

Palladium (II)—rare Earth Metal Catalyzed Copolymerization of CO and Styrene in [bmim]⁺PF₆⁻ Ionic Liquid

Jintang Guo, Guang Hu, Shan Gao, Peng Li

Department of Polymer Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China

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ABSTRACT: In this work, the copolymerization of carbon monoxide (CO) and styrene (ST) was performed in the presence of both rare earth metal and palladium as composite catalyst with 1-butyl-4-methylimidazole hexafluorophosphate ([bmim]⁺PF₆⁻) ionic liquid as solvent. The result proved that the addition of rare earth salt indeed enhances the catalytic activity. And compared with palladium metal, rare earth metal has a lower cost. Furthermore, the effect of various rare earth metals on catalytic activities was investigated. The results showed that rare earth metal Yb(P₂₀₄)₃ and [Pd(N-N)₂][PF₆]₂ composite catalyst was the optimal system yielding the highest catalytic activity 2040 g STCO/

gPd h. Meanwhile, the technological conditions (such as amount of rare earth metal, volume of ionic liquid, reaction time, amount of *p*-benzoquinone, and system pressure) of the copolymerization of CO and ST were studied. The optimum reaction conditions are as follows: Pd²⁺/RE³⁺ (mol/mol) = 1'styrene/ionic liquids (V/V) = 4, BQ/Pd²⁺ (mol/mol) = 75'reaction time = 2 h'p(CO) = 2MPa and the catalyst was still active at least up to four times of recycles. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2011

Key words: palladium; rare earth metal; ionic liquids; polyketone; carbon monoxide

INTRODUCTION

Polyketones prepared by CO and unsaturated monomers containing double bond are fascinating polymeric materials with excellent properties, including mechanical property, high pressure, and temperature resistance, especially bio/photo-degradation, etc.¹ The copolymerization is generally performed with palladium as main catalyst and bidentate nitrogen-donor as chelating ligand, which has obtained a relatively high activity.² However, it is the high cost, difficulty in separation, poor reusability of the catalyst that restricts the industrialization of polyketones severely. Exploration of a novel method of recycling palladium at no expense to productivity currently represents a knotty problem around the world.^{3–5}

Rare earth metals are inexpensive compared with some costly metals. However, it may cocatalyze the copolymerization when used with some expensive metals, which could reduce the consumption of

main catalyst and consequently lower the reaction cost.^{6–9}

Recent years, "green solvent" ionic liquids as replacement to conventional solvent in macromolecule field have drawn considerable attention, thanks to the unique combination of performance properties and above all, to the ability of improving productivity and reusability of the catalyst.^{10–13} Application ionic liquids to the copolymerization of CO/styrene casts light on recycling and reusing palladium catalyst with no variation of the productivity.

In our previous experiments, the effects of commercial Pd/C catalyst on catalytic activity were investigated in our previous research, and the result showed the highest total catalytic activity of directly purchased Pd/C catalyst can reach 1255.17 gPK/(gPd h).¹⁴

In this article, palladium-rare earth metal multiple catalyst system composing of rare earth metal cocatalyst and palladium catalyst was employed to promote the copolymerization. Moreover, effect of various factors in the system on catalytic activity and reusability of the catalyst were investigated in detail.

EXPERIMENTAL

Experimental materials

Carbon monoxide and nitrogen (>99.9%) was purchased from Beijing Analysis Instrument Company,

Correspondence to: J. Guo (jguo@tju.edu.cn).

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China. The methanol (Fluka) used for the catalytic reactions was purified by distillation from magnesium and iodine. Styrene, *N*-methylimidazole, pyridine, 2,2'-bipyridine were distilled prior to use. Palladium acetate of analytical grade from New Jersey ACROS Organics was used as received. Rare earth metal acetate RE(OAc)₃ (>99.9%, RE = Pr, Nd, Eu, Dy, Ho, Yb) were supplied by Baotou Research Institute of Rare earth metals, China. The other chemicals were of analytical grade or higher (Kewei, Tianjin, China), and were directly used without further purification.

Preparation of [Pd(*N-N*)₂][PF₆]₂

13 mmol of 2,2'-bipyridine¹⁵ were added into the beaker containing 100 mL methanol at the room temperature, and then the mixture was agitated until the 2,2'-bipyridine was completely solved. Totally, 20 mL of distilled water, 20 mL of HCl (37 wt%) and 19 mmol of KPF₆ were placed into the mixture successively. Next, after agitation for 30 min, half of amount of the solvent were removed by distillation under reduced pressure. After the remnants were cooled, the white crystal was obtained by filtration. The intermediate product of [(*N-N*)H][PF₆] was obtained after the white crystal was washed and dried.

Palladium acetate was dissolved in the acetone and the resultant solution was stirred for 30 min. Next, the prepared [(*N-N*)H][PF₆] was added into the mixture, and then a large amount of pale yellow crystal separated out promptly. After filtration, washing and drying, the catalyst of [Pd(*N-N*)₂][PF₆]₂ was obtained.

Preparation of RE(P₂₀₄)₃

Ten grams of rare earth metal RE(P₂₀₄)O₃¹⁶ was dissolved in the concentrated hydrochloric acid and the solution was evaporated until the RECl₃ was separated out. Totally, 150 mL of the mixed solution of alcohol and water (50 wt %) and 60 g of P₂₀₄ were added into the above solution, and then diluted ammonia water was added dropwise to the mixture until the value of PH achieve 6.5. after agitated for 5 h and placed for a while, the mixture was filtrated and the resultant product was washed with alcohol and dried *in vacuo*.

The molecular structure of RE(P₂₀₄)₃, as is shown in Figure 1.

Preparation of [bmim]⁺PF₆⁻ ionic liquid

A mixture of 1-methylimidazole and normal bromobutane^{17,18} was stirred at 90°C for 12 h. After cooling, the reaction mixture was washed with diethyl

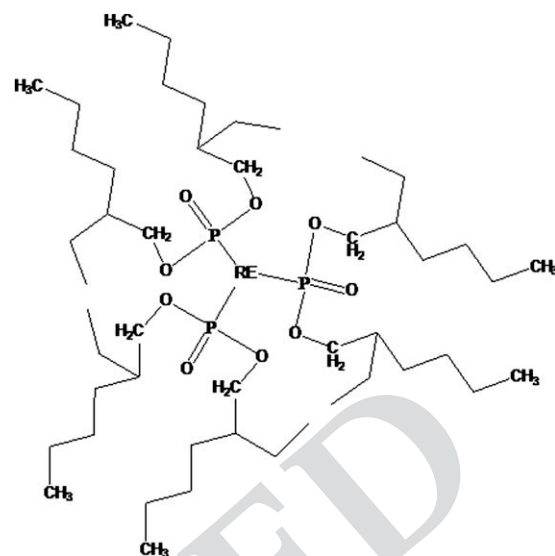


Figure 1 The molecular structure of RE(P₂₀₄)₃.

ether for three times and dried under vacuum for 24 h. The intermediate product 1-butyl-3-methylimidazole bromate was obtained.

To a solution of 1-butyl-3-methylimidazole bromate in water, potassium hexafluorophosphate was added and stirred at 60°C. After 6 h the solid that had formed was collected by filtration and washed with distilled water and then dried under vacuum for 48 h.

The copolymerization of CO/styrene and recycle of the catalyst

[Pd(*N-N*)₂][PF₆]₂, rare earth metal, *p*-benzoquinone, styrene and [bmim]⁺PF₆⁻ ionic liquid were added into 100-mL of stainless steel reactor. Carbon monoxide was blown up the system until the inner pressure reached 2.0 MPa. The mixture was stirred for 2 h at 60°C. Cooling to room temperature, the raw product was precipitated in ethanol and white powder (Polyketone, STCO) was obtained after filtering, washing and drying.

Filtrate was collected and then distilled under vacuum at 40°C until no distillate produced. The residual liquid was added into reactor and polyketones would be obtained again after addition of *p*-benzoquinone and styrene under the reaction conditions above.

Characterization

FTIR spectra were collected on a BIO-RAD FTS3000 FTIR spectrometer as potassium bromide pellets to characterize copolymer and ionic liquids.

¹CNMR analysis was acquired on Varian Infinity plus 300WB NMR spectrometer operating at 300 MHz to characterize polyketones; ¹HNMR analysis

TABLE I
Element Analysis of Catalysts

Sample	Mass fraction (%)		
	C (%)	H (%)	N (%)
[(N-N)H][PF ₆] ^a	39.70	3.00	9.27
[(N-N)H][PF ₆]	38.96	3.21	9.25
[Pd(N-N) ₂][PF ₆] ₂ ^a	33.90	2.28	7.91
[Pd(N-N) ₂][PF ₆] ₂	33.70	2.65	8.16

^a Calculated values.

was acquired on Varian 500 MHz spectrometer to characterize ionic liquids.

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

Thermogravimetric analysis of polyketones was recorded on Japan DaoJin TGA-50 analyzer. Heating rate was 10°C/min. Carrier gas was N₂. Gas flow rate was 10 mL/min.

PHI-1600 photoelectron spectrograph from USA PE Company was employed to analyze surface elements of the catalyst and identify their relative contents. Mg K_α was used as X-ray radiator ($E_b = 1253.6$ eV). Power was 300 W. Spot size was 0.8 mm². Vacuum degree was 667 nPa. Pass energy was 23.5 eV. Al 2p in Al₂O₃ ($E_b = 74.00$ eV) was as internal reference.

BI-200SM X-ray diffractometer from America Brookhaven Company was employed to character polyketones. Condition: Cu K_α target $\lambda = 0.15405$ nm/voltage = 40kV/electric current = 40mA/scanning speed = 6°/min/scanning scope: 5° ≤ 2θ ≤ 45°/12290.

JEM-2000FX transmission electron microscope was used to observe the microstructure and analyze the product sample. Measure voltage 200 kV, vacuum degree 5–10 Pa, resolution 0.19 nm.

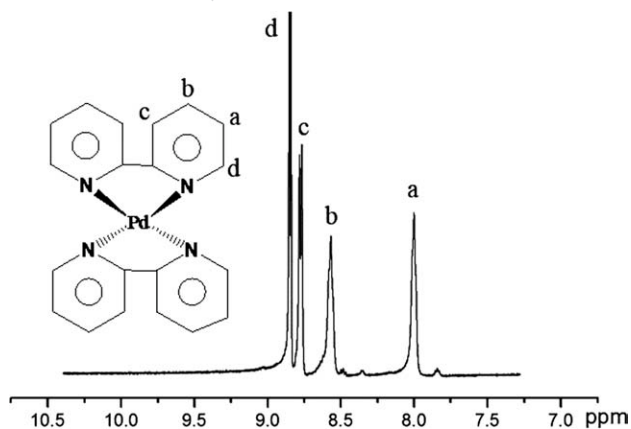


Figure 2 ¹H NMR spectrum of [Pd(N-N)₂][PF₆]₂.

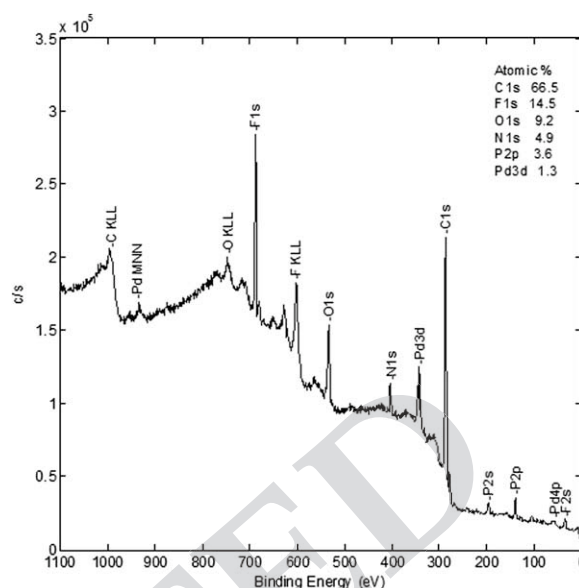


Figure 3 XPS spectrum of [Pd(N-N)₂][PF₆]₂.

Elemental Analysis was carried out on a Perkin-Elmer PE-2400 elemental analyzer to identify C, N, H elements in composite catalysts and also in copolymer.

Molecular weights and molecular weight distributions were measured with a Waters 1515 gel permeation chromatograph (GPC) equipped with a Waters 2410 differential refractometer as detector. Three Styragel columns (HR2, HR4, HR6) were used in series. GPC samples were run at a flow rate of 1 mL/min, and the columns were calibrated using narrow distribution polystyrene standards obtained from Polymer Laboratories, UK.

RESULTS AND DISCUSSION

Characterization of catalyst

In this article, composite catalyst [Pd(N-N)₂][PF₆]₂ was synthesized. Moreover, C/N/H elemental analysis of intermediate product [(N-N)H][PF₆] and final product [Pd(N-N)₂][PF₆]₂ were performed. The experiment data is in accordance with calculated values by and large, as is shown in Table I, which also proves the occurrence of desired product quantitatively.

In ¹H NMR spectrum of the catalyst (Fig. 2), δ values of four positions a, b, c, d of bipyridine are 7.97 ppm, 8.54 ppm, 8.75 ppm, and 8.82 ppm, respectively.

X-ray Photoelectron Spectroscopy (XPS) is mainly used to identify elements (except H, He) and their chemical states. XPS analysis of [Pd(N-N)₂][PF₆]₂ catalyst was carried out in this article. The XPS spectrum and content of each element are depicted in Figure 3, which proves that the substance under test is composed of elements C, F, N, Pd, P.

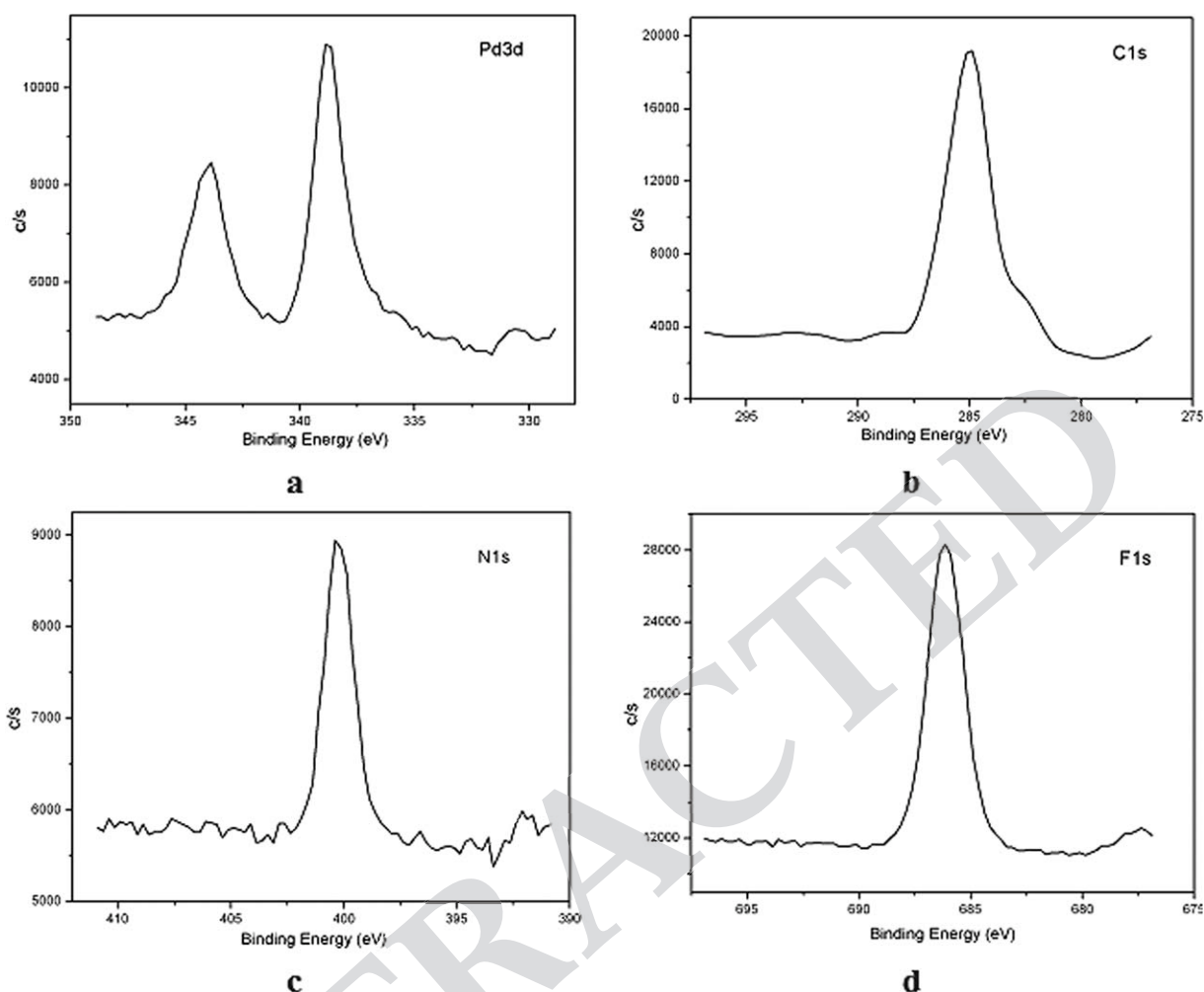


Figure 4 XPS Pd3 days, C1s, N1s, F1s core-level spectra of $[\text{Pd}(\text{N-N})_2][\text{PF}_6]_2$.

High resolution spectra of element Pd in Figure 4 shows that 343 eV and 383 eV represent bivalent Pd in $[\text{Pd}(\text{N-N})_2]$ and the two peaks are resulted from spin splitting of Pd(II). 285 eV and 400 eV correspond to atom C and N of bipyridine respectively. Peak at 686 eV represents F of minus-one valence, consisting with information in standard spectrum database. All of this further suggest the composite structure of $[\text{Pd}(\text{N-N})_2][\text{PF}_6]_2$.

Characterization of $[\text{bmim}]^+\text{PF}_6^-$ ionic liquid

FTIR spectra of $[\text{bmim}]^+\text{PF}_6^-$ was shown in Figure 5. The strong absorbent peak at 840.4 cm^{-1} results from the stretching vibration peak of P-F. The two absorbent peaks at 3170.4 cm^{-1} and 3124.3 cm^{-1} correspond to stretching vibration peaks of two kinds of C-H in imidazole ring. The absorbent peak at 1577.8 cm^{-1} corresponds to stretching vibration peaks of C=N in imidazole ring. The two absorbent peaks with 1168.1 cm^{-1} and 753.3 cm^{-1} result from inplane bending vibration and offplane bending vibration of C-H in imidazole ring, respectively.

^1H NMR data of $[\text{bmim}]^+\text{PF}_6^-$ was recorded, and the result was shown in Table II. The chemical shifts of eight kinds of hydrogen in ionic liquid have been acquired. The results indicate the obtained ionic

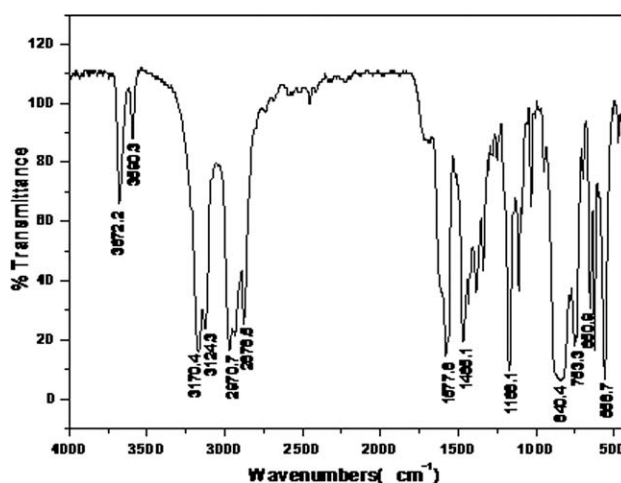


Figure 5 FT-IR spectrum of $[\text{bmim}]^+\text{PF}_6^-$.

TABLE II
 ^1H NMR Data of $[\text{bmim}]^+\text{PF}_6^-$

Number of H	Peaks	Chemical shift δ
1	NCHN, 1H, s	8.72
2	NCH, 1H, s	7.48
3	CHN, 1H, s	7.44
4	NCH ₂ , 2H, t	4.21
5	NCH ₃ , 3H, s	3.90
6	CH ₂ , 2H, m	1.86
7	CH ₂ , 2H, m	1.34
8	CH ₃ , 3H, t	0.93

liquid is desired one, which is consistent with literature.¹⁹

Characterization of copolymer

The IR spectrum of polyketones produced by CO/styrene copolymerization is shown in Figure 6. 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 =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 literature.²⁰

The elemental analysis of copolymer is shown in Table III, which indicates that the element contents of prepared copolymer are consistent with perfectly linear alternating copolymer. Thus it is certain that the product is rigid linear alternating copolymer prepared from CO and styrene.

The ^{13}C NMR spectrum of polyketone also confirms the desired product, as is presented in Figure

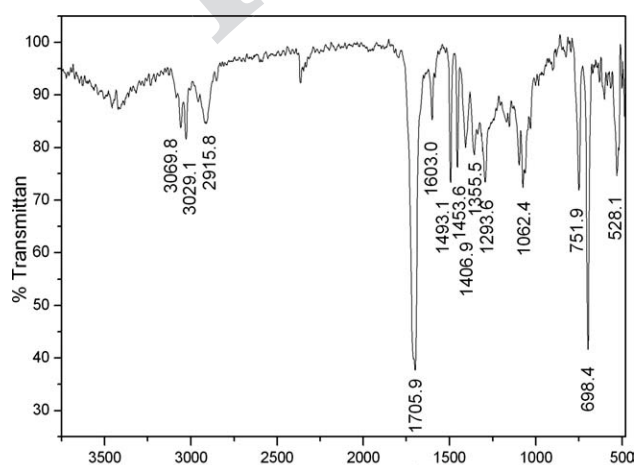


Figure 6 FT-IR spectrum of polyketone.

TABLE III
Elemental Analysis of Polyketone

Sample	Mass fraction (%)		
	C	H	O
Polyketone	81.87	6.03	12.10
Alternating copolymer ^a	81.82	6.06	12.12

^a Calculated values.

7. The absorption peak of carbonyl at $\delta = 208.5\text{ ppm}$ shows that the copolymer has group from CO. Absorption peaks at $\delta = 139.5\text{ ppm}$, $\delta = 133.0\text{ ppm}$, $\delta = 128.6\text{ ppm}$, $\delta = 126.9\text{ ppm}$ corresponding to those of benzene ring, which indicates that there is structure unit from styrene in the copolymer. The two peaks corresponding to ethylene at $\delta = 55.1\text{ ppm}$, $\delta = 45.1\text{ ppm}$ further prove the existence of styrene structure unit in the copolymer. So ^{13}C NMR spectrum of polyketone proves the copolymer is the desired one.

DSC and TG were carried out to analyze the polyketone (Fig. 8). Because the specific heat capacity of polyketones differ in melting state, elastic state and glass state, whose energy absorbent peak are presented respectively, on the curves. It is reported⁵ that polyketones are crystal polymers. But the crystal radiative peak is unobvious so a second heating must be conducted in the measurement. From Figure 8 one can conclude that the catalytic system in the presence of ionic liquids produces polyketone of glass transition temperature 107.55°C and of decomposition temperature 325°C .

The same conclusion could be drawn from X-ray diffraction spectra of polyketone sample, as shown in Figure 9. The diffraction peaks in Figure 9(a,b) are relatively sharp, which prove polyketones prepared in the two ways are highly crystal polymers and

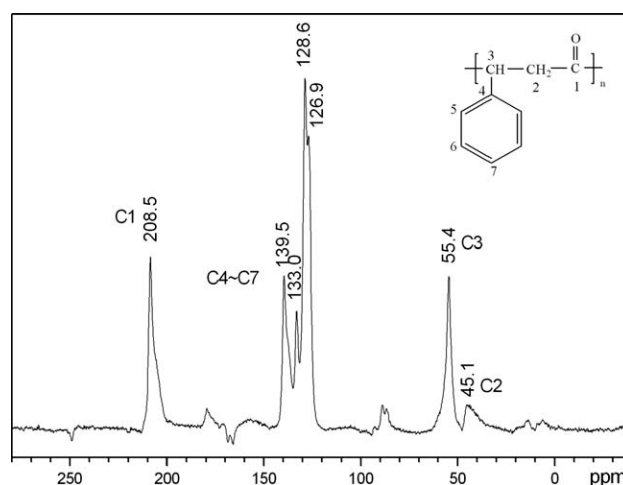


Figure 7 ^{13}C NMR spectrum of polyketone.

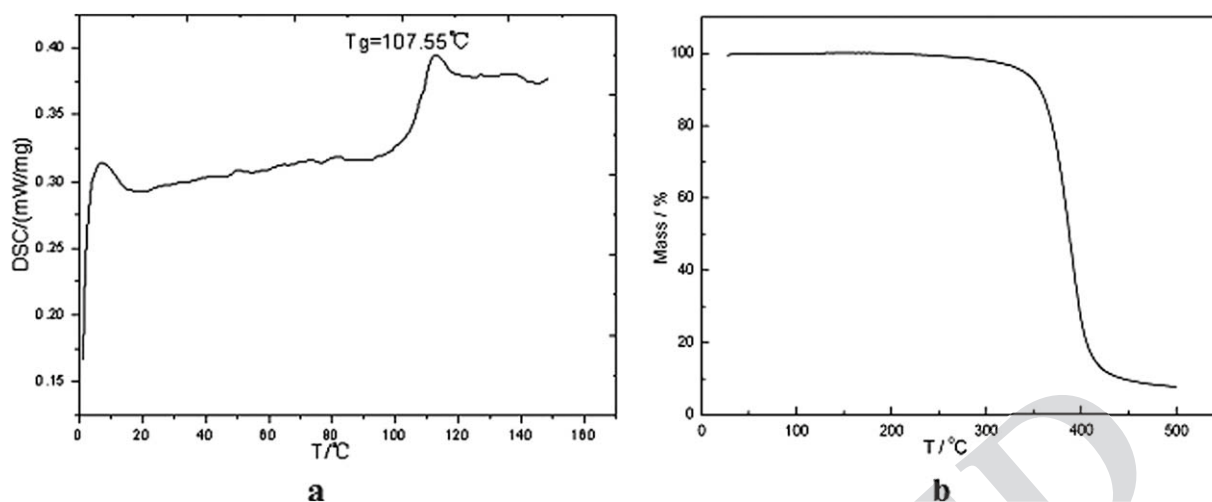


Figure 8 Differential scanning calorimetry curve (a) and thermogravimetry curve (b) of polyketone.

explain their immiscible behavior in organic solvents. In the X-ray diffraction spectrum obtained in different solvents, the strength, location, and even the sharpness of the diffraction peaks are quite similar, further confirming the same structure of polyketones prepared in ionic liquid and in traditional methanol.

From a general point of view, polyketones are high-crystal polymers which are immiscible with organic solvents such as benzene, butanone, chloroform. But people have not proved it by intuitionistic images according to literatures in existence. In the present work, the crystallization of polyketones was studied not only by X-ray diffraction spectra but also by transmission electron microscope (TEM) as well.

In the TEM images (Fig. 10) a large amount of crystallization area can be identified, forming stripe structure with small distance and large stack among layers. Electron diffraction spectrum shows the coexistence of diffraction spot and diffraction corona,

which further explains the high crystallization properties of polyketones.

Effect of components of catalyst system on copolymerization

Catalysts and ligands exist in homeostasis in palladium-catalyzed system. In other word, palladium and ligands can form chelating structure with double rings, which, however, has no active site for copolymerization. According to the Pearson Theory says: Soft acid reacts with Soft base, Hard acid reacts with Hard base. Rare earth cation and palladium cation fall into hard acid and soft acid respectively. Bidentate nitrogen-donor chelating ligand is hard base while CO and olefin belong to soft base. As a result, rare earth cation is prone to coordinate with bidentate nitrogen-donor chelating ligand while palladium cation is more likely to coordinate with CO and olefin. The following structure may come into being when the concentration of rare earth ion is

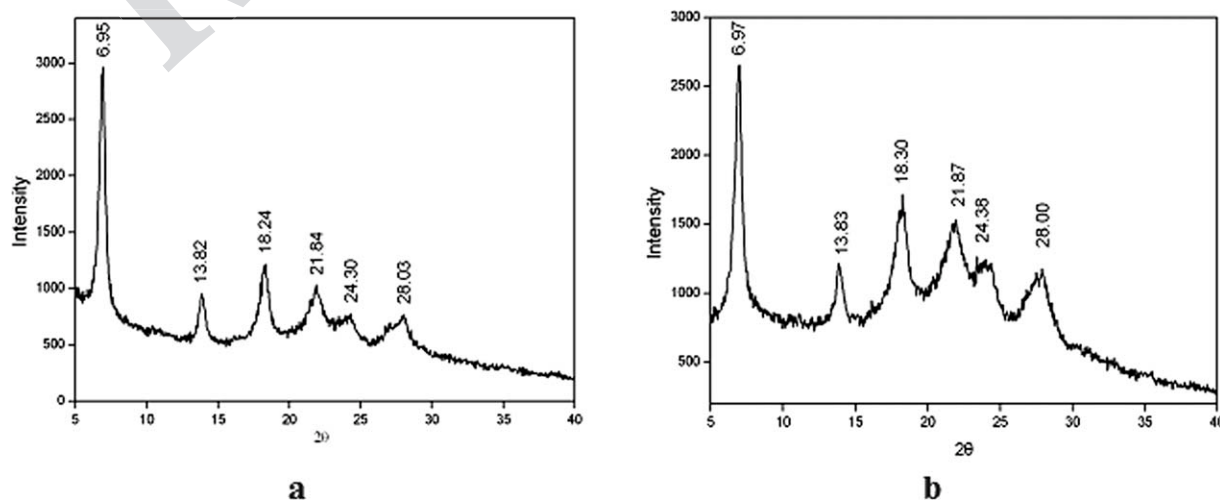


Figure 9 X-ray diffraction spectra of polyketone sample, (a) CH_3OH as solvent (b) ILs as solvent.

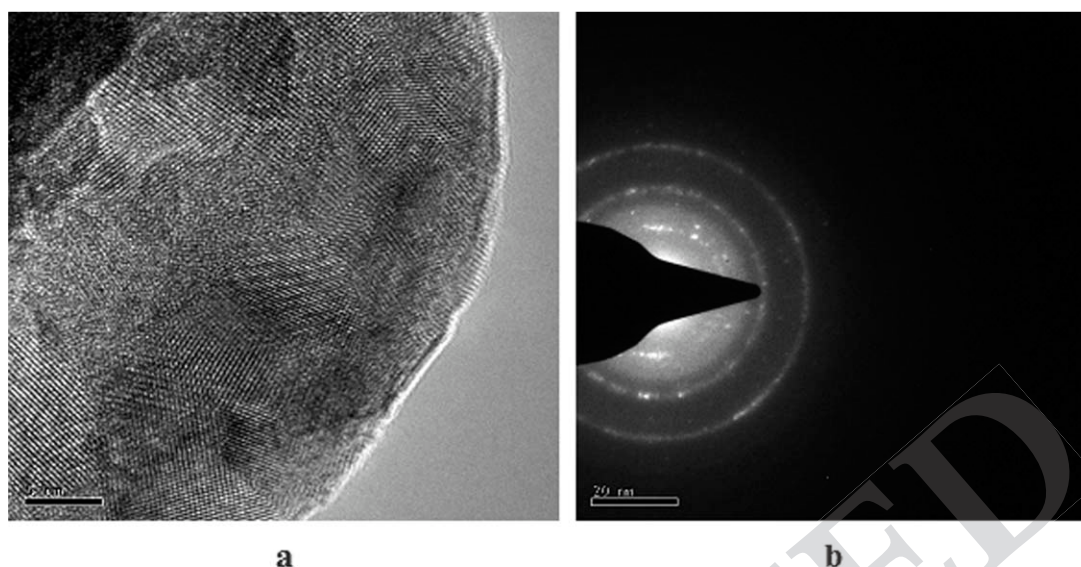


Figure 10 TEM spectra of polyketone.

lower than that of palladium (Take neodymium for example in Fig. 11):

When the electron cloud density is relatively high, copolymer chain is apt to terminate by β -H elimination. Electron withdrawing group in ligand favors the enhance of chain propagation rate and improve the productivity. Most rare earth metal have no five days electron (except for lanthanum $4f^05s^25p^6$). But the distribution of outer electrons is $4f^n5s^25p^6$ representing the lost of two 6s and one f electrons (for lanthanum it is five days electron). In catalytic reaction, the empty five days orbit of rare earth metal serves as electron transfer station whose electron withdrawing effect allows electron cloud to move towards rare earth metal. As a result, prolonged chain propagation together with weakened coordination between palladium ion and benzyl group favors the insertion of CO and improves catalytic activity.

Effect of nature of rare earth salts on copolymerization

Effect of various rare earth phosphates combined with palladium respectively, on the catalyst system was investigated in detail (Table IV).

Table IV shows that the addition of rare earth salts indeed enhances the catalytic activity but the effects

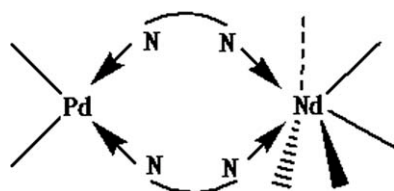


Figure 11 Coordination structure of Pd, ligand and rare earth.

differ. The catalytic activity and relative molecular weight increase with atomic number from praseodymium phosphate to ytterbium phosphate, among which ytterbium phosphate ($Yb(P_{204})_3$) is the best one with catalytic activity as high as 2060 gSTCO/gPd h while the counterpart of praseodymium phosphate ($Pr(P_{204})_3$) is just 630 gSTCO/gPd h. The main reason may be that the increased atomic number and decreased ionic radius ensure a more stable coordination structure with ligand and consequently improve the productivity.

Effect of amount of rare earth metal on copolymerization

In this article, influence of different molar ratio of rare earth salt to palladium composite catalyst on CO/styrene copolymerization was studied. Taken

TABLE IV
Effect of Different Rare Earths on Catalytic Activity^f

Catalyst ^b	NO. ^c	Electron configuration	CA ^d	Mn ^e	PDI ^f
$Pr(P_{204})_3$	59	$4f^36s^2$	630	5930	1.72
$Nd(P_{204})_3$	60	$4f^46s^2$	860	6205	1.75
$Eu(P_{204})_3$	63	$4f^76s^2$	1100	6310	1.61
$Dy(P_{204})_3$	66	$4f^{10}6s^2$	1880	6430	1.76
$Ho(P_{204})_3$	67	$4f^{11}6s^2$	2040	6760	1.54
$Yb(P_{204})_3$	70	$4f^{14}6s^2$	2060	6970	1.70

^aReaction condition: Pd^{2+}/RE^{3+} (mol/mol) = 1, styrene/ionic liquids (V/V) = 4, BQ/ Pd^{2+} (mol/mol) = 75, reaction time = 2 h.

^b $RE(P_{204})_3 + [Pd(N-N)_2][PF_6]_2$.

^c Atomic number.

^d Catalytic activity (g/gPd·h).

^e Determined by GPC relative to PS.

^f PDI is polydispersity index (M_w/M_n).

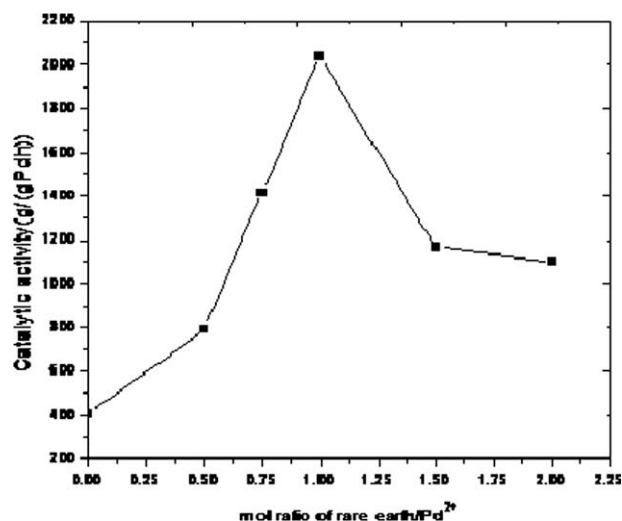


Figure 12 Effect of mol ratio of $\text{Re}^{3+}/\text{Pd}^{2+}$ on the catalytic activity. Reaction condition: styrene/ionic liquids (V/V) = 4, BQ/ Pd^{2+} (mol/mol) = 75, reaction time = 2 h, rare earth metal = $\text{Yb}(\text{P}_{204})_3$.

holmium phosphate for example herein, the results are shown in Figure 12.

As cocatalyst, if holmium phosphate (Re^{3+}) was used to catalyze the copolymerization of CO and styrene separately, the catalytic activity is pretty low with 645gSTCO/gPd h. Therefore, holmium phosphate itself cannot be used as catalyst independently, and it is only cocatalyst, not main-catalyst. So we investigated the effect of addition of cocatalyst holmium phosphate on catalytic activity, when the amount of main-catalyst palladium acetate (Pd^{2+}) was fixed. The experiment has demonstrated that with the molar ratio of $\text{Re}^{3+}/\text{Pd}^{2+}$ increasing, the catalytic activity is improved progressively. And it

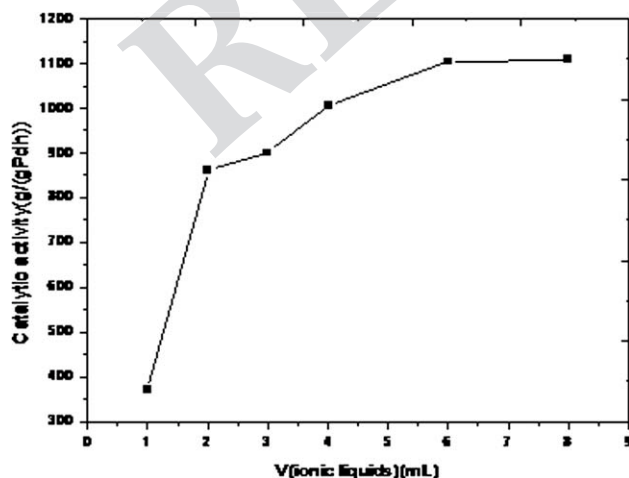


Figure 13 Effect of volume of ionic liquids ($[\text{bmim}]^+\text{PF}_6^-$) on catalytic activity of polyketones Reaction condition: $\text{Pd}^{2+}/\text{RE}^{3+}$ (mol/mol) = 1, BQ/ Pd^{2+} (mol/mol) = 75, reaction time = 2 h, rare earth metal = $\text{Yb}(\text{P}_{204})_3$.

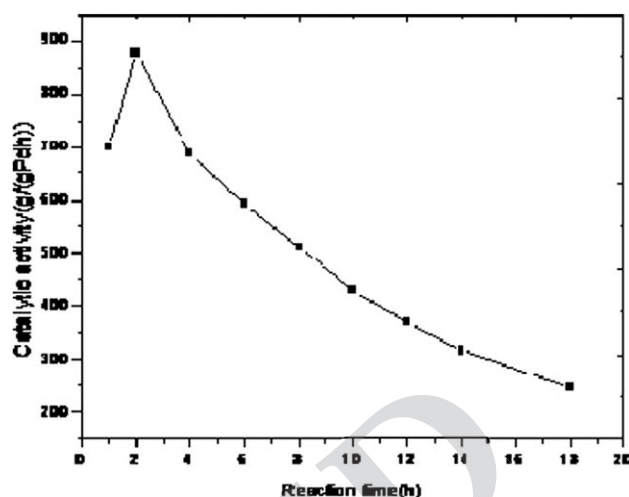


Figure 14 Effect of reaction time on catalytic activity and productivity of polyketone (a, PRODUCTIVITY; b, catalytic activity). Reaction condition: $\text{Pd}^{2+}/\text{RE}^{3+}$ (mol/mol) = 1, styrene/ionic liquids (V/V) = 4, BQ/ Pd^{2+} (mol/mol) = 75, rare earth metal = $\text{Yb}(\text{P}_{204})_3$.

reaches its maximum when the molar ratio of $\text{Re}^{3+}/\text{Pd}^{2+}$ is 1 : 1, with the highest catalytic activity 2040gSTCO/gPd h. When the molar ratio is larger than 1, the catalytic activity shows a downward trend.

In the copolymerization system, the added Re^{3+} and Pd^{2+} form binary metal complex which could fix the two adjacent covalence site efficiently. As a result, fewer ligands generate more highly active centers, namely the cocatalysis of rare earth metal. However, Re^{3+} can form a more stable complex with ligand compared with Pd^{2+} . So excess amount of holmium phosphate consumes more N-N ligand, which leads to the decomposition of Pd^{2+} active center from Pd (II) to Pd (0) and thus reduces the catalytic activity.

Effect of volume of ionic liquid on copolymerization

The volume of ionic liquid must play a key role in the copolymerization for ionic liquid is not only served as solvent instead of methanol but also takes part in the chain initiation. Figure 13 depicts the change of polyketone yield with the volume of $[\text{bmim}]^+\text{PF}_6^-$ ionic liquid. When less ionic liquid is consumed, the yield and productivity is accordingly low due to the incomplete dissolution of catalyst and bidentate ligands. Gradual increase of the ionic liquids enables palladium to disperse in the system equably and to catalyze the reaction adequately. As a result, the yield of polyketone increases.

Effect of reaction time on copolymerization

Study of the reaction time is significant to the copolymerization. Figure 14 presents the effect of

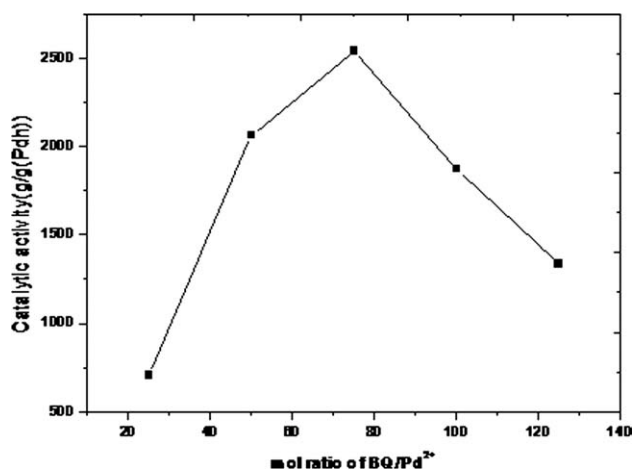


Figure 15 Effect of BQ on yield and catalytic activity. Reaction condition: Pd²⁺/RE³⁺ (mol/mol) = 1, styrene/ionic liquids (V/V) = 4, reaction time = 2 h, rare earth metal = Yb(P₂₀₄)₃.

reaction time on catalytic activity. As is shown in the figure, the catalytic activity of polyketone enhances first and then decreases with reaction. The highest catalytic activity 830 g STCO/(gPd h) is achieved when reaction time is 2 h. If time is too short, the copolymerization will not perform completely, which leads to the low catalytic activity. A properly longer time is beneficial for the reaction so the yield of polyketone increases with time at primary stage. When the copolymerization performs to the utmost, reaction time has little effect on yield. Furthermore, a partial inactivation of the active species occurs during longtime heating. Therefore, an appropriate reaction time must be determined to obtain reasonable yield as well as improve the reusability. 2 h is the optimal one under our experiment conditions.

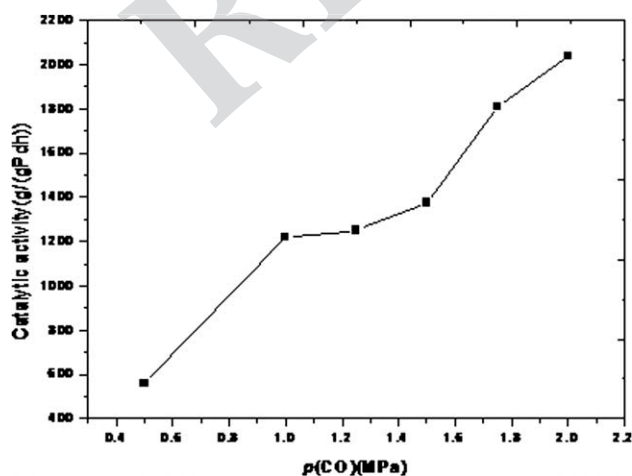


Figure 16 Effect of pressure (CO) on catalytic activity. Reaction condition: Pd²⁺/RE³⁺ (mol/mol) = 1, styrene/ionic liquids (V/V) = 4, BQ/Pd²⁺ (mol/mol) = 75, reaction time = 2 h, rare earth metal = Yb(P₂₀₄)₃.

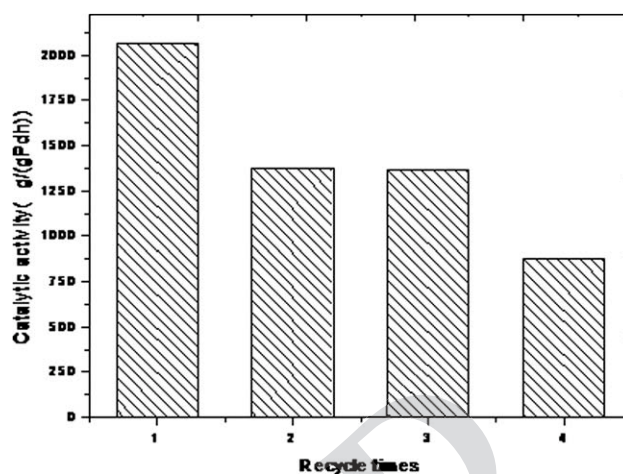


Figure 17 Recyclability of Pd²⁺ catalyst system in ionic liquids ([bmim]⁺PF₆⁻). Reaction condition: Pd²⁺/RE³⁺ (mol/mol) = 1, styrene/ionic liquids (V/V) = 4, BQ/Pd²⁺ (mol/mol) = 75, reaction time = 2 h, rare earth metal = Yb(P₂₀₄)₃.

Effect of amount of oxidant on copolymerization

Palladium acetate is prone to inactivate during the catalytic reaction, reduced to zerovalence. The addition of *p*-benzoquinone, nitrobenzene or naphthoquinone into the system can not only prevent Pd (II) from reduction efficiently by oxidizing Pd (II)-H to catalytic center Pd (II)-OMe, but also enhance selectivity of the reaction. Effect of *p*-benzoquinone on catalytic activity is presented in Figure 15. The activity increases first then falls with the addition of *p*-benzoquinone (BQ), when fixed the amount of palladium composite catalyst and other components. The highest catalytic activity 2040 g STCO/(gPd h) is achieved when $n_{\text{BQ}}/n_{\text{Pd}^{2+}} = 75$. Large amount of *p*-benzoquinone dissolved incompletely in solvent makes the system tend to be heterogeneous, consequently, reducing the catalytic activity.

Effect of the pressure of CO on copolymerization

The pressure of CO equally influences the productivity of catalyst notably (Fig. 16). The catalytic activity increases corresponding to CO pressure with the concentration of catalyst, reaction temperature, and copolymerization time fixed. The solubility of CO in ionic liquid increases with pressure at a certain temperature, depending largely on the CO pressure, according to the research of Kumefan.²² So we speculate on the relative low concentration in liquid phase when low CO pressure presented in the system ($P_{\text{CO}} \leq 0.5$ MPa) is responsible for the poor catalytic reaction rate.

Nevertheless, the catalytic activity increases more slowly as pressure rises gradually. Reaction is controlled by other factors rather than CO pressure

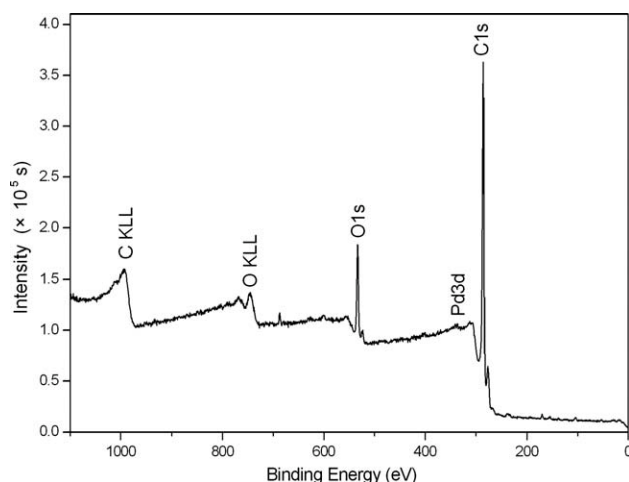


Figure 18 XPS spectrum of polyketone.

when the concentration of CO in liquid phase is beyond a certain value, which may account for the behavior that the increase of system pressure exerts subtle influence on reaction rate. In practical manufacture seeking for a proper pressure is necessary to reduce cost at no expense to reaction rate.

Effect of ionic liquid on reusability of copolymerization

The traditional copolymerization of α -olefin and CO used to employ alcohol (such as methanol, etc.) as solvent. Alcohol act as not only solvent but also chain transfer agent and precipitator. Methanol could participate in the chain initiation by reacting with coordinated acetate palladium to form active center. Nevertheless, it is difficult to reuse bivalent palladium in alcohol due to their flammability and volatility.

Ionic liquid is a kind of excellent solvent to most inorganics, organics and macromolecule materials due to their nonvolatility, high-stability and reusability. In the experiment, $[\text{bmim}]^+\text{PF}_6^-$ ionic liquids was used as solvent instead of traditional alcohol. It is certain that reuse of the catalyst has come true despite of the obscure chain initiation mechanism. Polyketones could still be obtained by pouring reaction liquid into reaction kettle after the removal of terminator by vacuum distillation. And the catalyst is active after four times of recycle but the activity declines compared with the former one, as is presented in Figure 17. The main reason may be that some bivalent palladium species are buried by polyketones in chain termination and fail to take part in recycle. This conclusion could also be drawn from XPS analysis of the sample (Fig. 18). There are 87.4% of C and 12.5% of O together with trace palladium metal respectively, in the polyketones, which also

suggests that contents of other residual elements are less than the relative sensitivity for XPS analysis.

In addition, partial bivalent palladium active centers decompose to Pd (0) during vacuum distillation, which also contributes to the inactivity and poor reusability of the catalyst.

Further study in our experiment showed that the increased consumption of precipitator methanol could reduce leakage of palladium into polyketones. Moreover, the addition of *p*-benzoquinone during vacuum distillation efficiently prevent Pd(II) from decomposing to Pd(0).

CONCLUSIONS

Copolymerization of CO/Styrene with palladium-rare earth metal as catalyst and $[\text{bmim}]^+\text{PF}_6^-$ as reaction medium excel at the following aspects: (1) Less amount of expensive palladium metal is required with cocatalyst rare earth metal, improving catalytic activity obviously. (2) The catalyst is easily separated from product. (3) The recycle of catalyst together with solvent reduces reaction cost.

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