

# Synthesis of Novel Bipyridyl Ligands and Application in Preparation of Polyketone

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**ABSTRACT:** In this article, novel 2,2'-bipyridyl derivatives were synthesized and the excellent bipyridyl ligands were chosen as catalyst to apply in the copolymerization of carbon monoxide (CO) and styrene (ST) to prepare polyketone. 4,4'-Dicarboxyl-2,2'-bipyridine(4,4'-dcp) was synthesized by use of synthesized 4,4'-dimethyl-2,2'-bipyridine(4,4'-dmp). The products (4,4'-dmp and 4,4'-dcp) were characterized by melting point, NMR, IR, GC-MS, and elemental analysis. The effects of different ligands and various reaction conditions including the usage of ligand, *p*-toluenesulfonic acid, solvent, *p*-benzoquinone, the CO pressure, and reaction

temperature on catalytic activity of the copolymerization were investigated. The catalytic activity of 4,4'-dmp, 4,4'-dcp and 2,2'-bipyridine were compared. The results showed that the addition of the electron-donating substituent can enhance catalytic activity, with the sequence as follows: 4,4'-dimethyl-2,2'-bipyridine > 2,2'-bipyridine > 4,4'-carboxy 2,2'-bipyridine. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 3292–3297, 2012

**Key words:** carbon monoxide; styrene; 4,4'-dimethyl-2,2'-bipyridine; 4,4'-dicarboxyl-2,2'-bipyridine; polyketone

## INTRODUCTION

Polyketone prepared by the copolymerization of carbon monoxide (CO) and olefin is a strictly alternating linear copolymers with good mechanical properties, solvent resistance, nontoxic nature, and so on.<sup>1</sup> The raw materials CO can be obtained widely and hence reduce the costs of the copolymerization compared with most synthetic materials using petroleum as raw materials. More importantly, the carbonyl in the main chain of polyketone gives it unique properties of photodegradation or biodegradation. It can be degraded to small molecules slowly such as ethene and CO<sub>2</sub>, which has great significance in environmental protection and medical health. In addition, the active carbonyl of polyketone enable it to be used as matrix material in a variety of chemical modifications to get lots of functional polymer materials,<sup>2,3</sup> especially in petrochemical, medical, food processing and many other fields. Therefore, from the aspects of energy conservation, environmental protection and the development of new medical

materials, research, and development of polyketone have great practical significance and broad prospects for development.<sup>4</sup> Besides, polyketone prepared by the copolymerization of CO and  $\alpha$ -olefin in the presence of cationic Pd(II)-bidentate nitrogen ligand complexes as catalyst has the advantages of regular structure, high crystallizability, good mechanical properties.<sup>1</sup>

During the past 20 years, the copolymerization of carbon monoxide and  $\alpha$ -olefin to prepare polyketone had attracted more and more attention both in academic research and industrial applications,<sup>1</sup> which also had achieve great progress.<sup>5,6</sup> Currently, the study of synthesis of polyketone mainly concentrates in two aspects: selection of catalytic system and performance optimization for product. For the copolymerization of styrene (ST) and carbon monoxide, activity of the cationic Pd(II)-bidentate nitrogen ligand complexes as catalyst is much higher. But because of its high cost, it has baffled the industrialization of alternating copolymerization of ST and CO. The study of resin-supported catalysts started earlier, which has obtained desired results in the reusability and recovery of the catalyst<sup>7</sup> but the catalyst still failed to radically reduce the product costs of polyketone. Thus it is very necessary to select bidentate nitrogen ligand which has higher catalytic activity and further make sure its mechanism in catalytic system of the synthesis of polyketone.

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At present, bidentate nitrogen ligands are mainly 2,2'-bipyridine categories and 1,10-phenanthroline categories. It has been proved that they have good catalytic properties in the system of copolymerization of CO and ST.<sup>8</sup> Bipyridyl derivatives as ligands used in the synthesis of polyketone have been studied less<sup>9-11</sup> than that of phenanthroline derivatives. Thus this paper started with the synthesis of the new bipyridyl ligands. Two new bipyridyl derivatives 4,4'-dimethyl-2,2'-bipyridine and 4,4'-carboxyl-2,2'-bipyridine were respectively, synthesized and further used as ligands in the synthesis of polyketone. The effects of CO pressure, ligand, *p*-toluenesulfonic acid, *p*-benzoquinone, solvent and temperature on the catalytic activity were investigated to optimize reaction conditions and their catalytic activity were compared with that of 2,2'-bipyridine. Because of the effects of different 4,4'-substituents on the *N,N* electron density, their role in the copolymerization of CO and ST are studied, respectively.

## EXPERIMENTAL

### Experimental materials

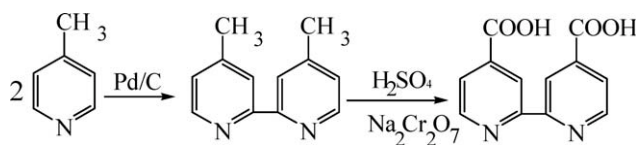
Raw materials 4-methylpyridine and 2,2'-bipyridine were purchased from Beijing Shi Ying Chemical Plant. Palladium carbon (Pd/C) catalyst was purchased from Baoji Ruike nonferrous metal limited liability company. Carbon monoxide (purity > 99.99%) was purchased from Beijing Analysis Instrument Company. Other raw materials were analytically pure. 4-methylpyridine was treated by vacuum distillation and cryopreservation in refrigerator for standby. The Palladium carbon (Pd/C) catalyst was treated by drying under vacuum at low temperature for standby. Other raw materials were used directly without further purification.

### Synthesis of 4,4'-dimethyl-2,2'-bipyridine 4,4'-dicarboxyl-2,2'-bipyridine

The reaction process referred to existed literature,<sup>12-14</sup> as is shown in Scheme 1.

### Synthesis of polyketone

Palladium acetate, 4,4'-dimethyl-2,2'-bipyridine (or 4,4'-dicarboxyl-2,2'-bipyridine), styrene, anhydrous methanol, benzoquinone and *p*-toluenesulfonic acid were mixed according to a certain proportion in a 100-mL stainless steel kettle with electromagnetic stirring and a certain pressure of carbon monoxide was kept. After 2 h the mixture was cooled to room temperature and the unreacted carbon monoxide was released to air. The reaction was terminated with ethanol and the precipitate as a white powder-



**Scheme 1** Synthesis route of 4,4'-dimethyl-2,2'-bipyridine and 4,4'-dicarboxylic acid-2,2'-bipyridine.

like product was filtered, washed, and dried under vacuum.

## RESULTS AND DISCUSSION

### Characterization

The melting points of the products were measured on RY-2 melting point machine made by Tianjin Analysis Instrument Factory. FTIR spectra were collected on a BIO-RAD FTS6000 FTIR spectrometer with potassium bromide pellets. <sup>1</sup>H-NMR data (the solvent of 4,4'-dimethyl-2,2'-bipyridine was CDCl<sub>3</sub>, and the solvent of 4,4'-dicarboxylic acid-2,2'-bipyridine was DMSO) was measured on INOVA liquid NMR spectrometer made by Varian company. Analysis of elements C, H and N were recorded on a Vanio-EL elemental analyzer made by Germany Heraeus Company. TG Analysis was obtained with SHIMADZU TG-50 analyzer. Heating rate was 10°C/min. The carrier gas was nitrogen. Air flow rate was 10 mL/min.

### Characterization of 4,4'-dimethyl-2,2'-bipyridine and 4,4'-dicarboxyl-2,2'-bipyridine

The bidentate nitrogen ligands were characterized by using mass spectrometry, FTIR, <sup>1</sup>H-NMR, and elemental analysis. The product catalyzed by palladium carbon catalyst is white needle crystal which can be dissolved in methanol, 4-methylpyridine and other organic solvents. The melting point of the product is 171°C, which is consistent with the reference.<sup>14</sup>

Figure 1 shows the mass spectrogram of the product, from which the following ion peaks can be found: 184 [M<sup>+</sup>], 169 [M<sup>+</sup>-CH<sub>3</sub>], 92 [M/2]<sup>+</sup>, 77 [M/2-CH<sub>3</sub>]<sup>+</sup>. The mass spectrogram of the product is 96% similar to the standard mass spectrogram of 4,4'-dimethyl-2,2'-bipyridine. It is proved that the product is just the objective product 4,4'-dimethyl-2,2'-bipyridine.

The characterization data of FTIR, <sup>1</sup>H-NMR, and elemental analysis are shown in Tables I and II.

### Characterization of polyketone

Figure 2 shows the IR spectra of the product polyketone. In Figure 2, the carbonyl strong absorption

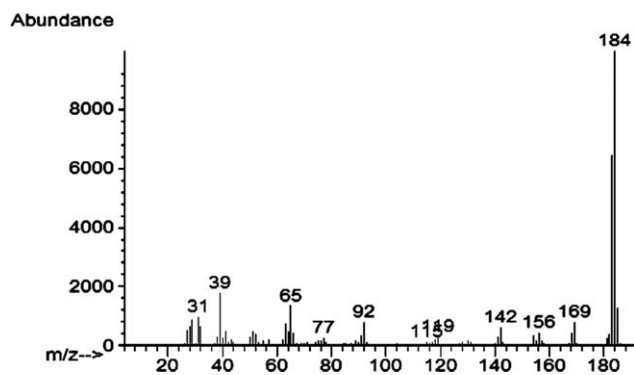


Figure 1 Mass spectrogram of 4,4'-dmpy.

peak at  $1706\text{cm}^{-1}$  gives evidence to the C=O in the product. In addition, the absorption peaks near  $697\text{cm}^{-1}$  and  $750\text{cm}^{-1}$  are caused by =CH plane bending vibration on the benzene ring, which are the characteristic absorption bands for single replacement of benzene ring. The peaks from  $1453\text{cm}^{-1}$  to  $1600\text{cm}^{-1}$  are the characteristic absorption bands of benzene ring caused by benzene ring skeleton vibration. It is shown that the copolymer contains the structure of benzene ring and carbonyl.

Thermogravimetric (TG) curves of polyketone suggested that the initial weight loss temperature of polyketone is  $300^{\circ}\text{C}$  and the complete weight loss temperature is about  $400^{\circ}\text{C}$  in nitrogen atmosphere when the heating rate is  $10^{\circ}\text{C}/\text{min}$ .

### Effect of different ligands on catalytic activity and polymer

In this article, the reaction of carbon monoxide and ST was performed with two bipyridine derivatives as bidentate *N,N* ligands, which were compared with the traditional ligand 2,2'-bipyridine. 2,2'-bipyridine is the matrix of the two new pyridine ligands, and the differences among the three ligands lie in the 4,4'-substituents. Based on the maximum catalytic activity of 2,2'-bipyridine as the ligand. The effects of the three ligands on catalytic activity are compared only changing the ligand type, without

altering other experimental conditions. And the results are shown in Table III.

In Table III, among the three types of pyridine ligands, the catalytic activity of catalyst used 4,4'-dimethyl-2,2'-bipyridine as ligand is higher than that of 2,2'-bipyridine and 4,4'-dicarboxylic acid-2,2'-bipyridine. The catalytic activity of 2,2'-bipyridine is slightly higher than that of 4,4'-dicarboxyl-2,2'-bipyridine. This is because in coordination copolymerization of CO/ST, bidentate nitrogen ligand can increase the electronic density of Pd (II) through substituent effect. It can help Pd (II) and carbon monoxide to form  $\pi$  complexes or coordinate with styrene. In the complex the chelating ring and conjugated  $\pi$  bonds are formed which further strengthen the Pd-N coordinating bonds and make Pd(II) complex stable. In other words, 4,4'-dimethyl-2,2'-bipyridine with electron-donor group could make Pd-ligand coordination structure more stable, which enable the catalytic system to have much higher activity and to gain larger molecular weight.

Therefore, introduce of the electron-donating substituents could enhance the catalytic activity of the system. The stronger the supplying electronic effect of 4,4'- substituents on pyridine ring, the higher net charge on pyridine ring; the stronger coordinate capacity of *N,N*- and Pd (II) ions, the higher stability of the catalytic system, and the higher catalytic activity of the catalyst system.

For the copolymerization of CO/ST, Figure 3 shows the two possible intermediate structures. The higher the stability of coordination intermediate formed by Bidentate nitrogen ligand and Pd (II), the longer it could exist in the chain growth process of coordinating copolymerization. It is difficult for chain termination reaction to occur. And relatively long molecular chains can be obtained. Therefore, the molecular weight of polyketone is larger. It is also proved by the experimental results, as is shown in Table III. Clearly, *N*-para-orienting groups of bidentate nitrogen ligand have important influence on the stability of catalyst system. Moreover the electron donating substituents are favorable for the stability of the catalytic system.

TABLE I  
IR Absorption Spectrum and  $^1\text{H-NMR}$  Analysis of Ligands

Ligands	IR absorbent peaks	Chemical shifts of H
4,4'-dmpy	$\nu_{(-\text{CH}-)} = 3054\text{cm}^{-1}, 1934\text{cm}^{-1}, 1592\text{cm}^{-1};$ $\nu_{(-\text{CH}_3)} = 1457\text{cm}^{-1}, 1367\text{cm}^{-1}$	$^1\text{H-NMR}$ ( $\text{CDCl}_3$ ): 8.53 (d, 2H, aryl H on $\text{C}_6$ and $\text{C}_6'$ ); 8.24 (s, 2H, aryl H on $\text{C}_3$ and $\text{C}_3'$ ); 7.14 (d, 2H, aryl H on $\text{C}_5$ and $\text{C}_5'$ ); 2.45 (s, 6H, $-\text{CH}_3$ ).
4,4'-dcpv	$\nu_{(-\text{CH}-)} = 3054\text{cm}^{-1}, 1893\text{cm}^{-1}, 1563\text{cm}^{-1};$ $\nu_{(-\text{COOH})} = 3111\text{cm}^{-1}, 1722\text{cm}^{-1}$	$^1\text{H-NMR}$ (DMSO): 8.91 (s, 2H, $-\text{COOH}$ ); 8.85 (s, 2H, aryl H on $\text{C}_3$ and $\text{C}_3'$ ); 8.58 (d, 2H, aryl H on $\text{C}_6$ and $\text{C}_6'$ ); 7.92 (d, 2H, aryl H on $\text{C}_5$ and $\text{C}_5'$ )

**TABLE II**  
Elemental Analysis of 4,4'-dimethyl-2,2'-bipyridine and 4,4'-dicarboxyl-2,2'-bipyridine

Elemental typed	4,4'-dmpy			4,4'-dcpy		
	C(%)	H(%)	N(%)	C(%)	H(%)	N(%)
Actual observed value	78.54	6.05	15.21	58.83	3.63	11.50
Theoretical computed value	78.26	6.52	15.22	59.01	3.33	11.50

### Effect of all kinds of reaction conditions on the catalytic activity

Considering that the use of 4,4'-dimethyl-2,2'-bipyridine can obtain much higher catalytic activity than that of others, it is used as ligand in the catalyst system. Effect of the amount of ligand, *p*-benzoquinone, *p*-toluenesulfonic acid, solvent, CO pressure, and reaction temperature on the catalytic activity are investigated (Fig. 4).

### Effect of Ligand amount on catalytic activity

In the copolymerization of carbon monoxide and styrene catalyzed by Pd/C catalyst, the coordination structure of bidentate nitrogen ligand and palladium acetate shows good catalytic effect. Amount of the bidentate ligand is directly related to the stability and the catalytic activity of the active center, as shown in Figure 4.

When there is no bidentate ligand in the catalyst system, no product will be produced. While the molar ratio of 4,4'-dmpy to Pd<sup>2+</sup> is less than 2, there is not enough 4,4'-dmpy to coordinate with palladium. As a result, Pd is apt to decompose and inactivate and its thermal stability is poor, resulting in the low yield of polyketone. With the increasing amount of

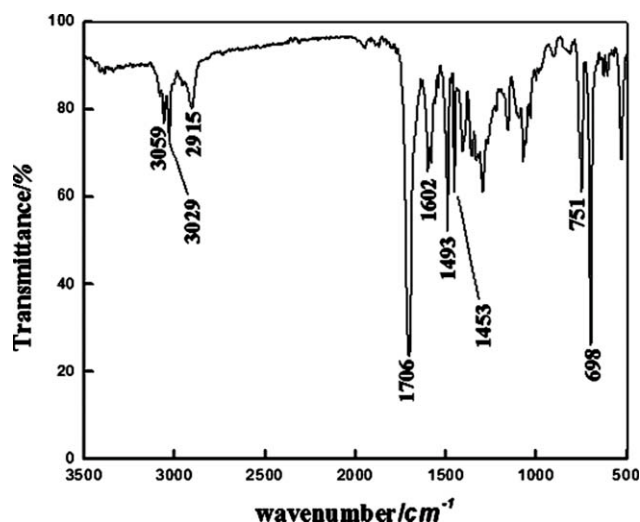


Figure 2 IR spectrum of product.

**TABLE III**  
CO/ST Copolymerization: Effect of the N-N Ligand

Ligand type	4,4'-substituents	Catalytic activity (gSTCO/gPd·h)	$M_w$ ( $M_w/M_n$ )
4,4'-Dimethyl-2,2'-bipyridine	-CH <sub>3</sub>	1,284	10,600 (1.6)
2,2'-Bipyridine	-	829	6,300 (1.6)
4,4'-Dicarboxylic acid-2,2'-bipyridine	-COOH	733	5,700 (1.5)

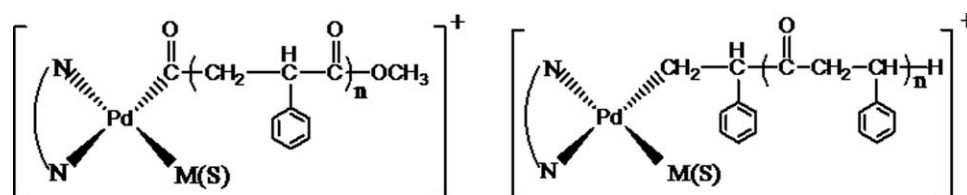
4,4'-dmpy, the productivity will also be improved. When the molar ratio of 4,4'-dmpy to Pd<sup>2+</sup> is 2, the catalytic activity of the system reaches to the maximum 939.8 g STCO/gPd h (Reaction conditions: Palladium acetate = 0.025 mmol; TsOH = 0.05 mmol; Benzoquinone = 2.5 mmol; P(CO) = 2MPa; Styrene = 8 mL; Methanol = 4 mL; Temperature = 60°C; Time = 2 h). Further increase of the amount of 4,4'-dmpy makes the catalytic activity decline.

In accordance to the coordination chemistry theory, increasing the amount of bipyridine is favorable to the formation of Pd chelating ring, which makes the central atom Pd tend to become more stable. The stability and activity of the catalyst are contradictory but also mutually restraining factors. When the amount of bipyridine is appropriate, it will come into being the chelate ring with the central Pd atom. The other two sites are the locations which can coordinate with monomer and copolymer growth chain, which make it more stable and active. When the consumption of bipyridine continues to increase, bipyridine will compete with monomer, and form double chelate ring with Pd, L<sub>2</sub>PdL<sub>2</sub>, leading to the decline of catalytic activity.

### Effect of *p*-toluenesulfonic acid (TsOH) on catalytic activity

Strong acid which coordinates weakly with palladium ions could be used as cocatalyst in the copolymerization of CO/ST. There are two main effects of TsOH on the catalysis system: (1) replace acetate ion and coordinate with palladium ions to form weaker palladium ligand, and then be replaced by monomer and solvent molecules to form vacancy with transposition catalytic role; (2) maintain electronic neutrality of the system.

The effect of the amount of TsOH on catalytic activity was investigated in this catalytic system. The change of catalytic activity is shown in Figure 4. With the molar ratio of TsOH to Pd<sup>2+</sup> increasing, the catalytic activity is improved obviously. And it reaches its maximum when the molar ratio is 5 : 1. When the molar ratio is larger than 5, the catalytic activity shows a downward trend with the increase of TsOH. This is because that in the copolymerization of CO/ST, TsOH anion provided by *p*-



**Figure 3** Structure of the Active Species (M was monomer (CO or Styrene), S was solvent).

toluenesulfonic acid coordinates weakly with  $\text{Pd}^{2+}$  center. It replaces the  $\text{CH}_3\text{COO}^-$  ion ligand and forms electrophilic  $\text{Pd}^{2+}$  cation coordinating center. Reaction equation is showed as follows:



At this time anionic ligand is easily replaced by monomer or solvent molecule and forms the catalytic coordinating vacancy. The binding energy of palladium and comonomers decreases because of the reduction of electron density of palladium center. Palladium reactive species formed in the catalytic cycle require low activation energy to initiate chain growth reaction, and the reaction rate increases. As a result, catalytic activity is improved with the increase of the amount of TsOH. On the other hand, because TsOH is a strong acid, it might affect methanol, styrene, and carbon monoxide to approach to the  $\text{Pd}^{2+}$  coordinating field when the amount of TsOH is excessive, which may result in the decrease of the palladium catalytic activity.

#### Effect of the pressure of CO on catalytic activity

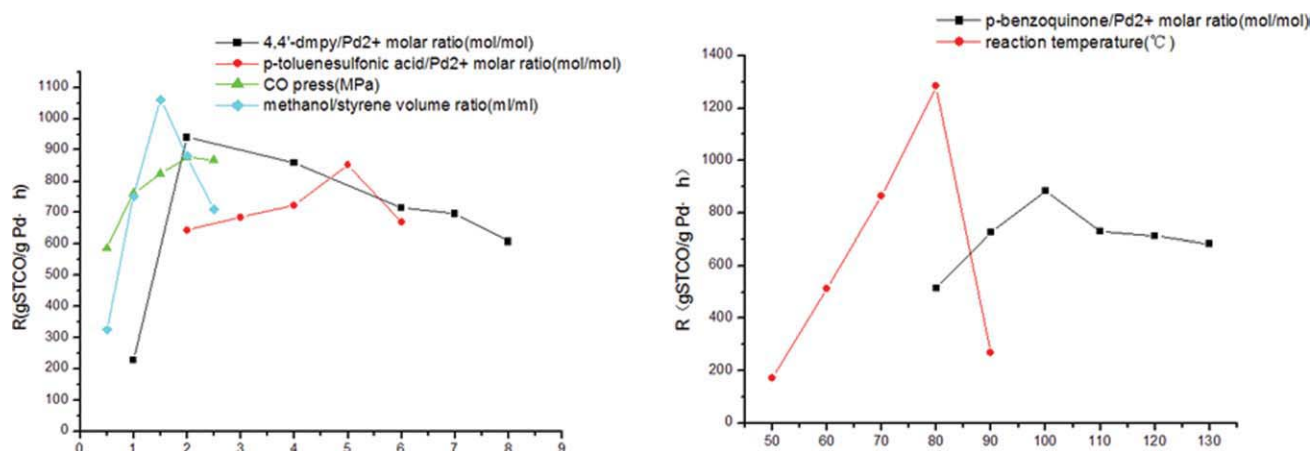
The pressure of CO has great influence on the catalytic activity in the copolymerization of CO/ST. The catalytic activity of the system increases with the CO pressure and reaches its highest catalytic activity 876 gSTCO/gPd h (Reaction conditions: Palla-

dium acetate = 0.025 mmol; 4,4'-dimethyl-2,2'-bipyridine = 0.175 mmol; TsOH = 0.05 mmol; Benzoquinone = 2.5 mmol; Styrene = 8 mL; Methanol = 4 mL; Temperature = 80°C; Time = 2 h) when the pressure of carbon monoxide is 2MPa. Further increase of the CO pressure fails to improve the catalytic activity of the system. This is because the solubility of carbon monoxide in styrene is limited. When the dissolution of carbon monoxide in styrene reaches to the utmost, increase the pressure will not have any impact on the copolymerization.

#### Effect of solvent amount on catalytic activity

In this experiment, methanol is employed not only as solvent but also as chain transfer agent and precipitator in the system. Methanol can coordinate with palladium acetate and generate catalytic active site. That is to say, methanol participates in the chain initiation process.

Figure 4 shows the changes of the system catalytic activity with the amount of methanol. When the amount of methanol is too small, the catalyst could not completely dissolve, especially the bidentate ligand could not dissolve in the reaction system, which results in low catalytic activity. When the amount of methanol is excessive, not only the chain propagation of polymer would stop ahead, but also the concentrations of catalyst and styrene are lower, which leads to the decrease of the yield of polyketone and the catalytic activity of catalyst. The system reaches its highest catalytic activity



**Figure 4** Effect of all kinds of reaction conditions on the catalytic activity. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

1060 gSTCO/gPd h. (Reaction conditions: Palladium acetate = 0.025 mmol; 4,4'-dimethyl-2,2'-bipyridine = 0.175 mmol; TsOH = 0.05 mmol; Benzoquinone = 2.5 mmol; P(CO) = 2 MPa; Styrene = 8 mL; Temperature = 80°C; Time = 2 h).

#### Effect of *p*-benzoquinone on catalytic activity

In the copolymerization of CO/ST, the addition of *p*-benzoquinone plays a key role in three aspects: (1) as a strong oxidant to prevent the Pd (II) from reduction; (2) as an effective resistant agents to prevent the homopolymerization of styrene; (3) to coordinate with Pd(0) and make palladium enter the catalytic system again by ion exchange with solvents.

Generally, the catalysate of the Pd (II) is Pd (II)-H, which catalyzes the chain termination reaction in the copolymerization of CO/ST. In the experiment, if it would not decompose to other kinds of active species, CO and ST can not insert into Pd (II)-H bond. So it can not initiate the copolymerization again. In addition, it would be easy to become Pd (0) which reduces the activity of catalysts. The *p*-benzoquinone could effectively oxide Pd (II)-H to the catalytic active center Pd(II)-OMe. So the addition of *p*-benzoquinone can greatly improve the catalytic activity.

The effect of the molar ratio of *p*-benzoquinone to palladium acetate on catalytic activity is shown in Figure 4. It is shown that when the amount of *p*-benzoquinone is small, the catalyst is easier to decompose and lose its catalytic activity, yielding a small amount of gray powder product. With the amount of *p*-benzoquinone increasing, the catalytic activity of the system increases and the product is white powder. Excess *p*-benzoquinone still leads to white powder but its yield is lower because *p*-benzoquinone in the system can not completely dissolve and the system becomes non-homogeneous hence affects the catalytic activity. The appropriate molar ratio of *p*-benzoquinone to palladium acetate is 100 under this experimental conditions, with the highest catalytic activity 883.5 gSTCO/gPd h. (Reaction conditions: Palladium acetate = 0.025 mmol; 4,4'-dimethyl-2,2'-bipyridine = 0.175 mmol; TsOH = 0.05 mmol; P(CO) = 2MPa; Styrene = 8 mL; Methanol = 4 mL; Temperature = 80°C; Time = 2 h).

#### Effect of reaction temperature on catalytic activity

In Figure 4, the system reaches its highest catalytic activity 1284 gSTCO/gPd h (Reaction conditions: Palladium acetate = 0.025 mmol; 4,4'-dimethyl-2,2'-bipyridine = 0.050 mmol; TsOH = 0.05 mmol; Benzoquinone = 2.5 mmol; P(CO) = 2 MPa; Styrene = 8 mL; Methanol = 4 mL; Time = 2 h) when the reac-

tion temperature is 80°C. It is adverse to the reaction whether the reaction temperature is too high or too low. When below 80°C the copolymerization is controlled by the activation energy of the reaction; while at higher temperature, the main influencing factors of catalytic activity are the decrease of CO solubility in liquid phase and the thermal decomposition of catalyst. When reaction temperature is low, catalyst can not play the role of catalysis very well; and when reaction temperature is too high, catalytic activity reduces because of the serious decomposition of catalyst.

## CONCLUSIONS

Two ligands 4,4'-dimethyl-2,2'-bipyridine and 4,4'-carboxyl-2,2'-bipyridine which were synthesized successfully in this paper were characterized by melting point, GC-MS, IR, NMR, and elemental analysis. Synthetic derivatives of the two bipyridine were used as bidentate nitrogen ligands in the copolymerization of CO/ST, which are compared with the traditional ligand 2,2'-bipyridine. Experiments show that the addition of the electron-donating substituent can enhance the catalytic activity with the sequence 4,4'-dimethyl-2,2'-bipyridine > 2,2'-bipyridine > 4,4'-carboxy-2,2'-bipyridine. The catalytic system consisting of palladium acetate, 4,4'-dimethyl-2,2'-bipyridine, *p*-toluenesulfonic acid, and *p*-benzoquinone catalyzes the copolymerization of CO/ST to prepare polyketone. Effects of the usage of each component of the catalyst system on catalytic activity were studied. By optimizing the reaction conditions, the catalytic activity can achieve the maximum 1284 gSTCO/gPd h.

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