



The Effects of Different Components in Pd²⁺/Rare Earth Catalytic System on Synthesis of a Polyketone

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ABSTRACT

The linear copolymer of styrene (ST) and carbon monoxide (CO) was prepared in the presence of palladium acetate, cupric *p*-toluenesulphonate and rare earth acetate RE(OAc)₃ (RE= Pr, Nd, Eu, Dy, Ho) multiplex catalyst system. The structure of products was characterized by ¹³C NMR and FTIR. It is found that the catalytic activity of the system increases with the increasing of atomic number and decreasing of the ionic radius from praseodymium to holmium. The best catalytic effect was obtained when the molar ratio of Pd²⁺: Ho³⁺: Cu²⁺ was 1:4:4, and the catalytic activity was 1194 g/(gPd·h). The effects of the different components including methanol, 2,2-bipyridyl, *p*-toluenesulphonic acid, and *p*-benzoquinone on the copolymerization were also studied in detail. To evaluate the influence of different components on the catalyst system, the principal component analysis method was employed. The experiments and data analysis performed have shown that three principal components are significant for evaluation of total variability of the catalytic system.

Key Words:

polyketone;
rare earth;
styrene;
carbon monoxide;
catalytic activity.

INTRODUCTION

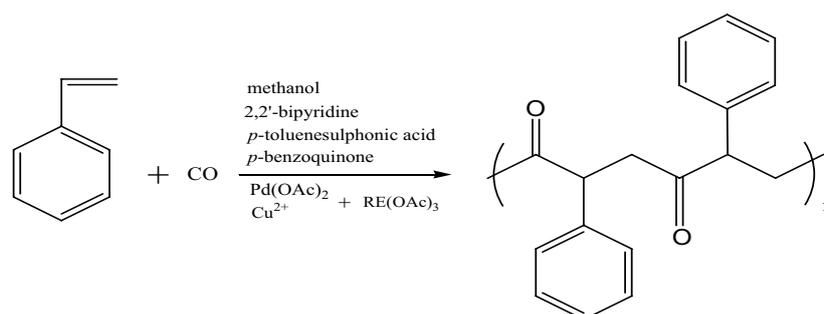
As one class of high performance materials, polyketones have attracted a great deal of attention due to their high thermal stabilities [1]. Polyketones also have the advantage of being easily converted to other functional polymers. Moreover, aliphatic polyketones have been used as photodegradable polymers [2]. Unfortunately, the

high price of palladium-based catalysts results in increasing cost of polyketone preparation. Therefore, improving the activity of the catalytic system has become the most important issue [3-6].

Since the excellent performance of the rare earth in the polymer synthesis was realized, the rare earth catalyst has been applied in

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Scheme I. Alternating copolymerization of styrene with CO in the presence of multiplex catalyst system.

the copolymerization of alkene with monomers like methyl methacrylate [7], lactide [8], propylene oxide [9,10], etc. exhibiting good catalytic activity.

Unfortunately, the activity of rare earth in the synthesis of polyketone was not satisfied. The poor promoting effect of neodymium acetate in the copolymer of styrene (ST) and carbon monoxide (CO) was observed by Yao et al. [11].

Apart from few exceptions [6], it is difficult to find in literature data concerning the activity of Pd²⁺ multiplex catalytic system. In order to improve the catalytic activity of ST/CO copolymerization, a novel Pd²⁺/Cu²⁺/rare earth multiplex catalytic system was developed. In the presence of the multiplex catalyst, a reaction features high activity and high productivity. In particular, the further insights into the influence of different components on the catalytic activity were investigated as well.

EXPERIMENTAL

Materials

Styrene (analytical grade) was distilled and dried over CaH₂ prior to use. Carbon monoxide (99.9+%) was purchased from Beijing Analysis Instrument Company, China. Rare earth acetate RE(OAc)₃ (RE=Pr, Nd, Eu, Dy, Ho) was prepared according to literature [12]. The other chemicals were of analytical grade or higher (Kewei Ltd., Tianjin, China), and directly used without further purification.

Copolymerization

Palladium acetate, rare earth salts, cupric toluenesulphate, 2,2'-bipyridine, *p*-toluenesulphonic acid, and *p*-benzoquinone were added to a solution of methanol

and styrene in a 100-mL stainless steel reactor. Carbon monoxide was blown into the system until inner pressure reached 2.0 MPa. The mixture was stirred for 2 h at 60°C. The steel reactor was cooled down to room temperature after the copolymerization was over and the unreacted CO was released. The raw product, as illustrated in Scheme I, was precipitated in ethanol and washed by Soxhlet extractor. The product was dried under vacuum and gave poly(1-oxo-2-phenyltrimethylene) as a white powder.

Measurements

FTIR Spectra were collected on a BIO-RAD FTS3000 FTIR spectrometer with potassium bromide pellets. Solid-state ¹³C NMR analyses were acquired on Varian Infinity plus 300WB NMR spectrometer operating at 75 MHz.

RESULTS AND DISCUSSION

Characterizations

The IR spectrum of the resultant copolymer is shown in Figure 1. The characteristic strong absorbent peak of carbonyl group in the backbone of the copolymer is merged at 1705 cm⁻¹. Two absorbent peaks appear at 698 cm⁻¹ and 751 cm⁻¹, respectively, which are phenyl characteristic absorbent peaks. These results indicate that the structure of the copolymer has the components of CO and ST, consistent with literature [13].

The polyketone obtained using rare earth as co-catalyst, exhibits poor solubility in polar organic solvents such as CH₃OH, CH₃CN, and THF. This is probably due to the relatively high molecular weight and regioregularity [14]. The ¹³C solid-state NMR

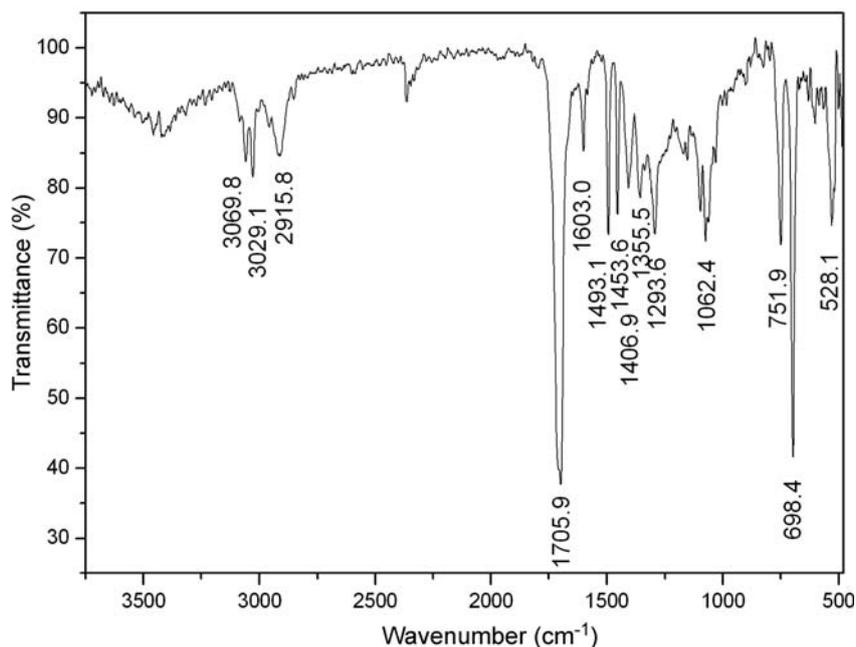


Figure 1. FTIR Spectrum of poly(1-oxo-2-phenyltrimethylene).

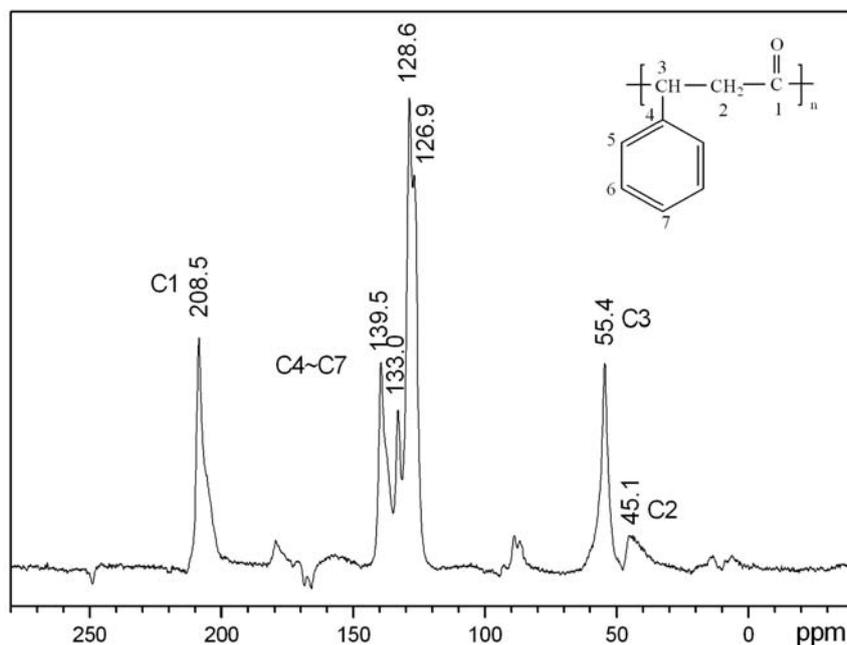
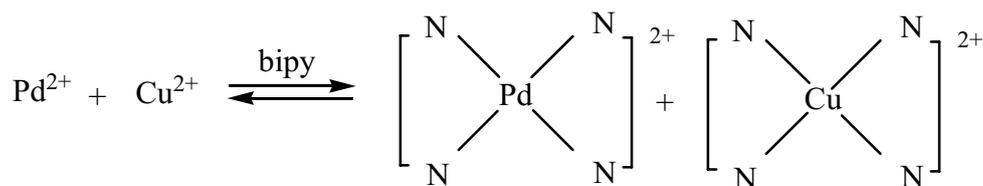


Figure 2. ¹³C Solid-state NMR spectrum of poly(1-oxo-2-phenyltrimethylene) synthesized using co-catalyst neodymium acetate.

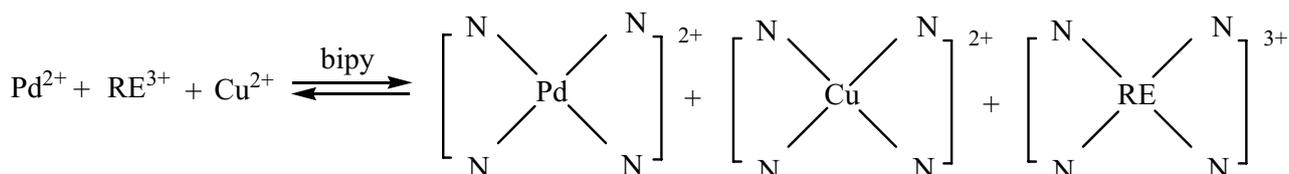
spectrum of the copolymer synthesized using co-catalyst rare earth is shown in Figure 2.

The resonances at 45.1, 54.4, and 208.5 ppm in the ¹³C NMR spectrum are assigned to backbone methylene, methylene, and carbonyl carbons, respectively, of the repeating molecular unit $-\text{CH}_2\text{CHphCO}-$. The aro-

matic carbon resonances are located at 126.9, 128.6, 133.0, and 139.5 ppm. Thus, the chemical shifts corresponding to the C atoms in various chemical environments in the chain of ST/CO confirm the regular structure of alternating copolymer of CO and ST, as it has been reported [15].



Scheme II. Schematic representation for the role of Cu²⁺ in the catalytic system.



Scheme III. Schematic representation for the role of RE³⁺ in the catalytic system.

Calculation of Catalytic Activity (CA)

$$CA = \frac{STCO(g)}{Pd(g) \times \text{reaction time}(h)}$$

Effects of Rare Earth Salts on the Copolymerization

Although palladium acetate was introduced instead of PdCl₂ in the multiplex catalyst system, the remarkable dependence of catalytic activity on the molar ratio of the rare earth in the multiplex catalyst system was obtained. It is shown in Table 1 that when Pd²⁺ to Cu²⁺ ratio was 1:4, the catalytic activity increased dramatically as the neodymium acetate molar amount increased. The mechanism of the reaction was probably that Scheme II which may be transformed into Scheme III. In this way, probably more than 1.5 times of the active centres could be kept in the catalytic system and so the catalytic activities were improved. The best catalytic effect was obtained when the Pd²⁺:Nd³⁺:Cu²⁺ ratio was 1:4:4, and the catalytic activity was 877 g/(gPd·h). The catalytic activity decreased when the amount of the neodymium acetate further increased. From Table 1, entries 2, 3, and 4, one can generalize that the cupric toluenesulphate affects the activity to a large extent as well. Similarly, the effect of Cu²⁺ on the system was also observed by Li et al. [6].

As a co-catalyst, different rare earth acetates RE(OAc)₃ (RE= Pr, Nd, Eu, Dy, Ho) were introduced

to the system in this work. Table 2 shows the effect of rare earth elements on the catalytic activity of the copolymerization catalytic system. From praseodymium to holmium, the catalytic activity of the system increases with the increasing of atomic number and decreasing of the ionic radius. On the other hand, the catalytic activity is also related to the chelating ability of the rare earth metal. Among them, the rare earth holmium has high chelating number, which consumes more 2,2'-bipyridyl and has the higher catalytic activity of 1194 g/(gPd·h).

Table 1. Effects of different Pd²⁺: Cu²⁺: Nd³⁺ molar ratios on the catalytic activity.

Entry	Pd ²⁺ : Cu ²⁺ : Nd ³⁺	W ^a	CA ^b
1	1:1:0	1.74	411
2	1:1:1	2.11	497
3	1:2:1	2.39	564
4	1:4:1	2.78	655
5	1:4:2	3.38	798
6	1:4:4	3.72	877
7	1:4:6	3.23	762

Reaction conditions: palladium acetate= 0.02 mmol, styrene=10 mL, methanol= 5 mL, *p*-toluenesulphonic acid= 0.24 mmol, *p*-benzoquinone= 4 mmol, 2,2'-bipyridine= 0.32 mmol, reaction time= 2 h, temperature= 60°C, P_{CO}= 2 MPa.

(a) Weight of polyketone (g).

(b) Catalytic activity (CA) defined as g polyketone/(gPd·h).

Table 2. Effects of different rare earth acetates on the catalytic activity.

Rare earth	Atomic number	Electron configuration	W	CA ^{a,b}
Pi ³⁺	59	4f ³ 6s ²	3.16	746
Nd ³⁺	60	4f ⁴ 6s ²	3.72	877
Eu ³⁺	63	4f ⁷ 6s ²	4.05	955
Dy ³⁺	66	4f ¹⁰ 6s ²	4.59	1082
Ho ³⁺	67	4f ¹¹ 6s ²	5.06	1194

Reaction conditions: palladium acetate= 0.02 mmol, rare earth acetate= 0.08 mmol, cupric toluenesulphate= 0.08 mmol, styrene= 10 mL, methanol= 5 mL, *p*-toluenesulphonic acid= 0.24 mmol, *p*-benzoquinone= 4 mmol, 2,2'-bipyridine= 0.32 mmol, reaction time= 2 h, temperature= 60°C, P_∞= 2 MPa.

(a) Weight of polyketone (g); (b) Catalytic activity (CA) defined as polyketone/(gPd·h); (c) Molar ratio of Pd²⁺: Cu²⁺: RE³⁺ is 1:4:4.

Effects of 2,2'-Bipyridine on the Copolymerization

The copolymerization of ST and CO requires palladium (II) catalysts with N-N chelating ligands to be used [16]. It is commonly agreed that the chain termination is induced more easily by the higher electron density on the phosphine-chelating palladium centre in comparison with nitrogen-chelating palladium [17]. In fact, the oligomers are generally obtained with palladium catalysts stabilized by chelating diphosphines [18].

2,2-Bipyridine was chosen as a catalytic complex ligand in this experiment. As shown in Table 3

(entries 1-7), the catalytic activity first increased and then decreased with the molar ratio of bipy: Pd²⁺ increasing from 4 to 24. Therefore, the optimum ratio of bipy/Pd²⁺ is important for catalytic activity in the copolymerization of ST and CO catalyzed by Pd²⁺ multiplex catalyst. For the reason of various rare earths with different ligand valencies we deduce that this optimum ratio of bipy/Pd²⁺ is not changed by different rare earths in the system.

Effects of *p*-Toluenesulphonic Acid on the Copolymerization

In the copolymerization of CO and ST, the strong acid plays important roles in the catalytic system (Scheme IV). It enhances the substitution of the acetate ions which is combined strongly with central metal or rare earth ions so that the reacting monomers can easily be activated by coordination to the central metal ion [19,20]. Furthermore, it maintains the neutrality of the catalytic system as well. Here, the highest catalytic activity 877 g/(gPd·h) is obtained in Table 3 (entries 8-13) when the molar ratio of *p*-toluenesulphonic acid to Pd²⁺ is 12:1.

Effects of Methanol on the Copolymerization

Methanol plays important roles in the copolymerization of CO and ST. According to the literature [21], methanol coordinates with Pd (II) to produce the active centre (Scheme V). In the catalytic system, Table 3 (entries 14-19) shows that the productivity of polyketone is critically influenced by the solvents.

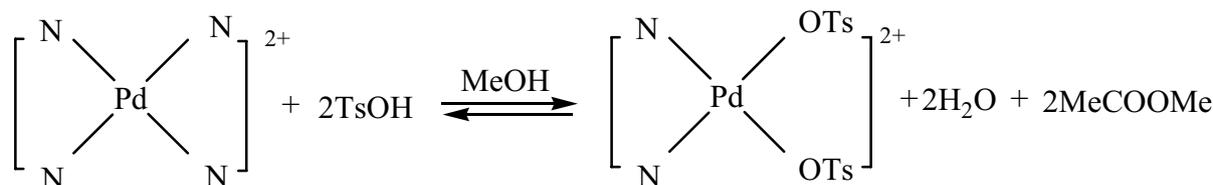
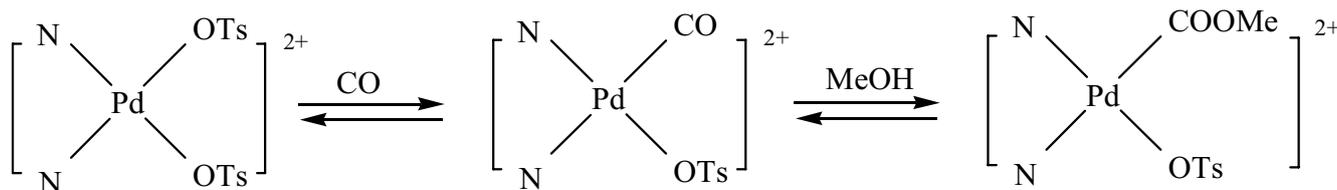
**Scheme IV.** Schematic representation for the role of TsOH in the catalytic system.**Scheme V.** Schematic representation for the role of MeOH in the catalytic system.

Table 3. Effects of different components on the catalytic activity.

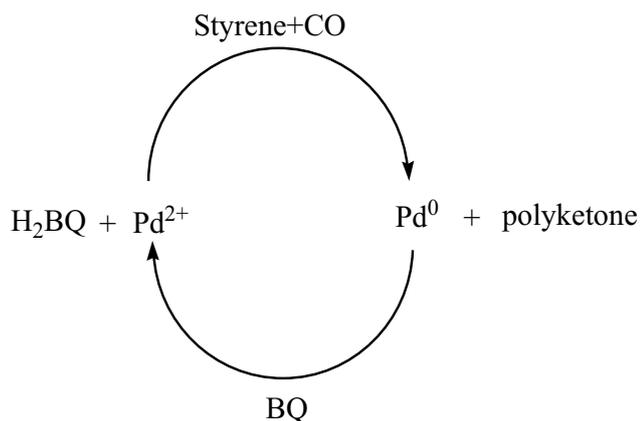
Entry	CA ^b	W ^c	Bipy ^d	pTSA ^e	MeOH ^f	BQ ^g
1	206	0.87	0.32	0.24	5	1
2	578	2.45	0.32	0.24	5	2
3	732	3.10	0.32	0.24	5	3
4	877	3.72	0.32	0.24	5	4
5	751	3.18	0.32	0.24	5	5
6	665	2.82	0.32	0.24	5	6
7	543	2.30	0.32	0.24	5	8
8	318	1.35	0.32	0.06	5	4
9	381	1.62	0.32	0.12	5	4
10	597	2.53	0.32	0.18	5	4
11	877	3.72	0.32	0.24	5	4
12	571	2.42	0.32	0.30	5	4
13	521	2.21	0.32	0.36	5	4
14	320	1.36	0.32	0.24	1	4
15	612	2.59	0.32	0.24	3	4
16	877	3.72	0.32	0.24	5	4
17	853	3.62	0.32	0.24	7	4
18	744	3.15	0.32	0.24	9	4
19	631	2.68	0.32	0.24	11	4
20	476	2.02	0.08	0.24	5	4
21	559	2.37	0.16	0.24	5	4
22	686	2.91	0.24	0.24	5	4
23	877	3.72	0.32	0.24	5	4
24	445	1.89	0.4	0.24	5	4
25	330	1.40	0.48	0.24	5	4
Mean	601.08	2.55	0.31	0.23	5.24	4.04
SD ^a	196.90	0.83	0.70	0.53	1.76	1.21

Reaction conditions: reaction time= 2 h, temperature= 60°C, P_{CO}= 2 MPa.

(a) Standard deviation; (b) Catalytic activity (CA) defined as g polyketone/(gPd.h); (c) Weight of polyketone (g); (d) Dosage of 2,2'-bipyridine (mmol); (e) Dosage of *p*-toluenesulphonic acid (mmol); (f) Volume of methanol (mL); (g) Dosage of *p*-benzoquinone (mmol).

Although no copolymer can be produced without methanol, but when volume of methanol is very high, the reaction rate will decline accordingly. As shown in

Table 3, when the volume of methanol is 5 mL, the catalytic activity reaches the highest value, 877 g/(gPd.h).



Scheme VI. Schematic representation for the role of BQ in the catalytic system.

Effect of *p*-Benzoquinone on the Copolymerization

All of these experiments were conducted with the addition of the oxidant, usually 1,4-benzoquinone, which has been reported to be essential in high amounts for achieving high productivities [22]. In this system, 1,4-benzoquinone can oxidize Pd (0) to Pd (II) again, and BQ itself is reduced to H₂BQ (Scheme VI). Therefore, the dosage of BQ is important to the copolymerization of ST and CO catalyzed by Pd (II).

It is found that high excess of the oxidant with respect to Pd²⁺ multiplex catalyst is required to have high yields of polyketones with $n(\text{benzoquinone})/n(\text{Pd}^{2+}) > 150$ (Table 3). For example, under the conditions reported in Table 3 (entries 20-25), the catalytic activity increases from 206 to 877 g STCO/gPd.h when benzoquinone/(Pd²⁺) molar ratio changes from 50 to 200. However, when the benzoquinone/ Pd²⁺ molar ratio is very high, the reaction rate will decline accordingly. The reason is probably that benzoquinone cannot dissolve in styrene completely and change the reaction system into a heterogeneous state.

The Evaluation of Different Components on the Catalyst System

Evaluation of the influence of different components on the catalyst system requires a large number of various data to be collected, and the results often are hard to analyze. In such situations, a principal component analysis (PCA) method is employed. Usually, 2 or 3 principal components are sufficient to explain the majority of total variability of original variables.

The effects of different components on the catalyt-

Table 4. Correlation matrix of the different components, weight of polyketone, and the catalytic activity^a.

Variable	CA	W	Bipy	pTSA	MeOH
W	1.000	—	—	—	—
bipy	-0.078	-0.078	—	—	—
pTSA	0.265	0.264	-0.019	—	—
Methanol	0.283	0.283	0.019	0.019	—
BQ	0.201	0.201	0.005	0.005	-0.005

(a) The labels correspond to variables listed in Table 3.

ic activity together with basic statistics for characterization of the variability of the samples analyzed are given in Table 3. In order to specify the relationships between the components and the catalytic activity of the system, the correlation analysis has been performed using pooled data for all 25 entries (Table 4). These relationships show that different components are independent under the present reaction conditions. It is an unexpected finding that the dosage of 2,2'-bipyridine is negatively related with any other variables.

Tables 5 and 6 report the principal component analysis results with Varimax rotation using SPSS15.0. It is established that three principal components are significant for explanation of total variability of the catalytic system (Table 5). By the first principal component 38.4% of the total variation is

Table 5. Results of PCA analysis using the data of different components, weight of polyketone, and the catalytic activity.

Principal component	Initial Eigen values		
	Total	Variance (%)	Cumulative (%)
PC 1	2.305	38.411	38.411
PC 2	1.019	16.989	55.400
PC 3	1.005	16.751	72.151
PC 4	0.963	16.044	88.195
PC 5	0.708	11.805	100.000
PC 6	5.30×10^{-6}	8.84×10^{-5}	100.000

Table 6. Coefficients of the first three principal components^{a,b}.

Variable	PC 1	PC 2	PC 3
CA	0.966*	0.000	0.008
W	0.966*	0.000	0.008
bipy	-0.114	0.816*	0.136
pTSA	0.401	-0.306	-0.261
Methanol	0.422	0.510	-0.374
BQ	0.297	1.36 × 10 ⁻⁶	0.882*

The main sources of variability indicated by asterisk (*); variable notations as indicated in Table 3. (a) Extraction method: Principal component analysis; (b) 3 Components extracted.

explained, 55.4% by the first two components and 72.1% by three components. Table 6 shows that for the first component (38.4% explained variation) the most important variables are: weight of polyketone and catalytic activity. The second component (17.0% explained variation) is mainly defined by one variable (dosage of 2,2'-bipyridine). For the third component (16.8% explained variation) the most important variable is the dosage of 1,4-benzoquinone.

CONCLUSION

The Pd²⁺/Cu²⁺/rare earth multiplex catalyst system showed high catalytic activity in the synthesis of poly(1-oxo-2-phenyltrimethylene). It is found that the ionic radius and the chelating number of rare earth salts affect the catalytic activity of Pd²⁺ catalyst directly for this reaction. The ratio of component in the multiplex catalyst system also shows great influence on the yield of polyketone. These results presented may be applied to find more suitable catalyst system in the copolymerization of CO with ST.

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REFERENCES

1. Belov G.P., Novikov E.V., Polyketones as alternating copolymers of carbon monoxide, *Russian Chem. Rev.*, **73**, 267-291, 2004.
2. Xu F.Y., Chien J.C.W., Photodegradation of α -olefin/carbon monoxide alternating copolymer, *Macromolecules*, **26**, 3485-3489, 1993.
3. Jerome D., Barbara M., The role of nitrogen-donor ligands in the palladium-catalyzed polyketones synthesis, *Coord. Chem. Rev.*, **250**, 542-560, 2006.
4. Bastero A., Ruiz A., Reina J.A., Claver C., Guerrero A.M., Jalon F.A., Manzano B.R., New catalysts for the alternating copolymerization of 4-tert-butylstyrene/CO, *J. Organomet. Chem.*, **619**, 287-292, 2001.
5. Hardacre C., Holbrey J.D., Katdare S.P., Seddon K.R., Alternating copolymerisation of styrene and carbon monoxide in ionic liquids, *Green Chem.*, **4**, 143-146, 2002.
6. Li L., Huang X.L., Li G.X., A new catalytic system for copolymerization of styrene with CO: PdCl₂/bipy/M(CF₃SO₃)_n, *J. Mol. Catal. A: Chem.*, **229**, 39-46, 2005.
7. Jiang L., Shen Z., Zhang Y., Polymerization of methyl methacrylate with a new rare-earth coordination catalyst, *Eur. Polym. J.*, **36**, 2513-2516, 2000.
8. Zhang L., Shen Z., Yu C., Fan L., Ring-opening polymerization of D,L-lactide by rare earth 2,6-dimethylaryloxyde, *Polym. Int.*, **53**, 1013-1016, 2004.
9. Liu B., Zhao X., Wang X., Wang F., Copolymerization of carbon dioxide and propylene oxide with neodymium trichloroacetate-based coordination catalyst, *Polymer*, **44**, 1803-1808, 2003.
10. Yasuda H., Tamai H., Characteristics of rare earth systems as polymerization initiators, *Prog. Polym. Sci.*, **18**, 1097-1139, 1993.
11. Yao F.L., Deng L.D., Men J.H., Feng Y.K., Sun

- J.W., Copolymerization of carbon monoxide and styrene with the Nd(III)-Cu(II) catalyst, *J. Appl. Polym. Sci.*, **82**, 8-13, 2001.
12. Seaton J.A., Sherif F.G., Audrieth L.F., Preparation of some basic and anhydrous rare earth acetates. Their properties and reactions in acetic acid as solvent, *J. Inorg. Nuc. Chem.*, **9**, 222-231, 1959.
 13. Guo J.T., Liu B., Wang X.Y., Sun J.W., The use of ion exchange resins in the recycle of palladium catalysts for the synthesis of polyketones, *React. Funct. Polym.*, **61**, 163-170, 2004.
 14. Bronco S., Consiglio G., Regio- and stereoregular copolymerisation of propene with carbon monoxide catalysed by palladium complexes containing atropisomeric diphosphine ligands, *Macromol. Chem. Phys.*, **197**, 355-365, 1996.
 15. Drent E., Budzelaar P.H.M., Palladium-catalyzed alternating copolymerization of alkenes and carbon monoxide, *Chem. Rev.*, **96**, 663-682, 1996.
 16. Sen A., Jiang Z., Palladium(II)-catalyzed alternating copolymerization and terpolymerization of carbon monoxide with α -olefins: Formation of syndiotactic copolymers as well as terpolymers with both syndiotactic and atactic segments, *Macromolecules*, **26**, 911-915, 1993.
 17. Nozaki K., Komaki H., Kawashima Y., Hiyama T., Matsubara T., Predominant 1,2-insertion of styrene in the Pd-catalyzed alternating copolymerization with carbon monoxide, *J. Am. Chem. Soc.*, **123**, 534-544, 2001.
 18. Nozaki K., Sato N., Takaya H., Highly enantioselective alternating copolymerization of propene with carbon monoxide catalyzed by a chiral phosphine-phosphite-palladium(II) complex, *J. Am. Chem. Soc.*, **117**, 9911-9912, 1995.
 19. Drent E., Budzelaar P.H.M., The oxo-synthesis catalyzed by cationic palladium complexes, Selectivity control by neutral ligand and anion, *J. Organometal. Chem.*, **593-594**, 211-225, 2000.
 20. Vavasori A., Cavinato G., Toniolo L., Carbon monoxide-ethylene copolymerization catalyzed by a Pd(OAc)₂/dppp/formic acid system [dppp=1,3-bis(diphenylphosphino) propane], *J. Mol. Catal. A: Chem.*, **191**, 209-215, 2003.
 21. Milani B., Anzilutti A., Vicentini L., O Santi A.S., Zangrando E., Geremia S., Mestroni G. Bis-chelated palladium(II) complexes with nitrogen-donor chelating ligands are efficient catalyst precursors for the CO/styrene copolymerization reaction, *Organometallics*, **16**, 5064-5075, 1997.
 22. Milani B., Corso G., Mestroni G., Carfagna C., Formica M., Seraglia R., Highly efficient catalytic system for the CO/styrene copolymerization: Toward the stabilization of the active species, *Organometallics*, **19**, 3435-3441, 2000.