Journal of Molecular Catalysis B: Enzymatic 87 (2013) 30–36

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Catalysis B: Enzymatic

journal homepage: www.elsevier.com/locate/molcatb

Enzymatic synthesis of phenol polymer and its functionalization

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ARTICLE INFO

Article history:
Received 1 July 2012
Received in revised form 9 October 2012
Accepted 29 October 2012
Available online 7 November 2012

Keywords:
Phenol
Horseradish peroxidase
Enzymatic polymerization
Supported catalyst
Heck reaction

ABSTRACT

In phosphate buffer (pH = 7.0) containing sodium dodecyl sulfate (SDS), an environmentally friendly system, enzymatic polymerization of phenol catalyzed by horseradish peroxidase (HRP) was efficiently performed. The obtained phenol polymer is partly soluble in common solvents, such as acetone, THF and DMF. IR analysis shows that the polymer is composed of phenylene and oxyphenylene units. The functionalization of the phenol polymer was performed by reacting with epoxy chloropropane and triethylene-tetramine following, and then insoluble aminated phenol polymer was obtained. The aminated phenol polymer was adopted as carrier to prepare a novel supported palladium catalyst (PP-N-Pd) for Heck reaction. PP-N-Pd shows high catalytic performance for Heck reactions of aryl iodides with acrylic acid or styrene and the yields of *trans*-products were higher than 90%. Under the optimized conditions, aryl bromides and activated aryl chloride also reacted with alkenes to give the yields of above 80%. XPS analysis indicates that the main coordination atom in PP-N-Pd is N and the chemical valence of palladium in PP-N-Pd is Pd^{2+}. The novel supported catalyst also shows good recyclability for Heck reaction.

1. Introduction

In the last decades, an enzyme-catalyzed polymerization has been developed as a new methodology for polymer synthesis [1–4]. By utilizing enzyme catalysis, many high-performance and useful polymeric materials have been synthesized successfully. Moreover, some of these polymers cannot be obtained by conventional chemical methods. Typically, peroxidase induces oxidative polymerization of various phenol derivates and produces a new class of phenol polymers with high thermal stability [5–12]. Now, such a synthetic strategy is expected to be an alterative method for preparation of polymer like phenolic resin without using toxic formaldehyde.

The enzymatic polymerization of phenol was usually performed by using HRP as catalyst and hydrogen peroxide as oxidant. For phenol, the simplest and most important phenolic compound in industrial fields, its enzymatic polymerization in aqueous media formed only dimers and trimers with extremely low yields [5,13]. Since HRP was reported to maintain its activity even in a mixture of buffer and water-miscible organic solvent [5], HRP-catalyzed phenol and phenol derivates polymerizations have been extensively studied in such mixture [14–16]. From the point of view of environmentally benign process for polymer production, the use of organic solvent is not preferred. To get rid of this disadvantage, templates assisted enzymatic phenol polymerizations in buffer have been achieved [13,17–21]. Unfortunately, complexes of the phenolic polymers and the templates are obtained and it is difficult to separate the pure target polymers from the complexes.

Recently, we reported the enzymatic phenol polymerization in aqueous micelle system using sodium dodecyl benzene sulfonate (SDBS) as surfactant [22]. In the present work, sodium dodecyl sulfate (SDS) is found to be a more competitive surfactant in contrast with SDBS. In addition, it was found that the synthesis and characterization of the enzymatic phenol polymers have attracted many scholars' attentions. However, the modification and application of the phenol polymer were limited.

Heck reaction is the coupling of various aryl halides with olefins and it offers a versatile method for the generation of new C—C bonds in organic synthesis [23]. Richard F. Heck is one of the winners of 2010 Nobel Prize in chemistry because of his outstanding contributions to the research field of Heck reaction. The reaction is usually catalyzed by palladium compound [$PdCl_2$ or $Pd(OAc)_2$] in homogeneous solution in the presence of phosphorus ligand. However, these expensive catalysts are hardly separated and reused. In recent years, polymer supported palladium complex have attracted much attention as a new type of recyclable catalyst for Heck reaction [24–27]. In our lab, several kinds of polymer supported palladium catalysts have been synthesized [28–31]. Here, as-synthesized phenol polymer was functionalized and adopted as carrier to prepare a

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http://dx.doi.org/10.1016/j.molcatb.2012.10.015

new polymer supported palladium catalyst. Finally, the catalytic performances of the catalyst for Heck reactions of various aryl halides were studied.

2. Experimental

2.1. Materials

Horseradish peroxidase (*RZ* = 2.5, activity = 200 U/mg) was purchased from Shanghai Guoyuan Biotechnology Co., Ltd. and used without further purification. Iodobenzene and *p*-chloronitrobenzene were chemical pure and were purchased from Sinopharm Chemical Reagent Co., Ltd. *p*-Iodoanisole (98%, Lancaster), *p*-iodotoluene (98%, J & K Scientific Ltd.), *p*-iodonitrobenzene (98%, Alfa Aesar), *p*-bromonitrobenzene (98%, J & K Scientific Ltd.) and *p*-bromoanisole (97%, Lancaster) were used without further purification. All other chemicals employed in this work were obtained from various commercial suppliers and were used as received.

2.2. Measurements

Infrared (IR) spectra were recorded on an Avatar 360 Fourier transform infrared spectroscopy (Nicolet Company, USA). Thermogravimetric (TG) analyses in nitrogen and air atmosphere were performed on a TGA/SDTA851e instrument (Mettler-Toledo Company, Switzerland) at a heating rate of 10 °C/min. The concentrations of phenol during the enzymatic polymerization were analyzed using a high-performance liquid chromatograph (HPLC; Agilent 1100, American) equipped with a C18-reverse phase column (2.1 mm × 150 mm, 5 μm). The eluent was composed of acetonitrile, distilled water and acetic acid (volume ratio 45:55:0.1, flow rate is 0.4 mL/min). Phenol was detected at 280 nm using an ultraviolet (UV) absorbance detector. Palladium content in PP-N-Pd was measured on an inductively coupled plasma (ICP) spectrometer (Optima 2100DV, Perkin-Elmer, America). X-ray photoelectron spectra (XPS) were acquired on an AXISULTRA spectrometer (Kratos Analytical, England) using mono-AlKα radiation. The C1s photoelectron line was used for energy calibration and the C1s binding energy was taken as 284.8 eV.

2.3. Enzymatic polymerization of phenol in aqueous micelle system

A proper amount of SDS and 5 mmol (0.47 g) of phenol were dissolved in 45 mL of phosphate buffer (0.1 M, pH 7.0). 1 mg of HRP was dissolved in 5 mL of phosphate buffer. Then, the enzyme solution and phenol solution containing SDS were mixed. To the resultant mixed solution, hydrogen peroxide (5%, 0.25 mL) was added every 5 min for a total of 14 times under mild magnetic stirring at room temperature. Resultant black mixture was stirred for an additional 0.5 h, followed by vacuum-filtering and thoroughly washing with water to remove HRP, SDBS, residual hydrogen peroxide and phenol. As-obtained black material was dried in vacuum at 60 °C to give the desired phenol polymer.

When the effect of dosage of HRP on the yield of phenol polymer was investigated, diluted enzyme solution was used. First, 2 mg of HRP was dissolved in 10 mL of phosphate buffer. 4, 3, 2 and 1 mL of the enzyme solution was taken out respectively. Then, the four samples of enzyme solution were all diluted to 5 mL with phosphate buffer. Finally, these diluted enzyme solutions were respectively mixed with 45 mL of phenol (5 mmol) solution containing SDS. As a result, for 5 mmol of phenol, the dosage of HRP is 0.8, 0.6, 0.4 and 0.2 mg respectively.

2.4. Titration of hydroxyl group in phenol polymer

The ratio of phenylene and oxyphenylene units (Ph/Ox) in as-prepared phenol polymer was determined by titration. Briefly, 0.10 g of as-prepared phenol polymer was dissolved in 5.0 mL of pyridine containing 2.5% acetic anhydride. Resultant solution was kept at 95 °C for 1 h under gentle magnetic stirring. After cooling to room temperature, 0.5 mL of water was added and the mixture was heated again at 95 °C for 10 min. Resultant solution was titrated with 0.20 M sodium hydroxide solution in ethanol in the presence of phenolphthalein as an indicator [32].

2.5. Preparation of aminated phenol polymer supported palladium complex

1.0 g of phenol polymer was dissolved in 10 mL of ethanol, then 10 mL of epoxy chloropropane and 20 mL of NaOH (20% aqueous solution) were added. The mixture was stirred at 50 °C for 5 h. The black phenol polymer turned into yellow powder. The powder was filtrated, washed with plenty of water and ethanol. After being dried at 60 °C in vacuum for 8 h, 1.2 g of epoxidated phenol polymer was obtained.

1.0 g of epoxidated phenol polymer was added into 20 mL of H_2O. The pH value of the mixture was adjusted to 10 with NaOH solution. After 5 mL of triethylene-tetramine was added, the mixture was heated to 50 °C and stirred for 8 h. The powder was collected and dried at 60 °C in vacuum for 8 h to give the aminated phenol polymer (abbreviated as PP-N).

0.5 g of aminated phenol polymer was added to the solution of $PdCl_2$ (0.05 g) in ethanol (20 mL). The mixture was stirred at 60 °C for 72 h in air. After being cooled to room temperature, the reaction mixture was filtered and washed with ethanol (3× 20 mL), H_2O (3× 20 mL) following. Then, the powder was dried at 60 °C in vacuum for 8 h to give 0.52 g of aminated phenol polymer supported palladium complex (abbreviated as PP-N-Pd).

2.6. Typical procedure for the Heck reaction of aryl iodides with acrylic acid

In a 50 mL of round bottomed flask, PP-N-Pd (0.015 g), acrylic acid (1.5 mmol), iodobenzene (1.0 mmol), $(n\text{-Bu})_3N$ (3.0 mmol) and solvent (0.2 mL) were added. The mixture was stirred and heated to 90 °C in air for 3 h. After the reaction mixture was cooled to room temperature, H_2O (25 mL) and Na_2CO_3 (1.0 g) were added. The mixture was stirred for 10 min, and then PP-N-Pd was separated by filtration. The filtrate was treated with 3 M HCl (5 mL) and the precipitate appeared. Then, the precipitate was filtered, washed with H_2O and dried in air to give the product.

2.7. Typical procedure for the Heck reaction of aryl halides with styrene

PP-N-Pd (0.015 g), styrene (2.25 mmol), iodobenzene (1.5 mmol), $(n\text{-Bu})_3N$ (3.0 mmol) and solvent (0.2 mL) were added into a 50 mL round bottomed three necked flask. The reaction mixture was stirred at 90 °C in air for 3 h. Then, the mixture was cooled to room temperature and ether (30 mL) was added. The ether layer was separated, concentrated, and recrystallized to give the final product.

3. Results and discussion

3.1. Preparation and characterization of phenol polymer

We first examined the effect of SDS on HRP-catalyzed polymerization of phenol in phosphate buffer at room temperature in air.

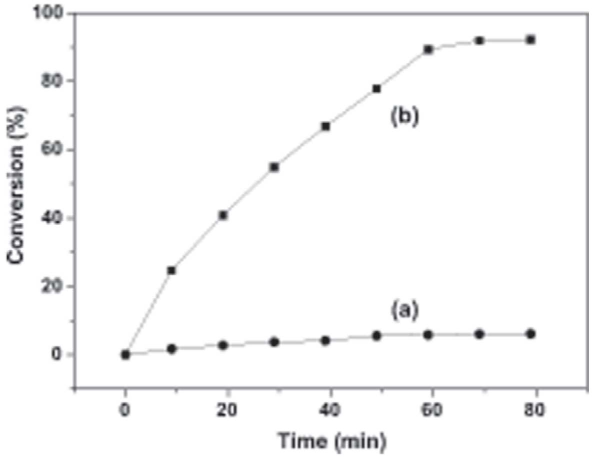


Fig. 1. Plots of conversions of phenol versus reaction time with amount of HRP is 1 mg: (a) dosage of SDS is 0 g and (b) dosage of SDS is 0.15 g.

The phenol conversions during the enzymatic polymerization are presented as Fig. 1. The polymerization of phenol catalyzed by HRP in the absence of SDS is shown as (a) curve. It can be seen that the polymerization in phosphate buffer (pH = 7) does not perform effectively; the final conversion of phenol is less than 6.0%. Curve (b) shows the conversion changes of phenol in phosphate buffer containing 0.15 g of SDS. We can see that the phenol polymerization is conducted effectively and the final conversion of phenol is higher than 90%. By utilizing SDBS as surfactant, we have reported that the final conversion was less than 50% on condition that the dosage of SDBS was 0.15 g [22]. The results show that SDS is a more competitive surfactant for enzymatic phenol polymerization in phosphate buffer.

To further investigate the effect of SDS on phenol polymerization in phosphate buffer, the dosage of SDS was varied from 0.10 to 0.40 g. Table 1 summarizes the results of HRP-catalyzed phenol polymerization in aqueous micelle system using SDS as surfactant. It is seen that the amount of SDS greatly affects the polymer yield. Yields of the product increase gradually by changing the dosage of SDS from 0.1 to 0.3 g. When the dosage of SDS is above 0.3 g, the polymer yield is almost constant. The solubility of sparingly soluble substance in water will increase when the concentration of surfactant solution is above the critical micelle concentration (CMC). The solubility of phenol in 100 mL of phosphate buffer containing 0.3 g of SDS at 25 °C is 11.2 g, which is higher than that of 8.0 g in phosphate buffer in the absence of SDS. The solubilization effect of micelle is the true reason for the effective enzymatic phenol polymerization in aqueous micelle system [22].

Table 1
Enzymatic polymerization of phenol in phosphate buffer in the presence of SDS.[a]

Entry	SDS (g)	Yield[b] (%)	Ph/Ox[c]	DSP[d] (%)
1	0.10	85.3	47/53	65.7
2	0.15	88.6	40/60	63.5
3	0.20	90.8	39/61	58.4
4	0.25	92.5	42/58	47.3
5	0.30	96.6	41/59	46.5
6	0.35	96.8	45/55	42.2
7	0.40	96.8	43/57	40.1

[a] Reaction conditions: phenol (5 mmol), phosphate buffer (pH = 7, 50 mL), HRP (1 mg), hydrogen peroxide (5% aqueous solution, 0.25 mL) was added every 5 min for 14 times at room temperature in air.

[b] The yield mentioned is actual isolated yield.

[c] Determined by titration.

[d] DMF-soluble part of the phenol polymer.

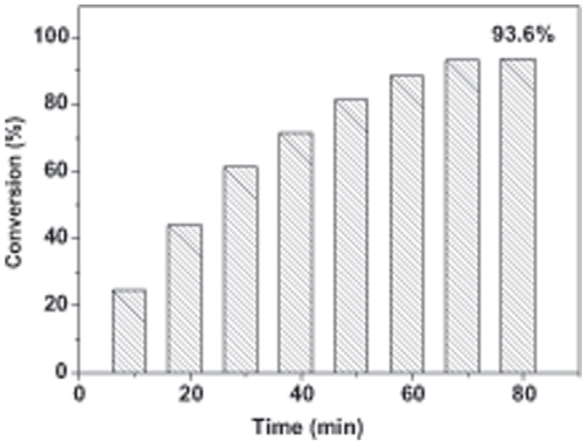


Fig. 2. Plot of conversions of phenol versus reaction time with dosage of HRP is 0.4 mg and SDS is 0.3 g.

It is well known that the mixture of organic solvent and buffer is feasible for enzymatic phenol polymerization, but the activity of HRP decreases slightly [5]. For 5 mmol of phenol or phenol derivate, the amount of HRP is usually higher than 5 mg as described in other papers [14–16]. In the present work, the amount of HRP was investigated as 0.8, 0.6, 0.4 and 0.2 mg respectively. The corresponding isolated yields of phenol polymer were 95.1, 94.3, 90.8 and 67.5%. The conversions of phenol during the reaction were investigated by HPLC with the amount of HRP is 0.4 mg and the results are shown as Fig. 2. We can see from Fig. 2 that phenol is consumed smoothly and the final conversion reaches 93.6%. Assuming the molecular weight of HRP is 4×10^4, the total turnover number is 4.68×10^5, which shows that the activity of HRP in phosphate buffer containing SDS is very high. The minor dosage of the HRP can reduce the cost greatly and will promote the application of the enzymatic phenol polymer.

The obtained phenol polymer is partly soluble in DMF, THF and acetone and insoluble in $CHCl_3$. The DMF-soluble part of the phenol polymers are listed in Table 1. The structure of the obtained phenol polymer was characterized by IR analysis. As seen from Fig. 3(a), a broad peak centered at 3420 cm^{-1} is ascribed to the vibration of the O—H bond. The peaks at 1588, 1489, 833, 753 and 692 cm^{-1} are assigned to various vibration modes of the C—H and C—C bonds of aromatic nuclei/rings. A peak at 1102 cm^{-1} corresponds to the symmetric vibration of the ether bond. The strong peak at 1207 cm^{-1} is due to the asymmetric stretching vibration of C—O—C and/or

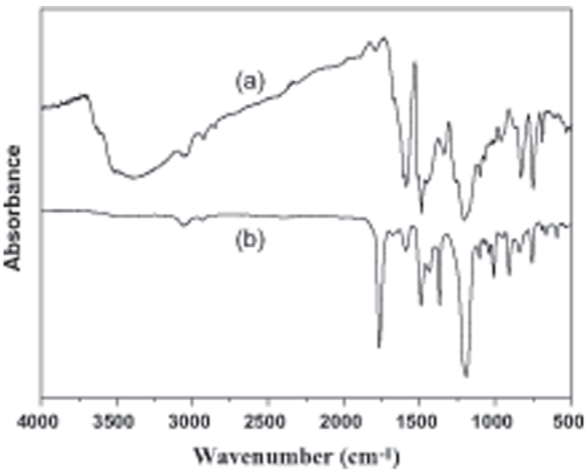


Fig. 3. IR spectra of the phenol polymer (a) and acetylated polymer (b).

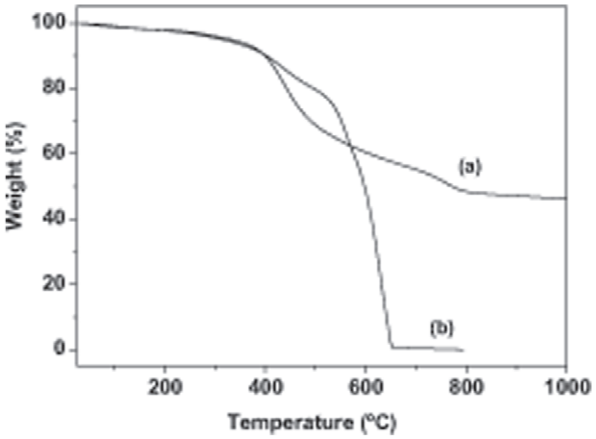


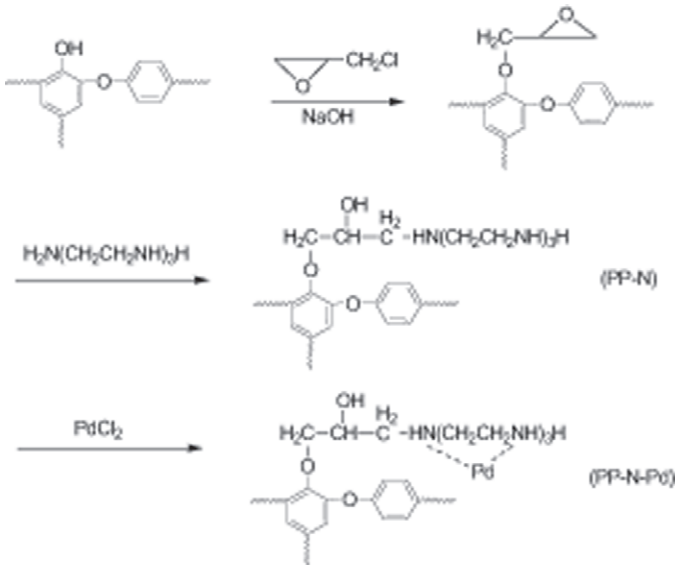
Fig. 4. TG curves of phenol polymer under nitrogen (a) and under air (b).

C—OH. These data mean that the structure of as-synthesized polymer is composed of a mixture of phenylene and oxyphenylene units [14]. The unit molar ratio of phenylene/oxyphenylene (Ph/Ox) was determined by titration of the hydroxyl group in the polymer. Fig. 3(b) shows FT-IR spectrum of the acetylated polymer. A peak at 1766 cm^{-1} corresponds to the stretching vibration of C=O. Meanwhile, the broad peak at 3420 cm^{-1} assigned to O—H bond disappeared, indicating that the acetylation is complete. Therefore, the phenolic hydroxyl group can be correctly determined by the titration method. The unit molar ratios of phenylene vs. oxyphenylene (Ph/Ox) determined by titration are listed in Table 1. In all cases, the ratios of the phenylene are in the range of 40–47%.

Thermal stability of as-synthesized phenol polymer (Entry 5 in Table 1) was evaluated by thermogravimetry (TG). The evaluations were performed under air and nitrogen respectively. The obtained TG curves were shown in Fig. 4. Temperature at 5% weight loss under air was observed at 314 °C, which was lower than that of 332 °C under nitrogen. These data show that the phenol polymer possesses high thermal stability. Under nitrogen, 46% weight of the polymer remained at 1000 °C, which is higher than phenol polymer obtained in organic system [14]. The polymer is completely decomposed at 625 °C under air.

3.2. Preparation and characterization of PP-N-Pd

The good thermal stability of the phenol polymer enlightens us to use it as a catalyst carrier for preparing a new catalyst for Heck reaction. Due to Heck reaction is usually carried out at high temperature, thermal stability of the catalyst greatly influences its catalytic performance and recyclability. Phenol polymer can be produced easily in aqueous micelle system and shows good thermal stability; we consider that it is suitable as a catalyst carrier. In order to enhance the coordination ability of the polymer, functional phenol polymer containing amino-groups was prepared by reacting with epoxy chloropropane first, and followed by the amination with triethylene-tetramine. Finally, the supported catalyst was synthesized via the coordination of aminated phenol polymer with $PdCl_2$. The whole synthetic route of aminated phenol polymer supported palladium complex (PP-N-Pd) is shown in Scheme 1.



Scheme 1. Synthetic route of PP-N-Pd.

Fig. 5(a) shows IR spectrum of epoxidated phenol polymer. A peak at 906 cm^{-1} assigned to asymmetric stretching vibration of epoxy group appears, while the peak due to the vibration of phenolic hydroxyl group decreases greatly, which indicates the epoxidation of phenol polymer occur. The aminated phenol polymer was obtained by epoxidated phenol polymer reacting with triethylene-tetramine. Fig. 5(b) shows IR spectrum of aminated phenol polymer. The peak at 906 cm^{-1} assigned to vibration of epoxy group disappears and the stretching vibration of N—H at 3300 cm^{-1} appears. These data show that the functional phenol polymer containing amino-group (PP-N) was successfully synthesized. The functional phenol polymer supported palladium complex was synthesized by reacting with $PdCl_2$ in ethanol. Pd content in PP-N-Pd measured by ICP method is 0.61 mmol/g.

To further study the chemical state of palladium in the supported catalysts and the coordination of macromolecular ligands with palladium, PP-N and PP-N-Pd were characterized by X-ray photoelectron spectroscopy (XPS). From Fig. 6, we can see that the binding energy of N1s in PP-N-Pd is 400.3 eV, which is higher than that of 399.1 in PP-N. The result shows that the lone-pair of electrons on nitrogen atom transfers and the electron cloud density around nitrogen atom decreases. Meanwhile, the binding energy of O1s in PP-N-Pd and PP-N does not show significant difference. We conclude that the main coordination atom in PP-N-Pd is N. The binding energy of $Pd3d_{5/2}$ in PP-N-Pd is 338.4, which suggests that the chemical state of palladium is Pd^{2+}.

Fig. 7 shows the TG curves of PP-N-Pd in nitrogen and air atmosphere. The thermal stability of PP-N-Pd is lower than pure phenol polymer because of the introduction of amino and alkyl groups.

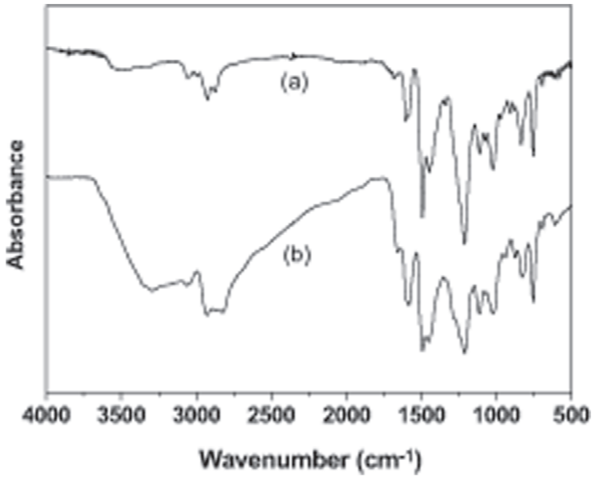


Fig. 5. IR spectra of epoxidated phenol polymer (a) and aminated phenol polymer (b).

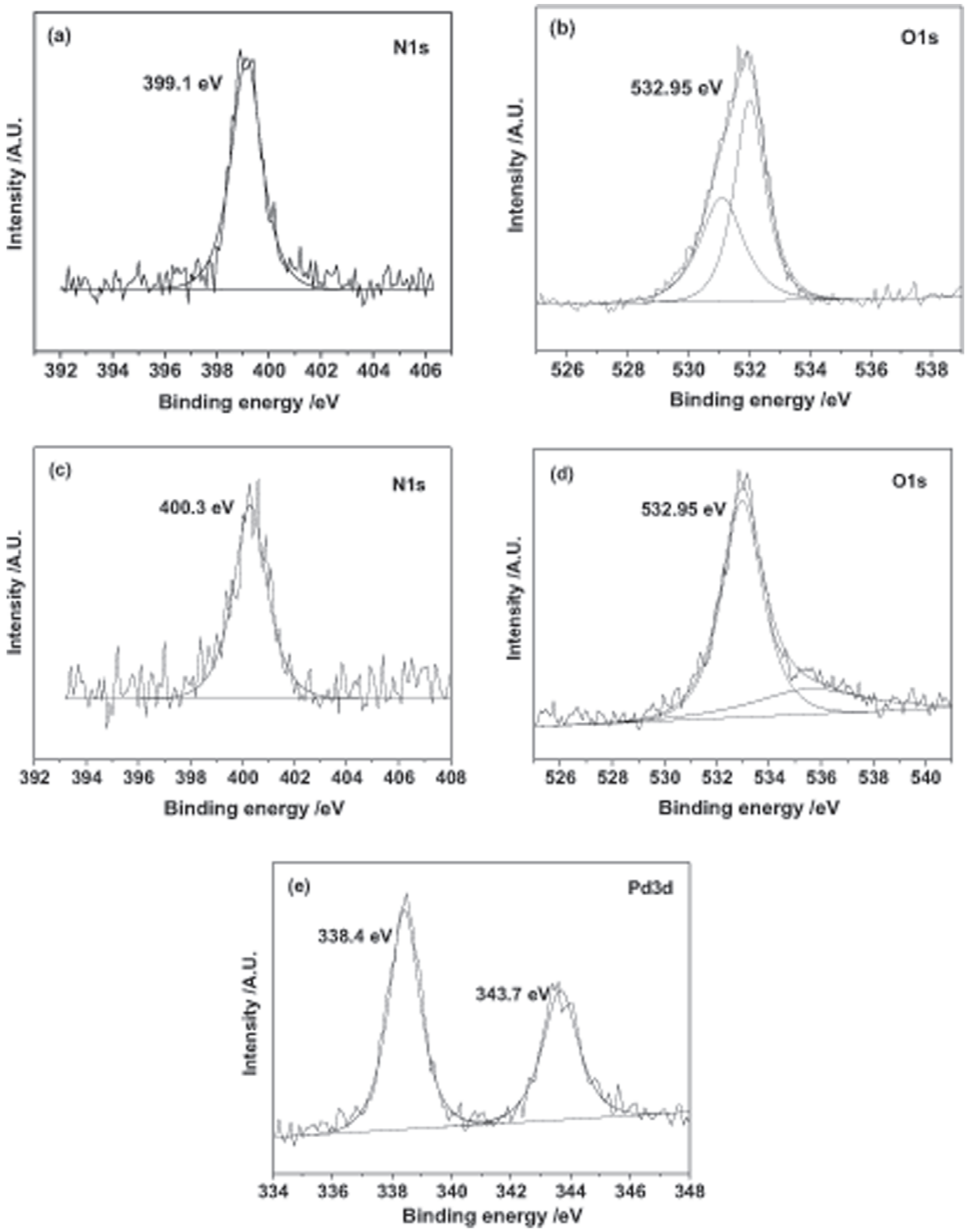


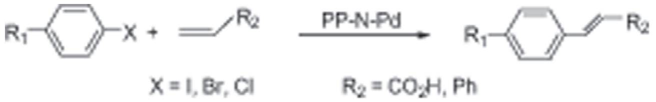
Fig. 6. XPS spectra of PP-N and PP-N-Pd: (a) N1s in PP-N; (b) O1s in PP-N; (c) N1s in PP-N-Pd; (d) O1s in PP-N-Pd; (e) Pd3d in PP-N-Pd.

Kobayashi also found the thermal stability of n-butylphenol polymer is lower than phenol polymer [32]. But even so, PP-N-Pd is still stable up to 200 °C. The high thermal stability can perfectly meet the high temperature condition which is required in Heck reaction.

3.3. *Catalytic performance of PP-N-Pd for Heck reaction*

The catalytic performance of PP-N-Pd for Heck reaction was investigated finally. The results of the Heck reactions of various aryl halides with olefins under different reaction conditions were summarized in Table 2. In the presence of the novel catalyst, PP-N-Pd, the reactions of aryl iodides with acrylic acid or styrene were carried out smoothly at 90 °C in DMF in air with short reaction time (Entry 1–8). For example, treatment of 4-iodotoluene with styrene afforded 92.6% yield of the corresponding product (Entry 3 in Table 2). For the substrates of aryl bromides and aryl chlorides, TBAB was chosen as solvent. In addition, the reactions were performed in nitrogen atmosphere at higher temperature due to the high bond energy of C—Br or C—Cl. Because of the high stability of the catalyst, the reactions of aryl bromides or aryl chloride could also be performed effectively. For the coupling of *p*-bromoanisole with styrene (Entry 12 in Table 2), the yield of the corresponding product was 85.2%. *p*-Chloronitrobenzene also reacted with styrene to give the moderate yield of 80.2% (Entry 14 in Table 2).

Table 2
Heck reactions of aryl halides with alkenes catalyzed by PP-N-Pd.[a]



Entry	Aryl iodide	Alkene	Temperature (°C)	Time (h)	Yield[b] (%)
1	C_6H_4I	CO_2H	90	3	90.0
2	4-$CH_3OC_6H_4I$	CO_2H	90	3	94.3
3	4-$CH_3C_6H_4I$	CO_2H	90	3	92.6
4	4-$O_2NC_6H_4I$	CO_2H	90	3	90.2
5	C_6H_4I	Ph	90	3	97.3
6	4-$CH_3OC_6H_4I$	Ph	90	3	94.2
7	4-$CH_3C_6H_4I$	Ph	90	3	92.8
8	4-$O_2NC_6H_4I$	Ph	90	3	97.0
9	C_6H_4Br	Ph	120	6	96.5
10	4-$CH_3OC_6H_4Br$	CO_2H	120	6	80.8
11	4-$O_2NC_6H_4Br$	CO_2H	120	6	86.6
12	4-$CH_3OC_6H_4Br$	Ph	120	6	85.2
13	4-$O_2NC_6H_4Br$	Ph	120	6	93.3
14	4-$O_2NC_6H_4Cl$	Ph	130	6	80.2

[a] Reaction conditions: PP-N-Pd (0.015 g), aryl halide (1.0 mmol), acrylic acid (1.5 mmol). When aryl iodides were adopted as substrates, the solvent is DMF. Tetrabutylammonium bromide (0.8 g) was used as solvent and the reaction was carried out in N_2 atmosphere on condition that aryl bromides or aryl chloride were adopted as substrates.

[b] Isolated yield was based on aryl halides.

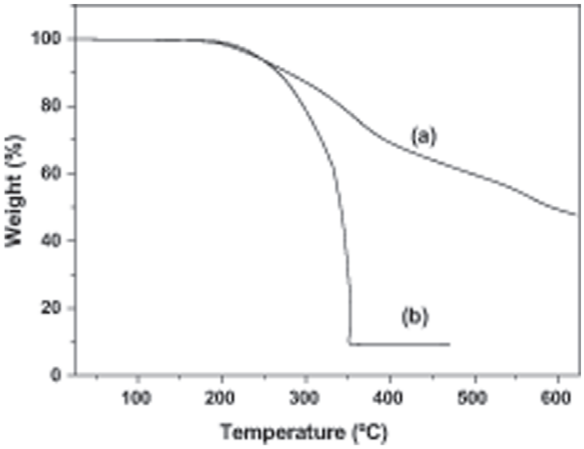


Fig. 7. TG curves of PP-N-Pd under nitrogen (a) and under air (b).

The recovery and reuse of the catalyst is highly important because of the high price of the palladium compounds. Therefore, the reusability of the catalyst was investigated using Heck reaction of iodobenzene with styrene as a model reaction (Table 3). After the reaction was completed, the catalyst was recycled easily by filtration, then washed with ethanol and dried in air. The recycled catalyst can be reused for Heck reaction of iodobenzene with styrene. The yield of *trans*-1,2-stilbene is high as 90.8% at the cycle of five. Moreover, the reusability of PP-N-Pd is better than that of our previously reported catalyst of poly(vinylidene dichloride)-diethylene triamine supported palladium complex [33]. The good catalytic activity and reusability of PP-N-Pd result from the effective coordination of PP-N with $PdCl_2$ and the high thermal stability of PP-N-Pd. Because of the high price of palladium complex, the high performance of PP-N-Pd can reduce the cost of the Heck reaction greatly.

Table 3
Reusability of PP-N-Pd for Heck reaction.[a]

Cycles	Time (h)	Yield[b] (%)
1	3	96.8
2	3	96.2
3	3	96.2
4	4	93.2
5	4	90.8

[a] Reaction conditions: PP-N-Pd (0.015 g), iodobenzene (1.0 mmol), styrene (1.5 mmol), $(n\text{-}Bu)_3N$ (3.0 mmol) and DMF (0.2 mL) in air at 90 °C;.

[b] Isolated yield was based on iodobenzene.

4. Conclusion

From phenol, the simplest and most important phenolic compound in industrial fields, its polymerization catalyzed by HRP was efficiently performed in aqueous micelle system using SDS as surfactant. Because of the solubilization effect of the micelle, phenol polymer was obtained with high yield. The obtained phenol polymer shows high thermal stability and is modified to generate a functional polymer possessing amino groups. As-synthesized functional phenol polymer supported palladium complex is a novel and efficient catalyst for Heck reaction. In the presence of the catalyst, various aryl iodides and aryl bromides reacted with alkenes to give the corresponding *trans*-products with moderate to high yield. We believe that the novel phenol polymer produced by enzyme catalysis must attract more attention and will be applied to many fields.

Acknowledgement

This work was supported by the open fund of State Key Laboratory of Molecular Engineering of Polymers.

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