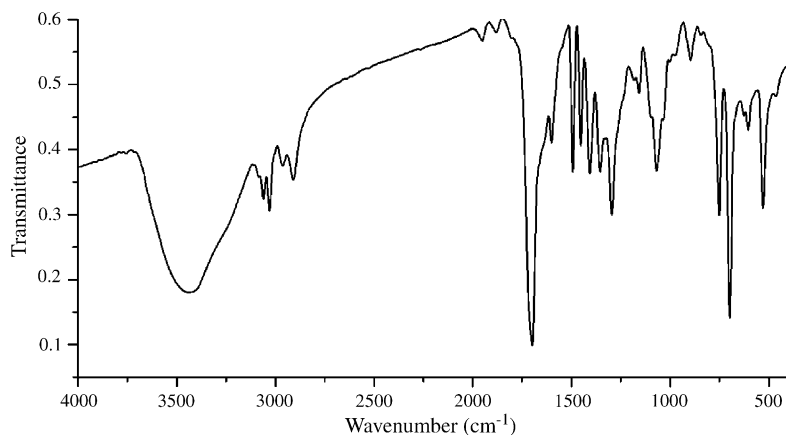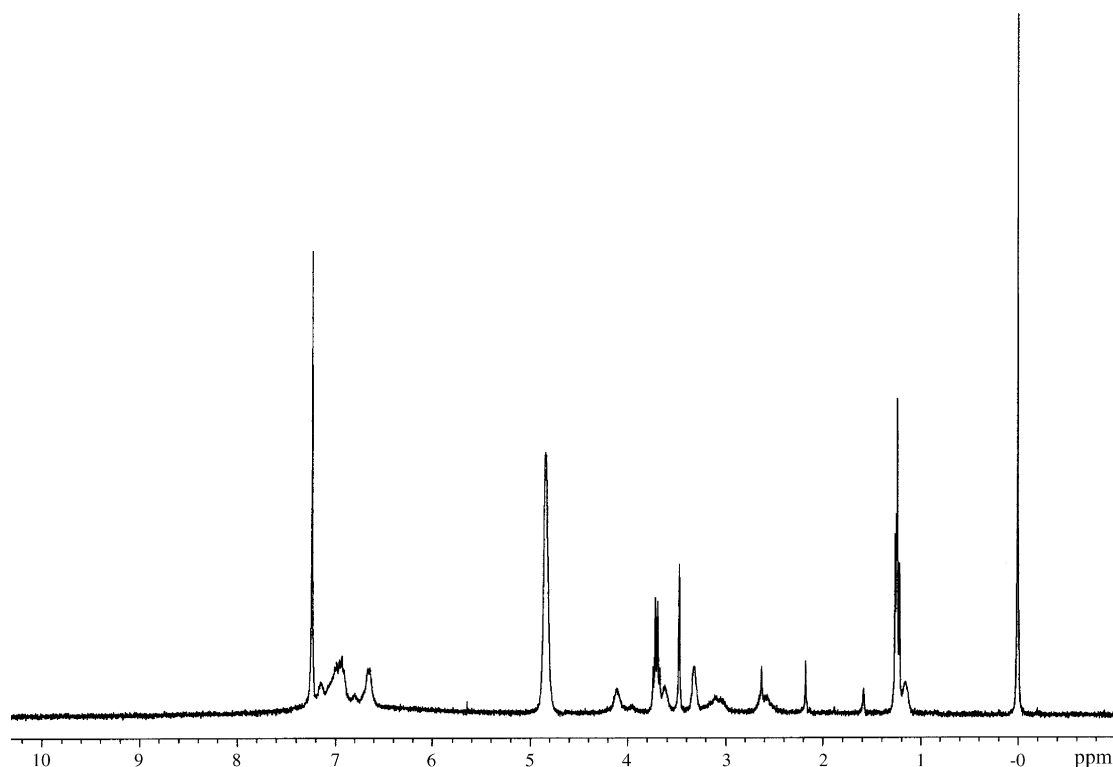

Fig. 1. IR spectrum of polyketone.

Fig. 2. ^{1}H NMR spectrum of polyketone.

from Fig. 3, the glass-transition temperature of the prepared polyketone catalyzed by $PdCl_2$/bipy/$M(CF_3SO_3)_n$ catalytic system is about 275 °C, the melting point is about 350 °C and the decomposition temperature is about 400 °C.

The thermal degradation of copolymer shows that there are three weight loss processes (Fig. 4). The weight loss occurring at temperatures below 300 °C is likely due to the elimination of a small amount of methanol used as solvent in the preparation of the polymer. The main thermal degradation takes place around 350–400 °C. The sample loses most weight very quickly. After the main thermal degradation, the weight-decreasing rate turns to be very slow again and the temperature of complete weight loss is about 550 °C.

3.2. Effects of $M(CF_3SO_3)_n$ on the copolymerization

$PdCl_2$/bipy/$M(CF_3SO_3)_n$ catalytic systems were studied with several different $M(CF_3SO_3)_n$ components. The results are listed in Table 2. It is shown that the
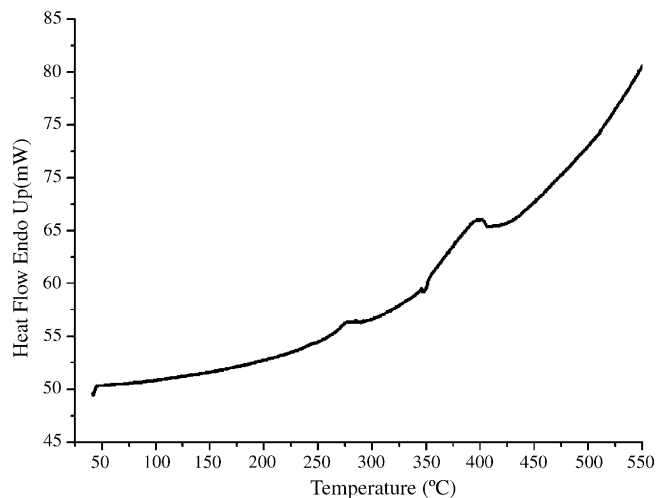

Fig. 3. Differential scanning calorimetry curve of polyketone.

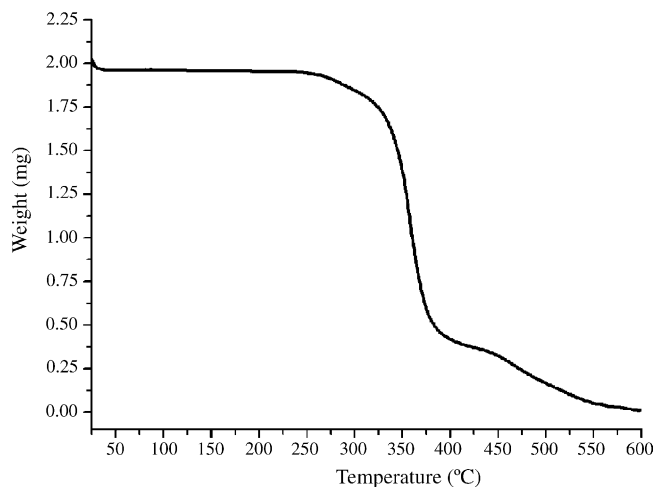Fig. 4. Thermogravimetry curve of polyketone.

Table 2
Effects of $M(CF_3SO_3)_n$ on catalytic activity

$M(CF_3SO_3)_n$	$CF_3SO_3^-$ (or AcO^-)/ $PdCl_2$ (mol/mol)	Reaction rate (gPK/molPd h)
CF_3SO_3H	4	Trace
$La(CF_3SO_3)_3$	4	2581
$Y(CF_3SO_3)_3$	4	3829
$Yb(CF_3SO_3)_3$	4	5136
$Zn(CF_3SO_3)_2$	4	13,734
$Cu(CF_3SO_3)_2$	2	1000
$Cu(CF_3SO_3)_2$	4	18,000
$Cu(CF_3SO_3)_2$	6	4388
$Cu(CF_3SO_3)_2$	8	1000
$Cu(OAc)_2$	4	Trace

$PdCl_2$: 1×10^{-4} mol; bipy: 5×10^{-4} mol; BQ: 3×10^{-3} mol; styrene: 10 ml; T: 338 K; P: 3.0 MPa; methanol: 4 ml.

$PdCl_2$/bipy/CF_3SO_3H system had a very low catalytic activity without $M(CF_3SO_3)_n$, and only trace of product was obtained. When $M(CF_3SO_3)_n$ was introduced instead of CF_3SO_3H, the $PdCl_2$/bipy/$M(CF_3SO_3)_n$ catalytic system exhibited high activity. With $Cu(CF_3SO_3)_2$, $Zn(CF_3SO_3)_2$, $Yb(CF_3SO_3)_3$, $Y(CF_3SO_3)_3$, and $La(CF_3SO_3)_3$, the activities of the corresponding catalytic systems were greatly increased and reached the values of 18,000, 13,734, 5136, 3829 and 2581 gPK/molPd h, respectively.

A remarkable dependence of catalytic activity on the nature of the carboxylate anion was also observed.

$Cu(OAc)_2$ showed a much lower catalytic activity than $Cu(CF_3SO_3)_2$. It has been pointed out that the anion which balances the charge of the metal complex should be the conjugate base of a strong acid and the anion should be weakly coordinating so that the reacting monomers can easily be activated by coordination to the central metal ion [8,9]. Obviously $CF_3SO_3^-$ is a weaker σ-donor ligand than AcO^-.

In order to explore a new catalytic system for copolymerization of CO with styrene, many researchers have studied the catalytic mechanism extensively [10]. They suggested that the active catalytic species were chelate cationic complexes of palladium(II) with ligands. A suitable bidentate ligand, e.g. bipy, had good stability on the palladium(II) center; suitable anions, e.g. $CF_3SO_3^-$, were easy to be removed to provide the coordination vacancy of palladium(II). Since Cl^- would be strongly coordinated with palladium(II) and was not easy to be removed to provide the coordination vacancy [11], the $PdCl_2$/bipy/CF_3SO_3H catalytic system had only very low ac-

tivity. When $M(CF_3SO_3)_n$ was introduced, the corresponding catalytic system showed a high activity. The reason was probably that $CF_3SO_3^-$ was a weakly coordinating anion, and that M^{n+} was probably coordinated with Cl^- more strongly than Pd(II) (see Eq. (1)) [12], allowing Pd(II) to produce its coordination vacancy for comonomers to give a high activity.

It was reported that suitable M^{n+} could coordinate with P–P ligand to produce a chelate ring complex, whose stability was probably between the monochelate ring and bis-chelate ring complexes of Pd(II) [12]. Similarly here Eq. (2) may be transformed to Eq. (3). In this way, probably more than half of the Pd(II) center could keep in the active monochelate ring state, so the activity of the catalytic system was improved.

$$PdCl_2 + M^{n+} \rightleftharpoons Pd^{2+} + MCl_n \qquad (1)$$
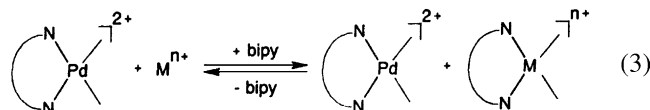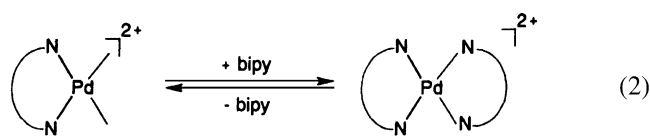
$$\qquad (2)$$

$$\qquad (3)$$

Table 3 shows the standard redox potentials of these metal ions under the conditions of 298 K and 100 kPa [13].

The higher is the redox potential, the stronger is the oxidation power of the metal ion. The highest potential of Pd^{2+}/Pd means that the oxidation power of Pd^{2+} is the strongest, so Pd^{2+} is likely to be reduced to Pd(0) under a CO atmosphere. 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 changed with the potential of M^{n+}/M. In order to keep the concentration of Pd(II) constant, it is necessary to introduce a kind of organic redox cocatalyst such as BQ [14] to oxidize M(0) to M^{n+}, thus realizing the circulation of Pd(II). As a matter of fact, our experimental results indicated that the large excess of BQ to Pd(II) is beneficial to the copolymerization.

A proposed mechanism for the redox reactions between Pd, M and BQ is shown in Scheme 1.

In the first step, Pd(II) catalyzes the reaction of styrene and CO to synthesize PK with concomitant reduction of Pd(II) to

Table 3
Redox potentials of the materials

Electrodes	Electrode reaction	Potential (V)
Pd^{2+}/Pd	$Pd^{2+} + 2e \rightleftharpoons Pd$	+0.987
Cu^{2+}/Cu	$Cu^{2+} + 2e \rightleftharpoons Cu$	+0.337
Zn^{2+}/Zn	$Zn^{2+} + 2e \rightleftharpoons Zn$	−0.763
Yb^{3+}/Yb	$Yb^{3+} + 3e \rightleftharpoons Yb$	−2.267
Y^{3+}/Y	$Y^{3+} + 3e \rightleftharpoons Y$	−2.372
La^{3+}/La	$La^{3+} + 3e \rightleftharpoons La$	−2.522
$Q,H^+/H_2Q$	$Q + 2H^+ + 2e \rightleftharpoons H_2Q$	+0.699
$CO_2,H^+/CO$	$CO_2 + 2H^+ + 2e \rightleftharpoons CO + H_2O$	−0.120
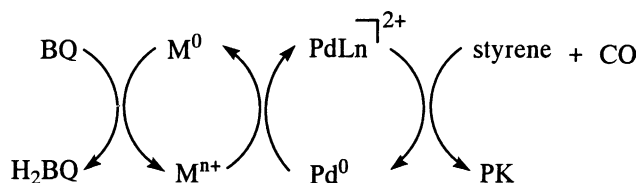
Scheme 1. Proposed mechanism for the redox reaction between Pd, M and BQ.

Pd^0. Then, Pd^0 is reoxidized to Pd(II) by M^{n+} as an inorganic redox cocatalyst at the reaction conditions. As a kind of 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.

The results in Table 2 show that the productivity is also strongly influenced by the concentration of $CF_3SO_3^-$. The highest productivity is obtained with a $CF_3SO_3^-$/Pd(II) molar ratio of 4. In the presence of a higher concentration of $CF_3SO_3^-$, the productivity decreases sharply. The beneficial effect of the acid anion may have several origins, one of which may be that it increases the concentration of $[Pd–H]^+$ species that reactivates the complexes of Pd(0) that inevitably form in the reducing reaction medium [15]. The fact that the productivity decreases with relatively large amounts of $CF_3SO_3^-$ may be due to the competition of $CF_3SO_3^-$ with the monomers for the coordination to the metal [16].

3.3. Effects of ligands on the copolymerization

Unlike aliphatic α-olefins, the copolymerization of styrene and its derivatives with CO requires palladium(II) catalysts with N–N chelating ligands to be used [17]. In fact low molecular weight oligomers are generally obtained with palladium catalysts stabilized by chelating diphosphines [18]. It is commonly agreed that termination by the β-H elimination prevails over propagation to polymer due to the higher electron density on the palladium center in phosphine-modified catalysts in comparison with nitrogen-modified catalysts [19]. It has also been suggested that the (diphosphine)Pd-styrenyl intermediates formed in the initial steps of the CO/styrene copolymerization are so strongly stabilized by π-benzylic coordination as to inhibit CO insertion. The termination process by the β-H elimination thus becomes favored and oligoketones are formed instead of polyketones [20].

Some N,N- and N,O-Schiff-bases as ligands in the catalytic copolymerization have been investigated, and the results are shown in Table 4. It is found that bipy has the highest catalytic activity. Phen and its derivatives have larger conjugated rings in comparison with bipy; therefore, it is not very advantageous to the insertion of monomers when they coordinated with Pd(II). This kind of structure leads to a lower yield of polyketone in copolymerization. On the other hand, the decreasing trend of the catalytic activity in the sequence of bipy, 5-NH2-phen, phen and 5-NO2-phen may be related to the electron-donor properties of the ligands in the same decreasing order [21]. Pyrazine-2-carboxylic acid and pyridine-2-carboxylic acid showed little catalytic activity. Due to the electron-withdrawing effect of the *ortho*-carbonyl, the electron density of N and O in these acids are decreased to some extent. It is not beneficial to the coordination with Pd(II) because the stability of Pd(II) complex has decreased. In fact, a large amount of black palladium was observed after the copolymerization when using pyrazine-2-carboxylic acid or pyridine-2-carboxylic acid as ligand.

When the concentration of Pd(II) is kept at 1×10^{-4} mol, the yield of polyketone increases at first and then decreases with the molar ratio of $bipy/PdCl_2$ increasing from 1 to 9. When the concentration of $PdCl_2$ is too high in comparison with bipy, there is not enough ligand to stabilize Pd(II). Therefore, $PdCl_2$ cannot convert into the catalytic intermediate rapidly and completely. The excess $PdCl_2$ tends to be reduced to Pd(0) in CO environment, which decreases the activity of catalyst. On the other hand, when the concentration of bipy is too high in comparison with $PdCl_2$, bipy tends to take up all the coordination vacancy of Pd(II), which results in no vacancy for the comonomers. Taking into account of the

Table 4
Effects of ligands on catalytic activity

Ligands	Ligand/PdCl2 (mol/mol)	Reaction rate (gPK/molPd h)
No	–	–
Pyrazine-2-carboxylic acid	5	Trace
Pyridine-2-carboxylic acid	5	Trace
5-NO2-phen	5	10,921
Phen	5	11,000
5-NH2-phen	5	14,037
Bipy	1	Trace
Bipy	3	2000
Bipy	5	18,000
Bipy	7	4833
Bipy	9	4267

$PdCl_2$: 1×10^{-4} mol; $Cu(CF_3SO_3)_2$: 2×10^{-4} mol; BQ: 3×10^{-3} mol; methanol: 4 ml; styrene: 10 ml; T: 338 K; P: 3.0 MPa.

yield of polyketone, the optimum molar ratio of bipy/PdCl$_2$ is about 5.

3.4. Effects of solvents on the copolymerization

According to the literature [22], we propose that the initiation steps of the copolymerization consist of three different equilibria. Firstly, the dissociation of one molecule of the nitrogen ligand from palladium generates a monochelated species with two available coordination sites in a cis configuration (Eq. (4)). Then, the coordination of CO is likely to happen on this species (Eq. (5)), followed by the interaction with alcohol and the subsequent formation of the monocationic carboalkoxy derivative and one proton (Eq. (6)).

$$\left[\begin{array}{c} N \\ Pd \\ N \end{array} \right]^{2+} \underset{}{\overset{L}{\rightleftharpoons}} \left[\begin{array}{c} N \\ Pd \\ L \end{array} \right]^{2+} + \ N\text{-}N \quad (4)$$

$$\left[\begin{array}{c} N \\ Pd \\ L \end{array} \right]^{2+} + \ CO \ \rightleftharpoons \left[\begin{array}{c} N \\ Pd \\ L \end{array} \right]^{2+} + \ L \quad (5)$$

$$\left[\begin{array}{c} N \\ Pd \\ L \end{array} \right]^{2+} + \ R\text{-}OH \ \rightleftharpoons \left[\begin{array}{c} N \\ Pd \\ L \end{array} \right]^{+} + \ H^{+} \quad (6)$$
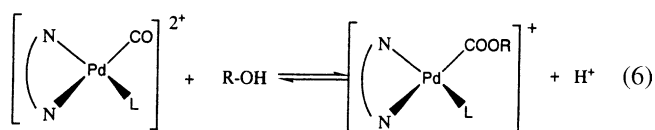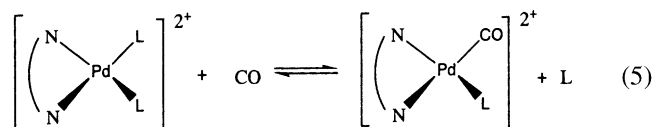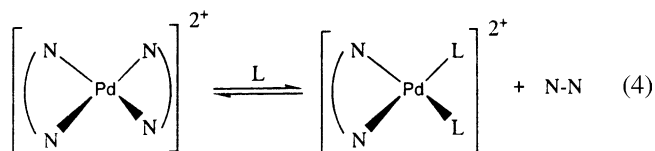
The carbomethoxy intermediate may be considered as the real active species. Coordination of styrene to the monocationic active species, followed by insertion, will lead to the propagation of the polymeric chain (Eq. (7a)). In contrast, coordination of CO leads to a carbonyl carbomethoxy intermediate, which, due to the unfavorable thermodynamics of the double carbonylation reaction [23], cannot proceed further (Eq. (7b)). This monocarbonyl carbomethoxy species has been isolated and characterized by Brookhart, who demonstrated that it was the resting state of the catalytic cycle [24].

$$\left[\begin{array}{c} N \\ Pd \\ N \end{array} \right]^{+} \underset{}{\overset{Ph}{\longleftarrow}} \left[\begin{array}{c} N \\ Pd \\ N \end{array} \right]^{+} \xrightarrow{\text{insertion}} \quad (7a)$$

$$\xrightarrow{\hspace{1cm}} \left[\begin{array}{c} N \\ Pd \\ N \end{array} \right]^{+} \xrightarrow{\text{insertion}} \quad (7b)$$
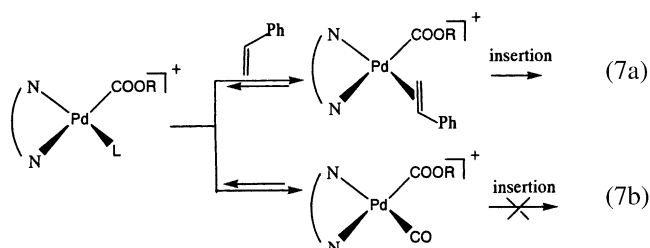
Table 5 shows that the productivity of polyketone is critically influenced by the solvents. Methanol plays important roles in the copolymerization of CO and styrene [25]: (1) Methanol coordinates with Pd(II) to produce the active center; (2) Methanol is the precipitator of the copolymer. From the results in Table 5, it can be seen that no copolymer can be produced without methanol. But when the amount of methanol is too high, the concentrations of catalyst and styrene will decrease, and the reaction rate will decline accordingly. As shown in Table 5, when the volume of methanol is 4 ml, the catalytic activity reaches the highest value, 18,000 gPK/molPd h.

Since organic solvent such as MB has capability to coordinate to Pd(II) because of its bare O, the activity of solution polymerization using MB is lower than that of precipitation polymerization. Although MB and PE are both ether compounds, PE is an apolar solvent which cannot coordinate with metal. On the other hand, PE does not dissolve in styrene and the reaction system is biphase; therefore, it has lower catalytic activity in comparison with MB. Since NB has an oxidative action which can prevent the decomposition of catalyst to some extend, its activity is higher than that of MB and PE [26].

Since the introduction of OCP can increase the solubility of the resultant copolymer, it can increase the reaction rate. In the case of too low amount of solvent, the system becomes viscous with the progress of reaction, and the center of catalyst is easily embedded in the copolymer, leading to a decrease of the reaction rate. In the case of too high amount of solvent, the concentration of the catalyst drops and this is not beneficial to the reaction. Therefore, it is important to introduce a suitable amount of solvent that can dissolve the product and keep the viscosity of the system low during the reaction. At the same time, solvents can react with Pd(II) to produce new active centers, and thus the stability and activity of Pd(II) is increased [27]. Under these conditions the optimal amount of OCP is 10 ml.

3.5. Effects of BQ/PdCl$_2$ ratios on the copolymerization

The oxidant, usually 1,4-benzoquinone, is claimed as an essential component of the catalytic systems based on N-donor ligands in methanol [28]. The effects of BQ/PdCl$_2$ ratios on the yields are presented in Fig. 5.

As already mentioned, in the reaction medium palladium could be present as both Pd(0) and Pd(II) species, and probably Pd(I) species of the type of the hydridecarbonyl dimer [29]. In this system, BQ can oxidize Pd(0) to Pd(II) and it can transform a [Pd−H]$^{+}$ species, which are produced in the
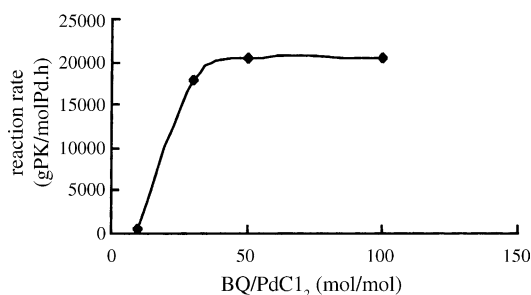

Fig. 5. Effects of BQ/PdCl$_2$ (mol/mol) on catalytic activity. PdCl$_2$: 1×10^{-4} mol; bipy: 5×10^{-4} mol; Cu(CF$_3$SO$_3$)$_2$: 2×10^{-4} mol; styrene: 10 ml; methanol: 4 ml; T: 338 K; P: 3.0 MPa.

Table 5
Effects of solvents on catalytic activity

Solvents	Solvents volume (ml/ml)	Reaction rate (gPK/molPd h)
–	–	–
Methanol	19	1500
Methanol	4	18,000
o-Chloride-phenol (OCP)/methanol	10/4	20,000
o-Chloride-phenol (OCP)/methanol	15/4	17,600
Nitrobenzene (NB)/methanol	15/4	11,991
Methoxybenzene (MB)/methanol	15/4	6005
Petroleum ether (PE)/methanol	15/4	3825

$PdCl_2$: 1×10^{-4} mol; bipy: 5×10^{-4} mol; $Cu(CF_3SO_3)_2$: 2×10^{-4} mol; BQ: 3×10^{-3} mol; styrene: 10 ml; T: 338 K; P: 3.0 MPa.

cessation reaction of copolymerization of styrene and CO catalyzed by Pd(II), into a $[Pd-OCH_3]^+$ species [30].

It is found that when the copolymerization is carried out in the presence of a relatively high amount of BQ the productivity is much increased. For example, under the conditions reported in Fig. 5, the reaction rate increases from 580 to 20,500 gPK/molPd h when $BQ/PdCl_2$ molar ratio changes from 10 to 100. This observation can be interpreted as a consequence of the possibility that in the presence of BQ the $[Pd-H]^+$ species, which are present in relatively high concentration under the conditions of maximum productivity, are transformed into $[Pd-(OCH_3)]^+$ species. It is noteworthy to observe that when the copolymerization is carried out in the presence of BQ the reaction rate is levelled to an average value of 20,500 gPK/molPd h irrespective of whether the $BQ/PdCl_2$ molar ratio is 50 or 100. The reason is probably that when concentration of BQ is too high, BQ cannot dissolve in styrene completely, and that the reaction system changes into a heterogeneous state resulting in a decrease in catalytic activity.

3.6. Effects of reaction temperatures on the copolymerization

It has been reported that the reaction temperature has important effects on both the activity of the system and the quality of polyketones [22]. An increase in temperature resulted in a remarkable increase in the activity and the reaction rate reached the highest value at about 65 °C (Fig. 6). The resultant cop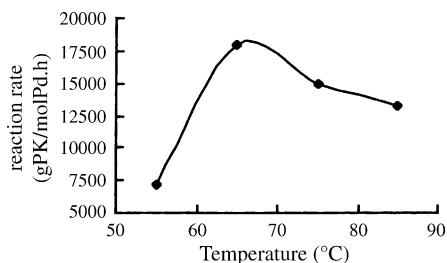olymer was white and contained little palladium. With the initial increase in reaction temperature, the rate constant increases accordingly and this is beneficial to the increase in catalytic activity.

It is not beneficial to the reaction when the temperature is too high or too low. At low temperatures the copolymerization is kinetically controlled and at higher temperatures the solubility of CO in the liquid phase decreases, and also the thermal decomposition of the catalyst becomes the main factor affecting copolymerization [31].

4. Conclusions

We have successfully demonstrated the possibility of $PdCl_2/bipy/M(CF_3SO_3)_n$ as a novel catalytic system in copolymerization of styrene and CO. This one-pot reaction could take place under mild conditions and the corresponding productivity of polyketone is reasonably high under optimal reaction conditions. This new three-component catalytic system with lower cost will promise significance in industrial application. Further studies are in progress in our laboratory.

Fig. 6. Effects of temperatures or catalytic activity. $PdCl_2$: 1×10^{-4} mol; bipy: 5×10^{-4} mol; $Cu(CF_3SO_3)_2$: 2×10^{-4} mol; BQ: 3×10^{-3} mol; styrene: 10 ml; methanol: 4 ml.

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