



Synthesis of polyketone catalyzed by Pd/C catalyst

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ABSTRACT

In the present work, polyketone (STCO) was successfully synthesized by use of carbon monoxide (CO) and styrene (ST) in the presence of Pd/C (5.4 wt%), bipyridine and *p*-toluenesulfonic acid. The final products were characterized by infrared Spectroscopy (IR), ¹³C nuclear magnetic resonance (¹³C NMR), elemental analysis, thermogravimetry (TG), differential scanning calorimetry (DSC), gel permeation chromatography (GPC) and transmission electron microscopy (TEM). The effects of various reaction conditions, including Pd/C catalyst usage, ligands, *p*-toluenesulfonic acid, reaction temperature and reaction time were investigated in detail, and the reusability of Pd/C catalyst in the copolymerization of CO and ST was also probed. It is found that the Pd/C catalyst shows higher catalytic activity and reusability in the copolymerization of CO and ST. It can be reused for 12 times with the highest catalytic activity of 1255.17 STCO/(g Pd h). The molecular weights and polydispersity index of the polyketone were as follows: Mn = 10,700, Mw = 19,079 and Mw/Mn = 1.78, respectively.

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1. Introduction

Polyketones are a kind of macromolecule with unique properties, including the excellent mechanical performance, resistance against pressure and heat, especially their biodegradation and photodegradation [1–8]. In the past 20 years, polyketones obtained by the copolymerization of carbon monoxide and styrene have received significant interest both in academic research and in industrial application. Meanwhile, they have made a great progress [9–16]. Nowadays, the copolymerization of carbon monoxide and styrene is usually promoted by Pd(II) complexes having N–N chelating ligand. However, because the catalyst cannot be reused and is prone to be buried in the products, the catalytic activity is reduced and the products cannot get high molecular weight leading to high cost, which seriously constrains its industrialization process.

The recycle and reuse of the catalyst, which appear as a way of reducing copolymerization cost, become a very attractive field of the research all over the world. Resin-supported palladium acetate and recycle of palladium in post-treatment fluid of absorption reaction were studied in our previous experiment [17,18]. The results show that the resin-supported palladium acetate is efficient in reusability. In the present paper, the copolymerization of carbon monoxide and styrene promoted by Pd/C catalyst was carried out. The effects of various components in the Pd/C catalytic system on the catalytic activity, properties of the product and the reusability of Pd/C were also investigated in detail.

2. Experimental

2.1. Starting materials

The carbon monoxide (99.9+%) used was purchased from Beijing Analysis Instrument Company, China. The Pd/C (5.4 wt%) catalyst was supplied by the Baoji Rock Pharmachem Co. Ltd. and it was dried under vacuum at room temperature prior to use. The styrene and 2-chlorophenol were vacuum distilled. The other chemicals are of analytical grade or higher, which were directly used without further purification.

2.2. Copolymerization of CO and styrene

A solution of methanol, styrene and 2-chloro-phenol, Pd/C, 2,2'-bipyridine, and *p*-toluenesulfonic acid were added into 100-mL stainless steel reactor. Carbon monoxide was blown up the system until the inner pressure reached 2.0 MPa. The mixture was reacted for 2 h at 70 °C under stirring. Then the reactor was cooled down to room temperature after the copolymerization was over and the unreacted CO was released. Pd/C catalyst was filtrated from the solution. The raw product was precipitated in ethanol and washed by a Soxhlet extractor. The product was dried under vacuum. Finally the dried polyketone was obtained in the form of white fine powder. ¹³C NMR: δ 208.1 (–CO–), 139.9, 133.1, 128.5, 126.6 (–Ph), 54.2 (–CHCH₂–), 45.4 (–CHCH₂–); Anal. Calc. for polyketone: C 81.82%, H 6.06% and O 12.12%; found: C 81.69, H 6.12 and O 12.19.

The mixture of *o*-chlorophenol and ethanol was distilled under reduced pressure to recycle *o*-chlorophenol and ethanol. The mixture of *o*-chlorophenol and ethanol was distilled under reduced

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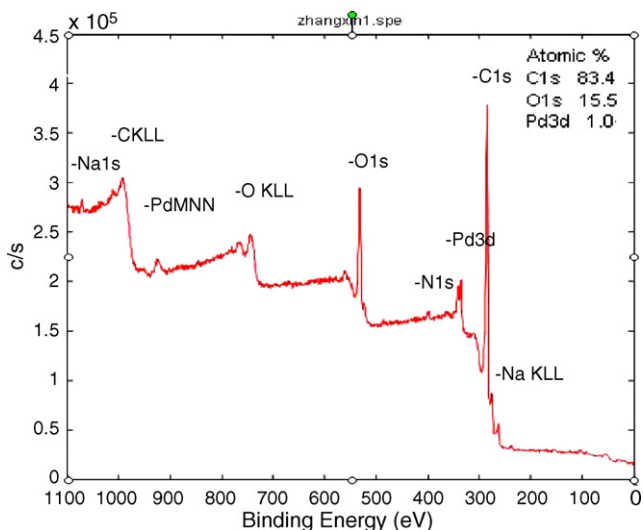


Fig. 1. XPS spectrum of Pd/C.

pressure. The filtrated Pd/C was dried under vacuum for 12 h and then it was used to catalyze the copolymerization of CO and styrene again along with bipyridine, *p*-toluenesulfonic, styrene and methanol following the above method.

2.3. Measurement

2.3.1. Characterizations of catalyst

PHI-1600 photoelectron spectrograph from USA PE company was employed to analyze surface elements of the copolymer and identify their relative content. Mg $K\alpha$ was used as X-ray radiator ($E_b = 1253.6$ eV), power 300.0 W, spot size 0.8 mm², degree of vacuum 667 nPa, pass energy 23.5 eV, Al 2p in Al₂O₃ ($E_b = 74.00$ eV) as internal reference. 180-80 atomic absorption spectrometer from Japan was used to analyze the content of Pd²⁺ from the surface of Pd/C every time that it was reused in the copolymerization.

2.3.2. Characterizations of copolymer

FTIR spectra were performed by using 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 300 MHz. The elemental analysis was carried out on a PerkinElmer PE-2400 elemental analyzer.

Differential scanning calorimetry (DSC) analysis was performed by NetzschDSC 204 F1 different thermal analysis meter from Germany. Heating rate 10 °C/min, carrier gas N₂, gas flow rate 10 mL/min.

Table 1
Content of Pd²⁺ from the surface of Pd/C catalyst.

Used time(s)	Content of Pd ²⁺
0	5.4%
1	0.7%
2	0.7%
6	0.4%
7	0.3%
8	0.3%
10	0.3%

Thermogravimetric analysis (TG) was performed in a Shimadzu TGA-50H thermal analysis system with nitrogen at the heating rate of 10 °C/min.

Agilent and GPC-MWA were both used to test molecular weight of the copolymer.

JEM-2000FX TEM made in Japan was used to observe microstructure of the chosen simple of polyketones and E-ray diffraction analysis of the samples was practised under test voltage of 200 kV, vacuum of 5–10 Pa, the resolution of 0.19 nm.

3. Results and discussions

3.1. Characterizations of catalyst

In the copolymerization of CO and styrene, the valency of Pd in Pd/C catalyst is mainly 2+, which performs good catalytic activity [19]. At first, the valency of Pd for the commercial Pd/C catalyst was validated.

X-ray photoelectron spectroscopy (XPS) was mainly employed to identify elements (except H and He) and their chemical state. In this paper, XPS analysis of Pd/C catalyst was carried out. The XPS spectrum and content of each element are shown in Fig. 1, which proves that the catalyst used in this experiment is composed of elements Pd, C and O. Fig. 2 is the high resolution spectra of Pd, C and O. High resolution spectra of element Pd (Fig. 2) show that 336 eV and 341 eV represent Pd²⁺ in Pd/C catalyst and the two peaks are resulted from spin splitting of Pd(II). It suggests that Pd(II) does exist in the Pd/C catalyst which can promote the copolymerization of CO and ST. Atomic absorption spectrometer (AAS) can be used to evaluate the content of many elements whether they are in some different compounds or just monomer. In the paper, AAS was employed to analyze the content of Pd²⁺ from the surface of Pd/C every time that it was reused in the copolymerization, and the results are shown in Table 1, which can explain that Pd²⁺ can be loaded very well in carbon activated, and Pd/C catalyst can be recycled. Although the content of Pd²⁺ in Pd/C catalyst was declined markedly when it was first used, the content from second time the catalyst was used keep stably correspondingly. So, it can be shown

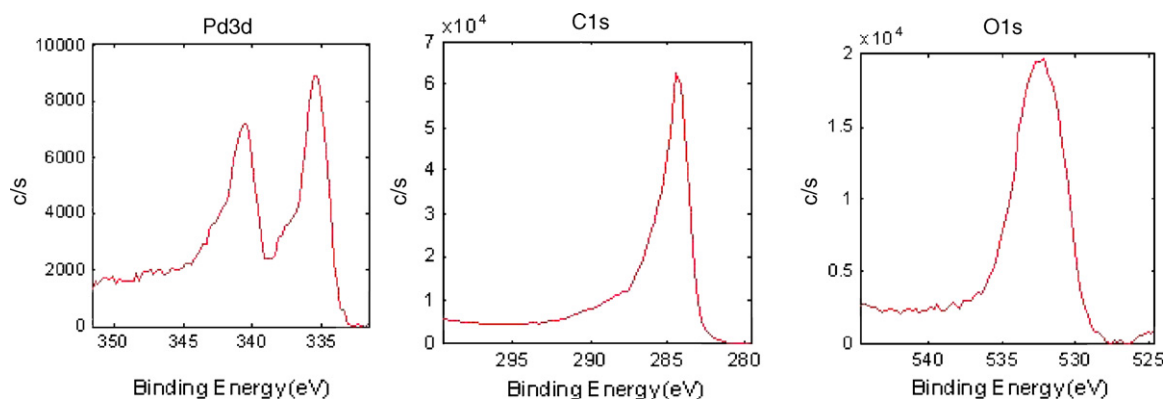


Fig. 2. XPS Pd 3d, C 1s, O 1s core-level spectra of Pd/C.

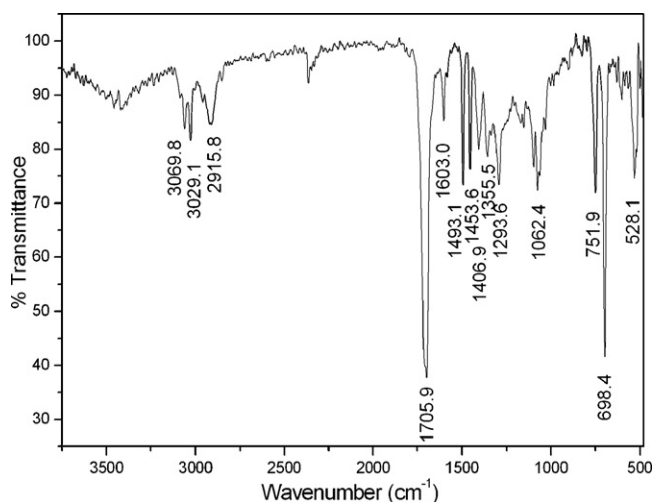


Fig. 3. The FTIR spectrum of polyketone.

in Table 1 that the active center of the copolymerization is Pd/C, but not forming active center of homogeneous catalyst.

3.2. Characterizations of copolymer

The IR spectrum of polyketones produced by CO/styrene copolymerization is shown in Fig. 3. The strong absorbent peak at 1705 cm^{-1} corresponds to carbonyl group which can prove the success of copolymerization. The two absorbent peaks at 698 cm^{-1} and 751 cm^{-1} correspond to offplane bending vibration peak of $=\text{CH}$, which are phenyl monosubstitution characteristic absorbent peaks. The absorbent peaks from 1453 cm^{-1} to 1600 cm^{-1} result from the vibration of phenyl backbone and they are its characteristic absorbent peaks. These results indicate that the structure of copolymer has the components from CO and ST, which is consistent with the literature [18].

DSC and TG were carried out on the polyketones, and the results are shown in Fig. 4. Due to the specific heat capacity of polyketones differing in melting state, elastic state and vitreous state, their energy absorbent peaks are presented, respectively, on the curves. It was reported that polyketones are crystal polymer [2], but the exothermic peak for crystallization is inconspicuous, so second

heating method for DSC must be conducted. It can be seen from Fig. 4 that the polyketones promoted by Pd/C have a glass transition temperature of 101.2°C and a decomposition temperature of 325°C .

It can be proved by the experiment that polyketone is a kind of high-crystalline polymers which is difficult to dissolve in many organic solvents such as benzene, butanone and chloroform, but the existing literature shows that no one have yet testified the visual image of this issue to that effect. In present experiment the crystal degree of polyketone was obtained by using TEM. In this paper, methanol was used as dispersant with suspension technique to prepare sample. 50 mg polyketone was added in 20 mL methanol, which was then placed in ultrasound generator for 10–15 min, and the small amount of solution was removed form the upper layer and dropped in copper network dedicated TEM tests. After vacuum drying 40 min, the sample could be measured by TEM test.

It can be observed from the TEM photo that crystal area does exist in polyketones, which results in a band structure of the small interval form every level and large accumulation on the level and then forming large crystal proportion. The electron diffraction analysis for the samples (Fig. 5) was also performed. The phenomenon of the diffraction spot coexistence with diffraction halo can be clearly seen from the figure, which more clearly and directly explain the high crystal nature of polyketone.

3.2.1. Effect of ligand on copolymerization

The copolymerization of ST and CO requires palladium(II) catalysts with N–N chelating ligands to be used, and then ST and CO insert the space for copolymerisation [19] which can be seen from Scheme 1. The nature and amount of N–N chelating ligand played important roles in the copolymerization, especially in the productivity and stability of catalytic system.

Fig. 6 shows the effect of 2,2'-bipyridine, acting as N–N chelating ligands in catalytic system, on the copolymerization. The fact that there is no polymer produced without chelating ligand in CO and ST catalytic system illustrates that CO and ST cannot be copolymerized without the coordination structure of Pd(II) and chelating ligands. When the value of 2,2'-bipyridine/ Pd^{2+} reached 2, the best catalytic effect is obtained with the highest catalytic activity $123.27\text{ gSTCO}/(\text{gPd h})$. However, further consumption of 2,2'-bipyridine can resulted in low catalytic activity. Though the increased amount of ligands ensured the stability of Pd due to the coordinating structure of Pd generates, the correlation between the

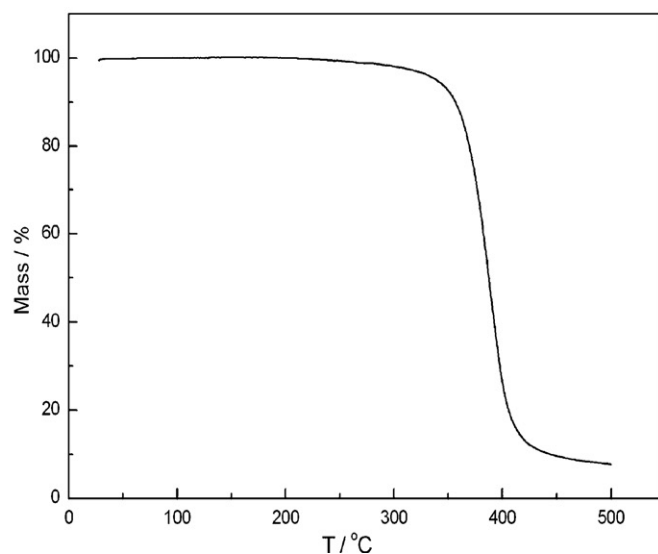
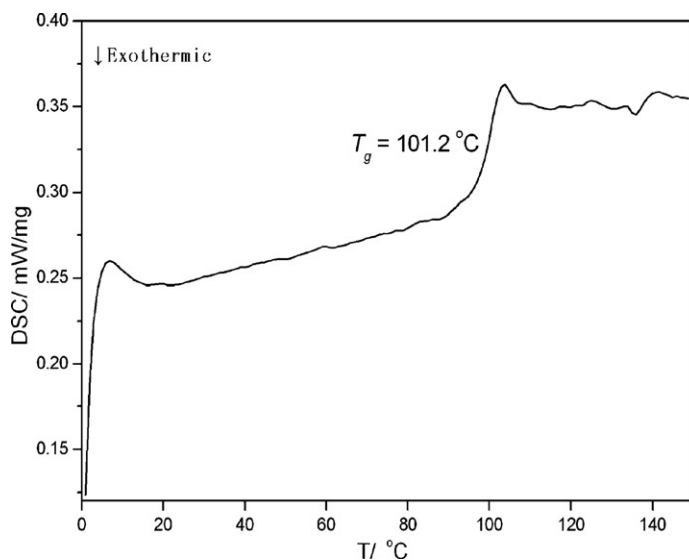


Fig. 4. The differential scanning calorimetry curve (a) and thermogravimetry curve (b) of polyketone.

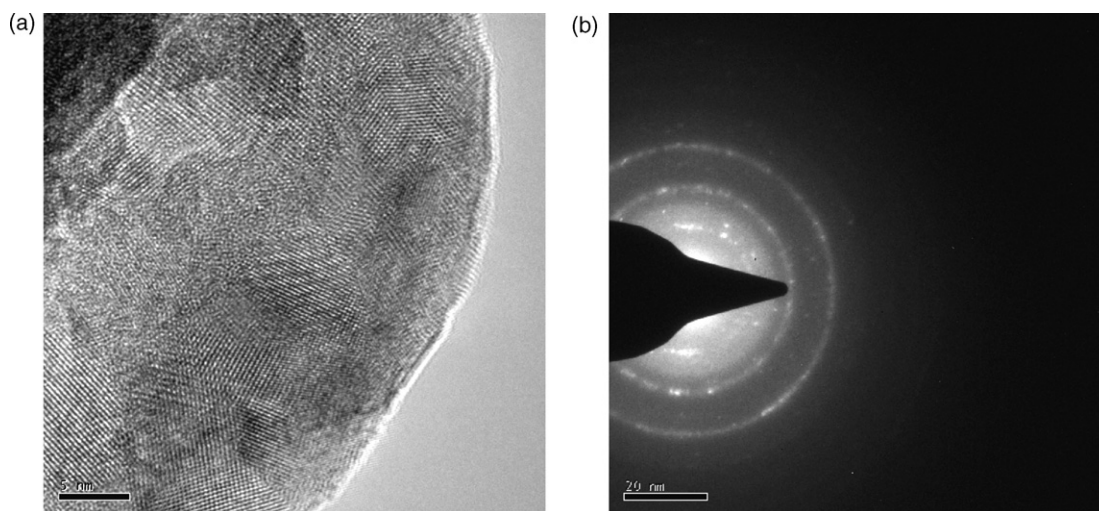
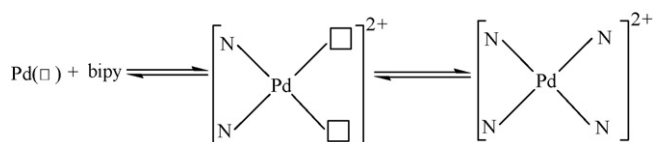


Fig. 5. TEM spectra (a) and the electron diffraction analysis spectra (b) of polyketone.



Scheme 1. Schematic representation for role of ligand.

stability of catalysts and the catalytic activity, however, is contradictory. Only when the amount of bipyridine is appropriate, the single-ring coordination structure with the coral atom Pd can be produced. The other two coordinating points of Pd existing in the coordinating state with polymer increasing chains and monomers make the catalyst stable and with high efficiency. But ligands

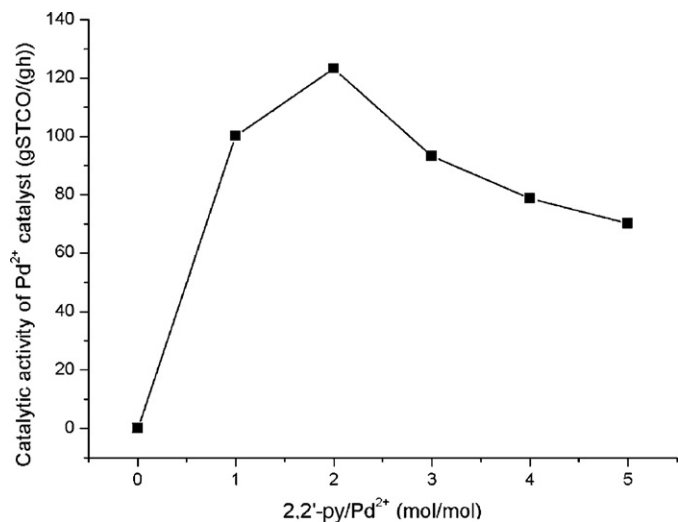


Fig. 6. Effect of 2,2'-bipyridine on the copolymerization.

Table 2
Effect of different ligands on the catalytic activity.

Various kinds of ligands	Weight of copolymer (g)	Catalytic activity (gSTCO/(g Pd h))
4,4'-2 hydroxymethyl-2,2'-bipyridine	1.9726	92.6974
4,4'-2 methyl-2,2'-bipyridine	2.9139	136.9314
2,2'-bipyridine	3.9726	186.6823
4,4'-2 carboxyl-2,2'-bipyridine	1.1380	53.4774

competed with monomers for the coordinating points. While the consumption of bipyridine goes up further, bipyridine will generate double-ring coordination structure L_2PdL_2 with Pd, resulting in lower catalytic activity.

In order to observe the structure and the coordination activity of different kinds of ligands, its effect on copolymerization is also shown in Table 2.

As it is illustrated in the table above that bipyridine without substituted ligand presents a better catalytic effect than those with substituted one. Because the Pd/C catalytic system loads Pd²⁺ to active carbon in ionic compound state, under the condition of this experiment, 2,2'-bipyridine is more suitable for the copolymerization system.

3.2.2. Effect of *p*-toluenesulfonic acid on copolymerization

In the copolymerization of CO and styrene, *p*-toluenesulfonic acid performed its function at the following two aspects: (1) substituting the negative ion which showed good coordinating activity with Pd, forming weaker coordinating state with Pd, and then being substituted by monomer and solvent molecule during the copolymerization for the purpose of forming cavity with catalytic and transfer function and (2) keeping the reaction system electric neutrality. In the experiment, the effects of different amounts of *p*-toluenesulfonic acid on copolymerization are investigated, and the results are shown in Fig. 7.

The catalytic activity is improved significantly as the molar ratio of *p*-toluenesulfonic to Pd²⁺ increase. The highest catalytic activity is achieved as high as 183.40 gSTCO/(g Pd h) when the molar ratio is 2.5. However, the catalytic activity becomes lower when the molar ratio goes up further. In the copolymerization of CO and ST, the *p*-toluenesulfonic negative ions offered by *p*-toluenesulfonic acid generate weak coordinating bond with Pd²⁺, so it is easily substituted by the monomers or solvent molecules and produce coordinating cavities which undertake catalytic function. The electronic density of Pd²⁺ is decreased and the binding energy between monomer and Pd is weakened, accordingly, the catalytic activity

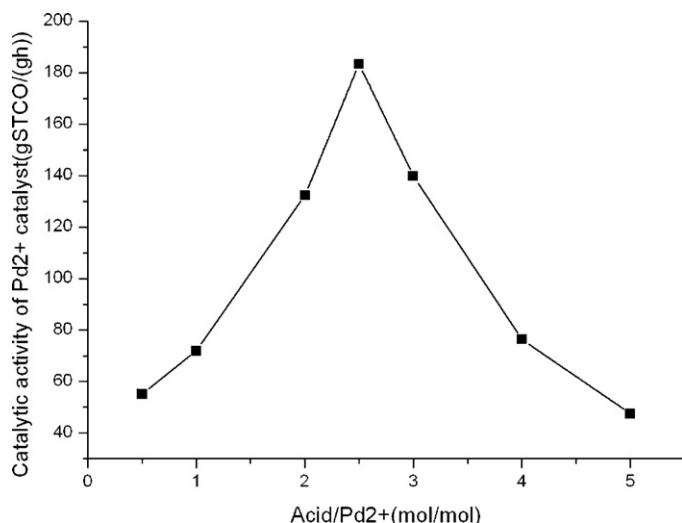


Fig. 7. Effect of *p*-toluenesulfonic acid on the catalytic activity.

rises as increasing in consumption of *p*-toluenesulfonic acid. The copolymer reduced when the consumption of *p*-toluenesulfonic acid goes up further. This is because when the excessive amount of *p*-toluenesulfonic acid exists in the system, a part of *p*-toluenesulfonic acid reacts with alkaline bipyridine so that the catalytic reactivity of Pd decreased.

3.2.3. Effect of reaction temperature on copolymerization

It shows that in Fig. 8 the effect of reaction temperature on the catalytic activity. When the copolymerization is carried out at a relatively low temperature, the activation energy will control the reaction mostly, and the catalyst will not play important role. Additionally, the lower energy of monomers and the slower reaction rate also result in the lower productivity. While the reaction is performed at a too high temperature, the concentration of CO in liquid phase reduces gradually. Moreover, the thermal decomposition of catalyst is possibly brought out by the high temperature, which also led to the decreased productivity. To be brief, either too low or high temperature is adverse to the reaction. It is proved that 70 °C is the optimum temperature to achieve the highest catalytic activity 183.40 gSTCO/(g Pd h).

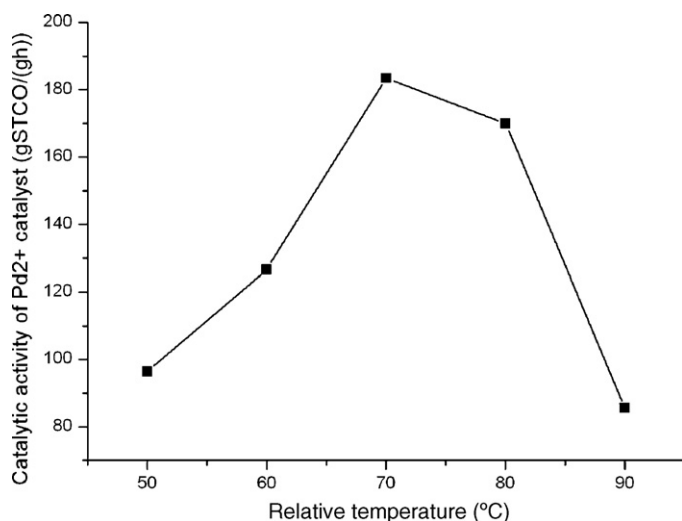


Fig. 8. Effect of reaction temperature on the catalytic activity.

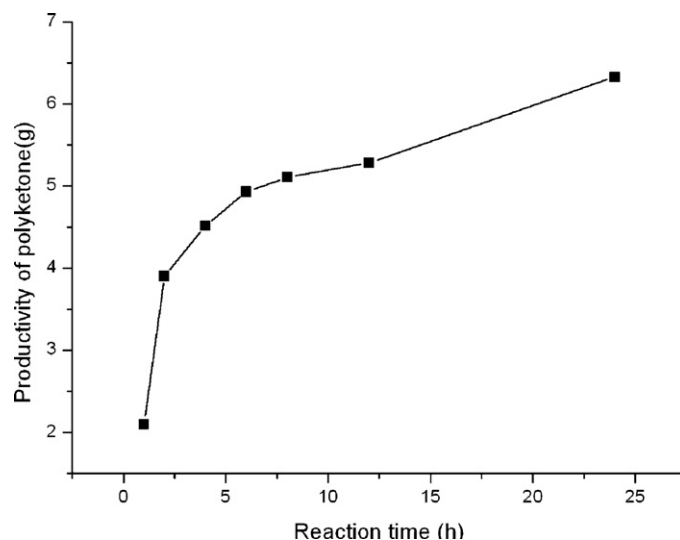


Fig. 9. Effect of reaction time on the productivity of polyketone.

3.2.4. Effect of reaction time on copolymerization

The effect of reaction time on the productivity of polyketones and the catalytic activity are shown in Figs. 9 and 10, respectively.

As is shown in Fig. 9, the productivity of polyketone increases first and then tends to be stable along with time. The yield is found to increase from 1 h to 6 h. After 6 h, the increase rate of polyketone weight slows down. However, when the reaction time is 2 h, the highest catalytic activity 183.40 gSTCO/(g Pd h) are achieved and then the catalytic activity decreases along with the reaction goes up. If the reaction time is too short, the copolymerization will not fully complete, which leads to a decreased product and low catalytic activity. A properly long time is benefit to the reaction. So, the yield of polyketone increases with time at the primary stage. When the copolymerization performs to the utmost, the reaction time has little effect on the productivity. Furthermore, as the concentration of monomers reduces, a certain part of Pd/C is apt to be inactivated during the longtime heating. So an appropriate reaction time should be determined to obtain more polyketone and enhance the reusability of the catalytic system. It can be seen from Fig. 5 that 2 h is the best time interval. The effects of various reaction times on molecular weight of polyketone are also investigated in the experiment. Table 3 suggested that reaction time does not have much

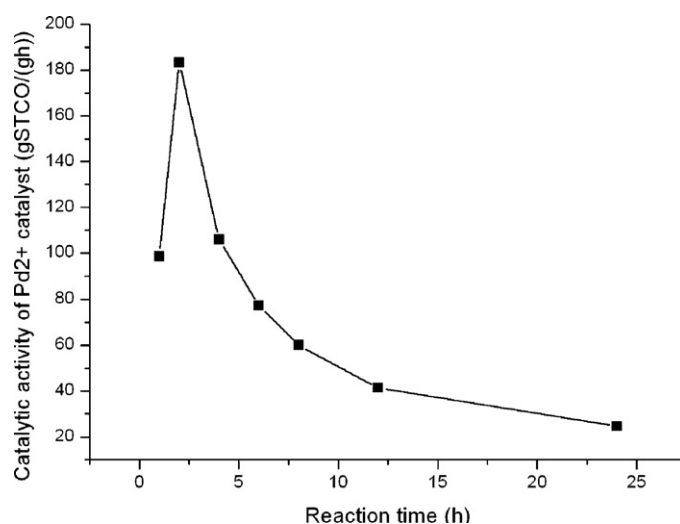


Fig. 10. Effect of reaction time on the catalytic activity.

Table 3
Molecular weight of polyketone.

Reaction time (h)	Mn	Mw	Mw/Mn
2	9882	15,533	1.57
8	9943	17,614	1.77
24	9487	15,793	1.66

Mn is the number average molecular weight, Mw is the weight average molecular weight, the ratio Mw/Mn is referred as polydispersity, expressed relative to a polystyrene equivalent.

Table 4
Molecular Weight of polyketone.

Different content of catalyst/mmol	Mn	Mw	Mw/Mn
Pd ²⁺ = 0.02	10,919	17,528	1.61
Pd ²⁺ = 0.05	10,062	16,492	1.64
Pd ²⁺ = 0.1	9,882	15,533	1.57

to do with molecular weight. So, a proper reduction of time can increase catalytic activity.

3.2.5. Effect of usage of Pd/C catalyst on copolymerization

In this work, Pd/C was used as catalyst for the copolymerization of CO and ST, and the effect of the amount of it on the copolymerization is shown in Fig. 11

Fig. 11 shows that the yield of polyketone increases with the addition of catalyst. However, after the amount of the catalyst reaches a certain value, the yield of polyketone increases just a little. As shown in Fig. 12, when the amount of Pd is 0.02 mmol, the highest catalytic activity of 698.26 g STCO/(g Pd h) is achieved. The reason is that with the increase of the Pd/C dosage, the volume of the Pd/C in autoclave grows. Due to the use of the magnetic stirrer, the Pd/C cannot be thoroughly stirred to form a homogeneous effective active center with increasing the amount of solid substance in the autoclave. It can be also proved by the experiment that there is no polyketone produced without Pd/C catalyst in the copolymerization.

The effect of consumption of Pd/C catalyst on the molecular weight of polyketone is shown in Table 4. It can be found that the molecular weight of the product decreases little with the increase of catalyst.

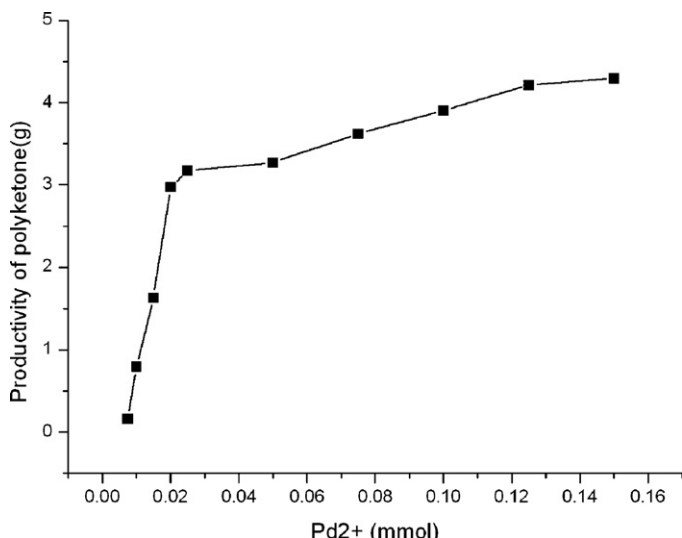


Fig. 11. Effect of Pd/C catalyst on productivity of polyketone.

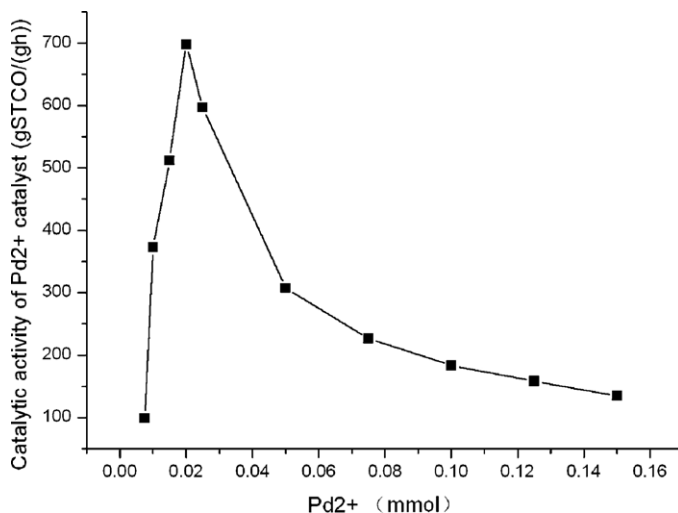


Fig. 12. Effect of Pd/C catalyst on the catalytic activity.

3.2.6. Reuse of Pd/C catalyst

Pd/C was used as loaded catalyst to promote the copolymerization of CO/styrene and Fig. 12 shows that it does have good catalytic activity for the copolymerization. The purpose of using the Pd/C catalyst is to recycle the palladium. The effect of reused times of Pd/C on catalytic activity is shown in Fig. 13. The catalyst Pd of the copolymerization of CO and ST is so expensive that its high cost influences the industrialization of polyketone directly. Therefore, it is essential to seek for a way of reusing the catalyst. In this work copolymerization of CO/styrene was promoted by Pd/C which was then recycled and reused after the reaction. The effect of reusability on catalytic system is presented in Fig. 13. The experiment shows that the catalyst Pd/C has good reusability and can be reused for 12 times with the highest catalytic activity of 1255.17 STCO/(g Pd h) and the highest molecular weights and polydispersity index of the copolymer are as follows: Mn = 10,700, Mw = 19,079 and Mw/Mn = 1.78, respectively, which shows the catalytic activity of Pd/C is higher than that of homogeneous catalyst (palladium acetate) [18].

Fig. 13 also suggests that the catalytic activity of Pd/C decreases after the seventh recycle. This is because Pd/C is a micro-crystalline catalyst. The metal Pd is distributed on the surface

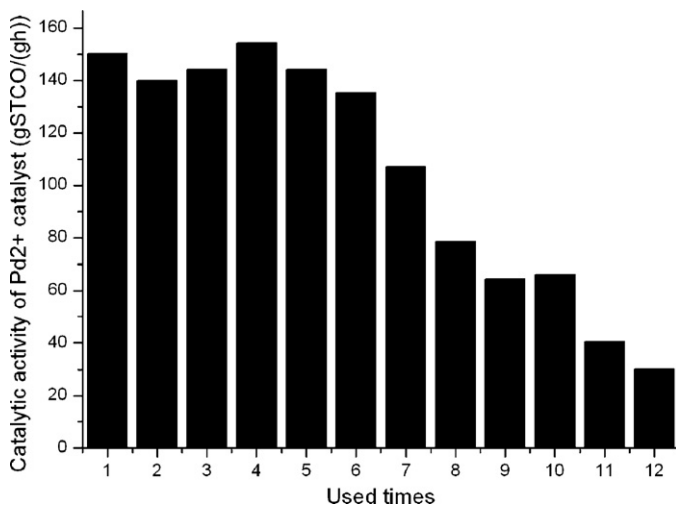


Fig. 13. Reusability of Pd/C catalyst.

Table 5
Molecular Weight of polyketone.

Recycle times	Mn	Mw	Mw/Mn
1	9,882	15,533	1.57
4	8,960	15,973	1.78
7	9,096	15,756	1.73
10	9,763	16,725	1.71
12	10,700	19,079	1.78

of coconut active carbon in the form of microcrystalline and the friction between the particles would cause abrasion. In the catalytic reaction, the agitation will bring intensive friction between the catalyst particles and generate carbon granules correspondingly, which may account for the losing of metal Pd. Therefore, the mechanical agitation and a proper stirring rate are employed in the experiment to reduce the Pd's losing as much as possible.

The virtues of Pd/C as catalyst to promote CO/styrene copolymerization are as follows: (1) The polyketones solve in *o*-chlorophenol accompany with reaction, which is favorable to the subsequent reaction. (2) The catalyst is not buried in the products. In other word, it is easy to separate catalyst from the products. (3) The reusability of catalyst and solvent *o*-chlorophenol can reduce the reaction cost.

The GPC analysis of polyketone for different catalyst recycle times are shown in Table 5. It can be found from the table that the molecular weight of polyketone increases gradually with catalytic recycle time. The part Pd²⁺ lost along with the increased recycle times of catalyst may account for the potential reason under the analysis. The concentration of Pd²⁺ decreases with recycle times of catalyst and the probability of chain termination are relatively low. Therefore, the coordination intermediates formed by 2,2'-bipyridine and Pd²⁺ can exist longer during the chain propagation of coordination polymerization to obtain a longer molecular chain accordingly and to yield polyketones of high molecular weight.

4. Conclusion

Pd/C presents high productivity and reusability in the copolymerization of CO/styrene. It can be reused for 12 times with a total catalytic activity of 1255.17 STCO/(gPd h) and the total yield of polyketone can achieve 26.7119 g. The molecular weight and its polydispersity index of the product are as follows: Mn = 10,700, Mw = 19,079 and Mw/Mn = 1.78, respectively. Generally, the catalytic activity of Pd/C is much higher than that of homogeneous catalyst (palladium acetate).

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References

- [1] G.P. Belov, E.V. Novikova, Polyketones as alternating copolymers of carbon monoxide, *Russ. Chem. Rev.* 73 (3) (2004) 267–291.
- [2] C. Bianchini, A. Meli, Alternating copolymerization of carbon monoxide and olefins by single-site metal catalyst, *Coord. Chem. Rev.* 225 (2002) 35–66.
- [3] A. Sen, The copolymerization of carbon monoxide with olefins, *Adv. Polym. Sci.* 73 (1986) 125–144.
- [4] J. Durand, B. Milani, The role of nitrogen-donor ligands in the palladium-catalyzed polyketones synthesis, *Coord. Chem. Rev.* 250 (3–4) (2006) 542–560.
- [5] E. Drent, P.H.M. Budzelaar, Palladium-catalyzed alternating copolymerization of alkenes and carbon monoxide, *Chem. Rev.* 96 (1996) 663–681.
- [6] C.E. Ash, Alternating olefin/carbon monoxide polymers: a new family of thermoplastics, *Polymer* 3 (30) (1995) 1–13.
- [7] A. Somazzi, F. Garbassi, Olefin-carbon monoxide copolymer, *Prog. Polym. Sci.* 22 (8) (1997) 663–669.
- [8] M. Brookhart, F.C. Rix, J.M. DeSimone, et al., Palladium(II) catalysts for living alternating copolymerization of olefins and carbon monoxide, *J. Am. Chem. Soc.* 114 (14) (1992) 5894–5895.
- [9] R. Senti, A.M. Romano, R. Garrone, et al., Copolymerization of styrene with CO catalyzed by palladium-substituted 1,10-phenanthroline bis(methoxycarbonyl) complexes [Pd(L-L)(COOMe)₂], *Macromol. Chem. Phys.* 200 (1) (1999) 25–30.
- [10] B. Milani, A. Anzilutti, L. Vicentini, et al., Bis-chelated palladium(II) complexes with nitrogen-donor chelating ligands are efficient catalyst precursors for the CO/styrene copolymerization reaction, *Organometallics* 16 (23) (1997) 5064–5075.
- [11] B. Milani, A. Scarel, G. Mestroni, et al., Very stable palladium(II)-(N–N) catalysts for the synthesis of high-molecular-weight CO/styrene polyketones, *Organometallics* 21 (7) (2002) 1323–1325.
- [12] S. Stoccoro, G. Alesso, M.A. Cinellu, et al., New complexes of palladium(II) with chelating heterocyclic nitrogen ligands. Characterization and catalytic activity in CO-styrene copolymerization. Crystal structure of [Pd(bipy)₂][BAr'₄]₂, Ar = [3,5-(CF₃)₂C₆H₃], *J. Organomet. Chem.* 664 (1–2) (2002) 77–84.
- [13] A. Aebly, G. Consiglio, Ethene and styrene insertion into the Pd-acyl bond of [Pd(COME)(PN)(solV)O₃SCF₃] and its role in the copolymerisation of olefins with carbon monoxide, *J. Chem. Soc., Dalton Trans.* (1999) 655–656.
- [14] S. Kacker, J.A. Sissano, D.N. Schulz, Synthesis and properties of copolymers of ethylene/carbon monoxide with styrene/carbon monoxide, *J. Polym. Sci. A: Polym. Chem.* 38 (4) (2000) 752–757.
- [15] A. Aebly, A. Gsponer, G. Consiglio, et al., From regioselective to regioirregular alternating styrene-carbon monoxide copolymerization, *J. Am. Chem. Soc.* 120 (42) (1998) 11000–11001.
- [16] Y. Feng, J. Sun, Y. Zhu, et al., Alternating copolymerizations of styrene derivatives and carbon monoxide in the presence of a palladium (II) catalyst, *J. Polym. Sci. A: Polym. Chem.* 35 (7) (1997) 1283–1291.
- [17] J.T. Guo, B. Liu, X.Y. Wang, et al., Recycle of Pd²⁺ catalyst in synthesizing of polyketone, *J. React. Funct. Polym.* 61 (2) (2004) 163–170.
- [18] J.T. Guo, F.T., H.X. Zhang, B. Wang, Copolymerization of polyketones catalyzed by polyacrylonitrile resin-supported palladium acetate, *J. Funct. Mater.* 38 (2) (2007) 279–282.
- [19] E. Drent, J.A.M. Van Broekhoven, M.J. Doyle, Efficient palladium catalysts for the copolymerization of carbon monoxide with olefins to produce perfectly alternating polyketones, *J. Organomet. Chem.* 417 (1–2) (1991) 235–251.