

The Effect of Ligand Molecular Weight on Copper Salt Catalyzed Oxidative Coupling Polymerization of 2,6-Dimethylphenol

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ABSTRACT: Polyphenylene oxide (PPO) was prepared via oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper salt. The ligand was a novel series of random copolymers (PSVP) of styrene and 4-vinylpyridine prepared by reversible addition-fragmentation chain transfer (RAFT) copolymerization. The copolymers with well-controlled molecular weight (MW) were used to study the effects of ligand molecular weight on the catalytic activity and selectivity. It was found that the catalytic activity increased with the molecular weight but there existed an upper MW limit above which no further increase in activity could be achieved. With PSVP of $F_{\text{VPy}} = 0.39$, the critical MW was about 5000 g/mol. The

mechanism involved in the successive complexation of copper ions and PSVP was elucidated and the equilibrium constants were estimated by pH titration. It was found that the macromolecular ligand was in favor of bridging Cu^{II} ions that formed catalytically active dinuclear copper-amine complexes. However, the catalytic selectivity was almost independent of the ligand MW. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 3473–3481, 2010

Key words: poly(phenylene oxide); oxidative coupling polymerization; macromolecular ligand; reversible addition-fragmentation chain transfer polymerization (RAFT); catalysis

INTRODUCTION

Polyphenylene oxide (PPO) is an engineering plastic that has outstanding chemical and physical properties,^{1,2} such as good mechanical strength, excellent chemical and moisture resistance, high glass transition temperature, and self-extinguishing performance. PPO materials of high molecular weight are produced by the C–O oxidative coupling polymerization of 2,6-dimethylphenol (DMP) catalyzed by copper ions complexed with amines,³ as shown in Scheme 1. However, an undesirable red-colored by-product, diphenoquinone (1–4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadieneone, DPQ), often resulted from the C–C coupling of two DMP molecules. The by-product severely degrades PPO during high-temperature processing and therefore must be minimized.

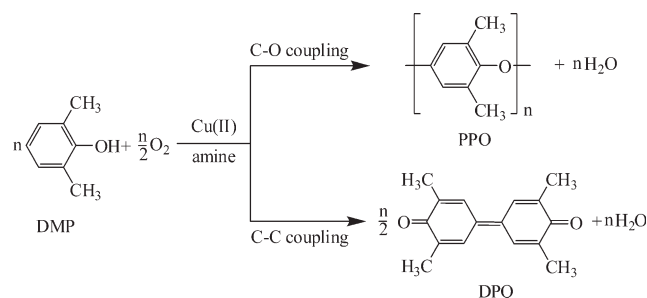
It is well known that the activity and selectivity of the copper catalyst are determined to a large extent by the ligand type. The most widely used ligands include pyridine,^{3–5} *N,N,N',N'*-tetramethylethylenediamine,^{6,7} *N*-methylimidazole,^{8–10} *N,N*-dibutylethylenediamine,^{11,12} etc. Macromolecular ligands have also attracted much attention because of their low volatility, ease in separation from small molecular products and flexibility in chemical modification, even with inferiority in solution viscosity as compared to small ligands. The macromolecular ligands reported in the literature for the oxidative coupling polymerization include poly(styrene-*co*-4-vinylpyridine),¹³ poly(styrene-*co*-*N*-vinylimidazole),¹⁴ poly(*N*-distributed iminotrimethylene),¹⁵ and polystyrene-bound-4-(*N,N*-dimethylamino)pyridine (PS-*b*-DMAP).¹⁶ Koning et al.¹⁶ found that PS-*b*-DMAP exhibited a comparable catalytic selectivity but an improved catalytic activity over its corresponding small molecule of DMAP.

Another advantage of macromolecular ligand is its effectiveness in developing supported copper-amine catalysts for continuous synthesis of PPO. In the case of small molecules, such as monoamines and diamines,^{17,18} a certain amount of free amine needs to be added to activate the supported copper-amine catalyst because four nitrogen atoms are required to form the active dinuclear copper center¹⁹ but the chemically supported small amines do not have an

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Scheme 1 The oxidative coupling polymerization of DMP catalyzed by copper-amine complex.

adequate density and flexibility to coordinate the copper ions. In contrast, macromolecular ligand can fulfill the coordination requirement owing to multiple coordinating points on a single flexible chain. In addition, the existence of free small amine results in another problem: leaching of copper ions from the support and, therefore, diminishing of catalytic activity. Clearly, such problem does not exist for chemically supported macromolecular ligand. Therefore, supported copper-amine catalyst with macromolecular ligand is more practical than that with small molecular ligands. It was reported that poly(styrene-*co*-*N*-vinylimidazole) supported on silica particles have been used in the polymerization of 2,6-disubstituted phenols in a continuous stirred tank reactor (CSTR).²⁰ The supported catalyst remained in the reactor by a filter mounted at the outlet and was found to be stable for at least 6 days.

The effects of macromolecular ligand in the catalysis are determined by its chain microstructure, such as composition and molecular weight (MW). As disclosed in the literature,²¹ the composition plays a significant role in catalytic activity of oxidative coupling polymerization. Koning et al.²² found that molecular weight of polystyrene-bound-DMAP did not influence catalytic activity when it ranged from 3.3×10^{-4} to 12.4×10^{-4} g/mol. However, Tsuchida et al.²³ observed an increase of catalytic activity with MW in the case of quarternized poly(vinylpyridine). The effects of ligand molecular weight on the catalytic activity and selectivity of copper-amine complexes are still not clear and remain to be resolved. The major challenge is the difficulty in synthesizing macromolecular ligands with well-defined composition and well-controlled molecular weight. Fortunately, the advent of controlled/living radical polymerization (CLRP) in the last decade makes it possible. Reversible addition-fragmentation chain transfer free radical polymerization (RAFT)²⁴ is one of the most effective CLRP and has been used to (co)polymerize most vinyl monomers including styrene^{25–27} and 4-vinylpyridine.^{28–31}

The objectives of this article are to synthesize a novel series of poly(St-*co*-vPy) (PSVP in abbrevia-

tion) samples with well-controlled composition and molecular weight via RAFT copolymerization of styrene (St) and 4-vinylpyridine (vPy) and to use these samples as ligand to systematically investigate the effects of ligand molecular weight on catalyst activity and selectivity in the oxidative coupling polymerization of DMP. We aim at providing insight into the mechanism involved in the successive complexation of copper ions and PSVP. As far as we know, this is the first report on the use of macromolecular ligand with well-controlled molecular weight in the oxidative coupling polymerization of DMP.

EXPERIMENTAL SECTION

Materials

Styrene (St, 99%, Shanghai Ling Feng Chemical Reagent Co., China) and 4-vinylpyridine (vPy, 95%, Acros) were purified by vacuum distillation before use. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Shanghai Si He Chemical Reagent Co., China) was purified by recrystallization three times from methanol. The RAFT agent, 1-phenylethyl phenyldithioacetate (PEPDTA) was synthesized following the procedure reported in the literature.³² 2,6-Dimethylphenol (DMP, Acros, 99%) was purified by recrystallization from *n*-hexane. All the other chemicals were of analytical grade and used without further purification.

Copolymerization of styrene and 4-vinylpyridine mediated by PEPDTA

The copolymerization was conducted in bulk using AIBN as initiator and PEPDTA as RAFT agent. The amount of PEPDTA in recipe was determined by the target molecular weight, and the amount of AIBN was maintained at the molar ratio of 1 : 5 to PEPDTA. St (0.14 mol) and vPy (0.06 mol), PEPDTA and initiator were charged to a 50 mL flask equipped a condenser, a thermometer, and a magnetic stirrer. The mixture was first degassed by nitrogen bubbling at 0°C for 1 h and then heated to 60°C under nitrogen atmosphere. Owing to similar reactivity ratios of St ($r_{St} = 0.54$) and vPy ($r_{vPy} = 0.70$),³³ the composition drifting in copolymer would not be significant as long as the monomer conversion is not too high. To maintain constant copolymer composition, all the polymerization runs were stopped before 50% monomer conversion. The reaction mixture was slowly poured into excess of *n*-hexane with continuous stirring. The precipitate was washed with *n*-hexane for three times and dried at 70°C in a vacuum oven for over 12 h.

Oxidative coupling polymerization of DMP

The oxidative coupling polymerization of DMP was carried out at 25°C in an oxygen uptake apparatus

according to the following procedure. CuCl_2 was dissolved in methanol, NaOH was dissolved in methanol, and DMP was dissolved in toluene. Then 1 mL CuCl_2 solution, 8 mL toluene, and a preset amount of PSVP were transferred to a jacketed reactor that was equipped with a suite of gas measuring equipment³⁴ and a jacketed constant pressure funnel. NaOH (1 mL) and 5 mL DMP solutions were transferred into the funnel. The reactor was purged with oxygen at 25°C for 1 h before reaction. After sealing the apparatus, the monomer solution was added to the reactor within 30 sec. The oxygen consumption was monitored immediately by gas measuring equipment as a function of time to estimate the reaction rate. When the oxygen assumption was no longer observed, the reaction mixture was sampled for estimation of DPQ yield. Except for otherwise described, the following standard reaction conditions were employed: $T = 25^\circ\text{C}$, $P = 1 \text{ atm}$, $[\text{DMP}]_0 = 0.06 \text{ M}$, $[\text{CuCl}_2]_0 = [\text{NaOH}]_0 = 3.32 \times 10^{-3} \text{ M}$; 15 mL toluene/methanol (13/2, v/v) mixture as solvent.

In addition, the catalyst samples were prepared for analysis according to the following procedure. A catalyst solution was prepared by mixing CuCl_2 salt and PSVP in toluene/methanol (13/2, v/v), similar to the recipe for oxidative coupling polymerization. The catalyst components were obtained by agitating the mixture for 0.5 h, followed by slow evaporation of solvents at 40°C in vacuum to constant weight.

pH titration for successive complexation of Cu^{II} and PSVP

The successive complexation of Cu^{II} ions and PSVP was studied with pH titration (PHS-2C pH meter equipped with a E-201-C combination electrode) employing a modified Bjerrum method.^{35,36} A typical pH titration process was performed as follows. The PSVP sample (including $5 \times 10^{-4} \text{ mol}$ pyridine rings) and KCl ($5 \times 10^{-3} \text{ mol}$) were charged to a 50 mL volumetric flask and dissolved with 37.5 mL dioxane. Five milliliter of CuCl_2 aqueous solution (0.02M) and 5 mL of hydrochloric acid (0.128M) were transferred to the flask. After it was filled with water up to the tick mark, the mixture was shaken for homogenization. The pH titration was then conducted by adding NaOH solution (1.2M) to the prepared solution. After pH value reached constant in every addition step, it was recorded versus the volume of added alkaline solution.

Characterization

The molecular weight and molecular weight distribution of PSVP samples were determined at 30°C by GPC (Waters 1525/2414/2487) with a refractive

index detector. THF was used as an eluent at a flow rate of 1 mL/min. The molecular weight was calibrated by a series of narrow polystyrene standards (Polymer Laboratory) with molecular weight ranging from 162 to 43,900 g/mol.

$^1\text{H-NMR}$ spectroscopy (Advance DMX500 spectrometer operated at 500 MHz) was used to determine the composition of PSVP in deuterated dimethyl sulfoxide at 25°C. TMS was used as an internal standard. The sample at the end of the oxidative coupling polymerization was diluted in toluene/methanol (13/2, v/v) and analyzed via UV/visible spectrophotometer (UV751GW). An obvious absorption peak at 420 nm was observed. The ultimate yield of DPQ was estimated from its absorbency according to the Beer's law (molar extinction coefficient $\epsilon = 60131 \text{ L mol}^{-1} \text{ cm}^{-1}$).

RESULTS

Chain properties of macromolecular ligands

Nine PSVP samples with various molecular weights were synthesized and the molecular characteristics were summarized in Table I. The polymerization was controlled at low monomer conversion, and therefore, the copolymer composition remained approximately constant ($F_{\text{vPy}} = 0.39 \pm 0.05$). The number-average molecular weights (M_n) agreed well with the calculated ones ($M_{n,\text{cal}}$) and the polydispersities (PDI) were lower than 1.26, indicating well-controlled RAFT copolymerization.

The compositions (F_{vPy}) of PSVP samples were estimated from their $^1\text{H-NMR}$ spectra. Figure 1 shows a typical spectrum. The signals characteristic of the pyridine ring were observed at 8.3 ppm and 6.6 ppm, and those of phenyl at 7.1 ppm and 6.6 ppm. The F_{vPy} was estimated from the relative intensities of the signals. It was noted that the phenyl from PEPDTA contributed to the signal at $\delta = 7.1 \text{ ppm}$, so its H atoms were excluded in the estimation of F_{vPy} values. According to the values of M_n and F_{vPy} , the average number of pyridine rings per PSVP chain, \bar{N}_0 , was calculated from eq. (1), where M_{PEPDTA} and M_{vPy} were the molecular weights of PEPDTA and vPy, respectively.

$$\bar{N}_0 = F_{\text{vPy}}(M_n - M_{\text{PEPDTA}})/M_{\text{vPy}} \quad (1)$$

Effect of ligand molecular weight on catalytic activity

In the oxidative coupling polymerization, DMP was predominantly converted into the product PPO, but at the same time, partially into the by-product DPQ. The O_2 uptake as a function of time was directly

TABLE I
The Chain Properties of PSVP Designed Via RAFT Polymerization and Employed
in this Work as Ligand

PSVP sample	Conversion (%)	$M_{n,cal}$ g/mol	M_n (g/mol)	PDI	F_{vPy}	\bar{N}_0
P1	50.0	1830	1310	1.12	0.44	4.4
P2	33.6	2370	1710	1.11	0.39	5.3
P3	44.6	3060	2530	1.11	0.39	8.4
P4	30.4	4070	3310	1.18	0.40	11.7
P5	37.6	4970	4080	1.19	0.40	14.7
P6	49.8	6490	5430	1.19	0.38	18.9
P7	42.6	9130	7520	1.24	0.38	26.5
P8	41.8	13310	10100	1.20	0.35	32.9
P9	43.4	18330	19040	1.26	0.35	62.1

measured during the polymerization to determine the total reaction rate which was twice of the O_2 consumption rate according to Scheme 1. A typical O_2 uptake curve is shown in Figure 2. The reaction basically remained a constant rate within 40% reaction degree. The initial reaction rate R_0 was therefore determined from the initial slope of the O_2 uptake curve. The result is shown in Figure 2.

Figure 3 illustrates the effect of PSVP M_n on the initial reaction rate R_0 under various N/Cu ratios (the molar ratio of total pyridine rings in PSVP to Cu^{II} ions, ranged from 0.35 to 28). The catalytic activity was gradually enhanced by increasing M_n and then leveled off when the M_n reached a critical value ($M_{n,cr}$). The critical molecular weight $M_{n,cr}$ of PSVP with F_{vPy} of 0.39 was found to be about 5000 g/mol, independent of the N/Cu ratio. In addition, the catalytic activity was improved by increasing N/Cu, which was similar to the oxidative coupling polymerization using small molecular amines as ligand.

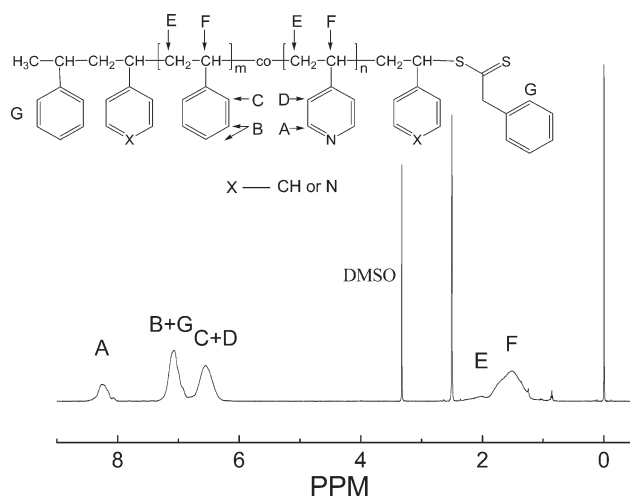


Figure 1 Typical 1H -NMR spectrum of PSVP synthesized via RAFT polymerization.

The effect of ligand molecular weight on catalytic selectivity

The amount of DPQ at the end of the reaction was determined via a UV/visible spectrophotometer. The yield of DPQ (DPQ%) was calculated from the amount of DPQ formed and the initial DMP fed to the reactor, $2[DPQ]/[DMP]_0$. Figure 4 shows the selectivity data in terms of PPO%. It indicated that the catalytic selectivity for PPO (i.e., $(100 - DPQ)\%$) increased significantly with the N/Cu ratio, but was nearly independent of the M_n of PSVP. The selectivity ranged from 82 to 94% when the N/Cu ratio was increased from 3.5 to 28.

Both C—O coupling and C—C coupling reactions contributed to the total reaction rate R_0 , but their individual reaction rates could hardly be isolated from the total R_0 data as only the final selectivity was known. Fortunately, R_0 approximated the initial reaction rate of C—O coupling because of the high selectivity. So the total rate data were used in the

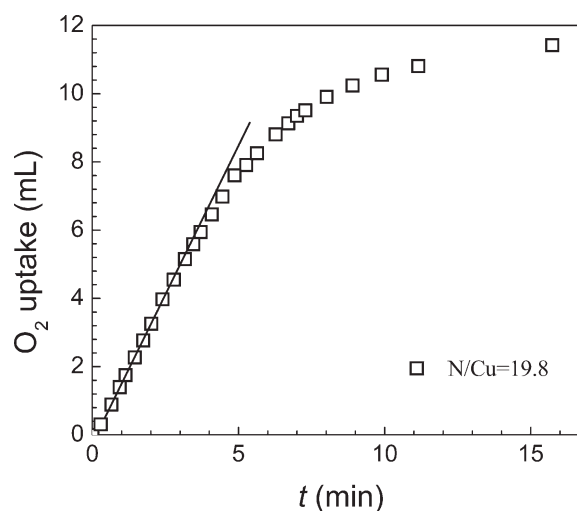


Figure 2 The O_2 uptake curves in the oxidative coupling polymerization of DMP catalyzed by Cu-P6 complex.

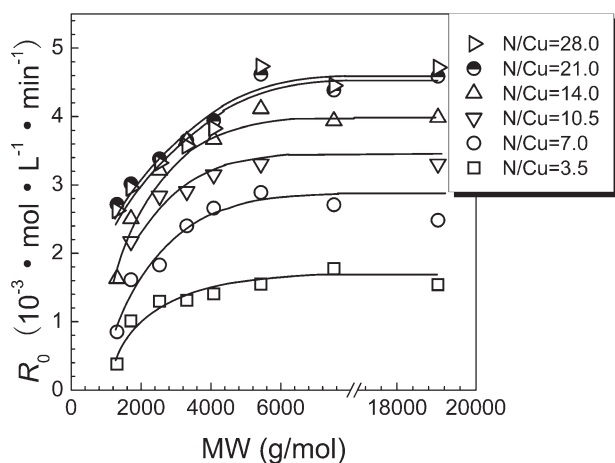


Figure 3 The R_0 vs ligand M_n in the oxidative coupling polymerization of DMP with copper-PSVP complex as catalyst at various N/Cu ratios.

following section to analyze the effects of the molecular weight of PSVP ligand.

Comparison between macromolecular and small molecular ligands

Figures 5 and 6 give the comparisons of the catalytic activity and selectivity in the oxidative coupling polymerization catalyzed by Cu-P7 and Cu-pyridine complex at various N/Cu ratios. The catalytic activity increased with the N/Cu ratio, reached a maximum and then decreased again in both P7 and pyridine systems. The selectivity for PPO also increased with the N/Cu ratio for both ligands. However, there were obvious differences. The selectivity in the P7 system was entirely higher than that in pyridine. In particular, at the N/Cu ratios lower than 40, P7 was advantageous for a high catalytic activity. The catalytic activity for P7 decreased with the N/Cu ra-

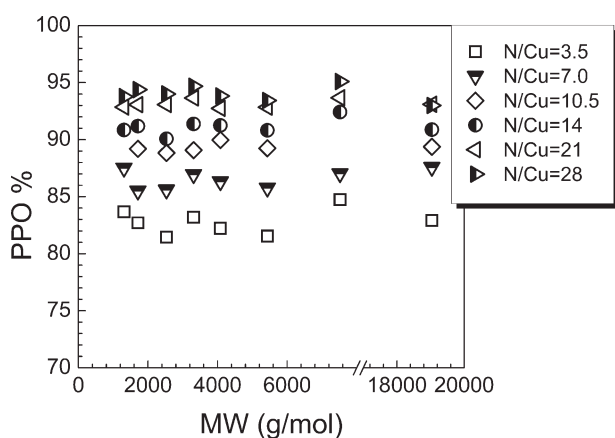


Figure 4 PPO% vs ligand M_n in the oxidative coupling polymerization of DMP with copper-PSVP complex as catalyst at various N/Cu ratios.

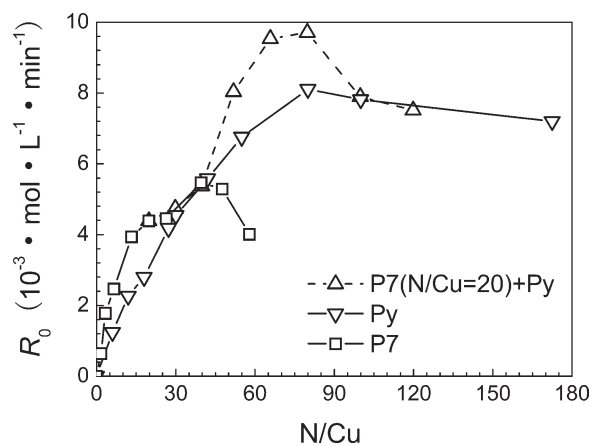


Figure 5 R_0 vs N/Cu in the oxidative coupling polymerization with pyridine (Py), P7 or their mixture as ligand.

tio over 40 because of a high solution viscosity. The content of P7 was up to 2.4 wt % in the solution when N/Cu ratio reached 40 and the macromolecular ligand chains might experience significant interaction and entanglement. The oxygen transportation could be adversely affected and, as a result, the reaction rate was retarded. In the absence of this limitation, the activity continuously increased for pyridine up to the N/Cu ratio of 80 as just pyridine ligand was used.

PSVP appears to be especially applicable at low N/Cu ratios, whereas pyridine has advantage at high N/Cu ratios because of its low viscosity. Therefore, the use of pyridine/PSVP mixture could possibly optimize the catalytic activity. As shown in Figure 5, when additional pyridine was added into Cu^{II}-P7 system with N/Cu of 20, the activity increased from 4.4×10^{-3} to 9.70×10^{-3} mol L⁻¹ min⁻¹ with N/Cu of 80 and the selectivity only decreased a little.

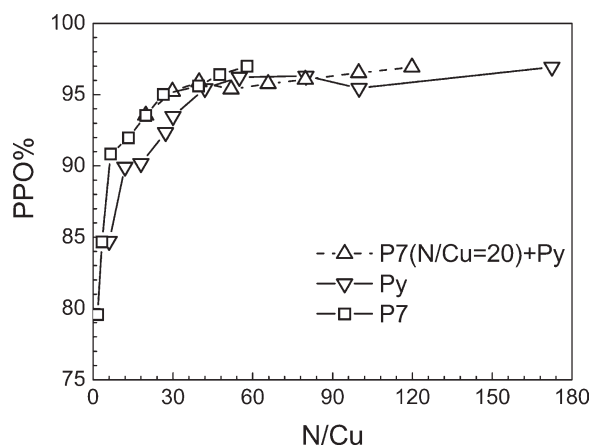
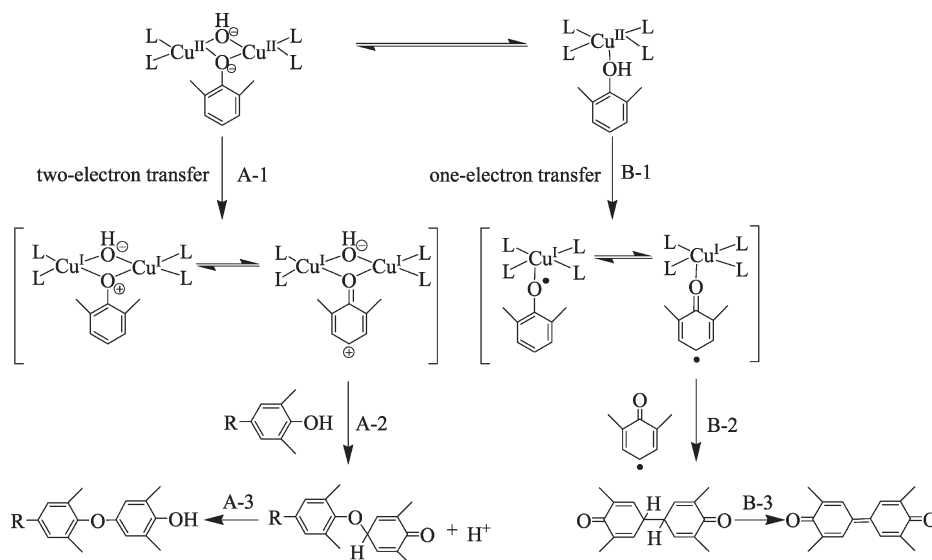


Figure 6 PPO% vs N/Cu in the oxidative coupling polymerization with pyridine (Py), P7 or their mixture as ligand.



Scheme 2 A-1~3: the ionic pathway for the formation of PPO; B-1~3: the radical pathway for the formation of DPQ. L: pyridine ring.

DISCUSSION

The features of oxidative coupling of DMP

In the polymerization of DMP, the dominant C—O coupling of two DMP molecules forms PPO while the minor C—C coupling results in DPQ. There are two types of catalytic active species: dinuclear copper-amine complex and mononuclear copper-amine complex.^{19,37} A phenolate anion is formed by deprotonation of DMP with NaOH and then coordinates with two Cu^{II} ions with four ligand moieties and one OH⁻. The complex experiences a two-electron transfer process and is oxidized to phenoxonium cation which is susceptible to nucleophilic attack. The nucleophilic attack of the electronegative oxygen atom on the paraelectropositive carbon atom is responsible for the C—O coupling reaction. The mechanism is illustrated in Scheme 2. Vigalok et al.³⁸ isolated the stabilized phenoxonium cation, which supports the ionic pathway for the C—O coupling.

At the same time, the C—C coupling reaction is catalyzed by the mononuclear copper-amine complex via a radical mechanism.³⁹ Namely, a DMP molecule coordinates with a Cu^{II} ion and experiences a one-electron transfer process to produce a phenolic radical, which is eventually transformed to DPQ. This has been validated by the fact that DPQ becomes the predominant product when a radical agent like benzoyl peroxide is used instead of the copper-amine catalyst.⁴⁰

In this study, we elucidated the mechanism through the effects of the OH/Cu molar ratio (initial NaOH/Cu^{II} ratio) on the catalytic activity and selectivity. Figure 7 shows the R_0 and DPQ % data with Cu-P8 complex. The initial reaction rate R_0 increased

dramatically with the OH/Cu ratio and reached a maximum at the OH/Cu ratio of 1. It suggests that the hydroxide ions not only deprotonated DMP molecules to produce phenolate anions (colorless DMP solution turned yellow after addition of NaOH) but also bridged Cu^{II} ions to form the dinuclear Cu^{II} complex. As a result, the Cu^{II} ions were mostly converted to the dinuclear Cu^{II} complex and the R_0 reached its maximum value at the OH/Cu ratio of 1 according to the coordination mechanism shown in Scheme 2. However, excessive OH⁻ ions hydrolyzed the catalyst because they were strong electron-donors. When two-fold of NaOH was used, blue-colored hydrolyzed product Cu(OH)₂ was precipitated out of the reaction solution. Therefore, the R_0

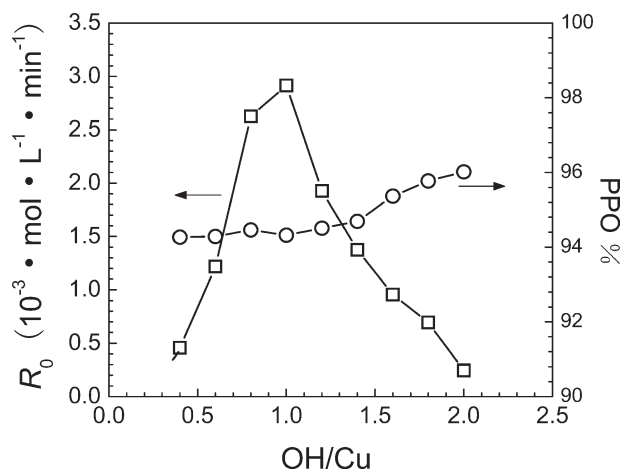
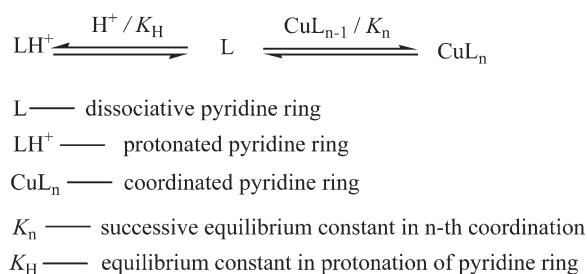


Figure 7 R_0 and PPO % vs OH/Cu in the oxidative coupling polymerization of DMP employing Cu-P8 complex as catalyst. $[\text{Cu}]_0 = 3.32 \times 10^{-3} \text{ M}$. N/Cu = 8.



Scheme 3 The dissociation and coordination equilibriums of pyridine ring in the pH titration process.

dropped remarkably when the OH/Cu ratio exceeded 1.

The catalytic selectivity was also improved by increasing the OH/Cu ratio. It indicates that high basicity was conducive to the ionic pathway for C—O coupling, rather than the radical pathway for C—C coupling. The selectivity was improved continuously with the increased N/Cu ratio up to 28 or higher (Fig. 4) as PSVP was a ligand of weak basicity.

Coordination capacity of PSVP

The effect of PSVP molecular weight on oxidative coupling of DMP lies in how the PSVP chains with different molecular weights participated in the formation of copper-amine complexes. We applied a modified Bjerrum pH titration method^{35,36} to three typical PSVP samples (P1, P3, and P8) to study the successive formation mechanism of copper-amine complexes. A dioxane/water solution of PSVP (0.01 M of pyridine rings) and CuCl₂ (0.002 M, N/Cu = 5) buffered with KCl was first acidized/protonized with excessive hydrochloric acid (0.0128M), and then titrated with NaOH aqueous solution. In comparison, the titrations were also carried out in absence of CuCl₂.

According to the dissociation and coordination equilibriums of pyridine rings in the pH titration process as shown in Scheme 3, the concentrations of free pyridine rings ([L]) and protonized pyridine rings ([H⁺L]) were calculated.³⁵ The [H⁺] in the presence of Cu^{II} was higher than that in the absence of Cu^{II}, but the [L] and [H⁺L] were lower (data not shown). The differences could be attributed to the coordination of pyridine rings to Cu^{II} that drove the equilibriums in Scheme 3 to the right-side.

The average number of pyridine rings bound to each Cu^{II} ion (\bar{n}) was thus calculated³⁵ and is shown as a function of log[L] (symbols in Fig. 8). The \bar{n} value was extrapolated to about 4 in P3 and P8, suggesting the formation of mononuclear copper-amine complex (CuL₄) with excessive pyridine rings.

If only the mononuclear coordination was considered for simplicity, the \bar{n} could be calculated from

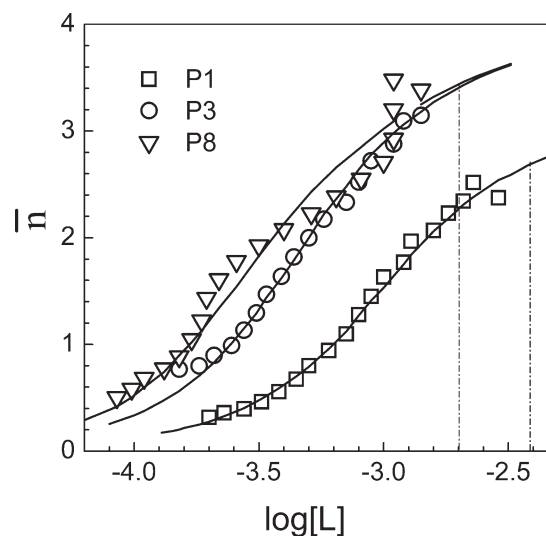


Figure 8 The average number of pyridine rings bound to per Cu^{II} ion (\bar{n}) as function of log[L] for P1, P3 and P8 systems. Symbols: experimental data; curves: fitted with eq. (2).

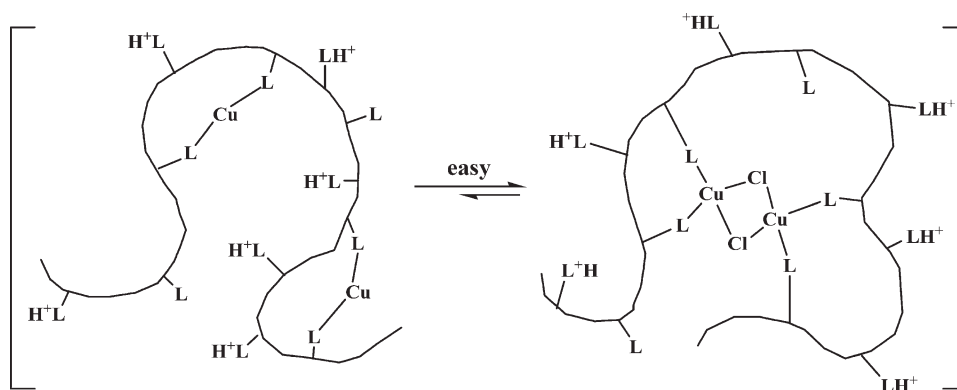
eq. (2), based on the equilibrium of copper-amine complexes. The successive formation constants, K_1 , K_2 , K_3 , and K_4 , were estimated from the experimental data by applying a least-square curve-fitting technique. The fitting curves are also shown in Fig. 8 (lines) with the parameters given in Table II. The overall formation constant, β_4 , is the product of K_1 , K_2 , K_3 , and K_4 .

$$\bar{n} = \frac{K_1[L] + 2K_1K_2[L]^2 + 3K_1K_2K_3[L]^3 + 4K_1K_2K_3K_4[L]^4}{1 + K_1[L] + K_1K_2[L]^2 + K_1K_2K_3[L]^3 + K_1K_2K_3K_4[L]^4} \quad (2)$$

The theoretical result agreed well with the experimental data in the P1 system, suggesting that mononuclear copper complexes are predominant species with PSVP samples of low molecular weight. Four pyridine rings appropriately spaced are needed in one PSVP chain to form an intramolecular CuL₄ complex. Although there are 4~5 pyridine rings ($N_0 = 4.4$) along a P1 chain, the chain is too short to assure four appropriately spaced pyridine rings because of random distribution of vPy units in the copolymer chain. Therefore, the value of log K_4 (=

TABLE II
The Successive and Overall Formation Constants Estimated for the Mononuclear Copper Complexes

	\bar{M}_n	\bar{N}_0	log K_1	log K_2	log K_3	log K_4	log β_4
P1	1310	4.4	3.08	3.00	2.95	1.00	10.02
P3	2530	8.4	3.40	3.48	3.30	2.88	13.06
P8	10100	32.9	3.40	3.90	3.30	2.88	13.48



Scheme 4 The equilibrium between intra-molecular mononuclear and dinuclear Cu-P8 complexes.

1.0) for P1 was about two orders of magnitude lower than that for P3. The max \bar{n} for P1 was less than 4. CuL_4 complexes could be formed only through intermolecular complexation by multiple P1 chains. Because the coordination number of dinuclear Cu^{II} complex (Cu_2L_4) is four identical with that of CuL_4 complex, just intermolecular Cu_2L_4 complexes with a considerably low overall formation constant could be formed by P1 chains. The quite small amount of catalytically effective Cu_2L_4 complexes in the P1 system resulted in a very slow reaction rate R_0 in oxidative coupling polymerization (Fig. 3).

The theoretical result in titration also agreed with the experimental data in the P3 system with a small deviation observed. However, a significant deviation was observed in the P8 system, which does not support the simplified mononuclear model. In addition, the experimental data for P8 clearly deviated from those for P3 ranged from $\bar{n} = 1$ to $\bar{n} = 2$. K_2 for P8 was also larger than that for P3 though the other successive formation constants were the same. This result suggests that a small quantity of dinuclear complexes Cu_2L_4 occurred in P3, but such complexation became dominant in P8 (Scheme 4).

There are two crucial aspects to effectively form Cu_2L_4 complexes. First, at a given Cu^{II} concentration, polymer chains (coils) should be adequately large to contain two or more Cu^{II} ions. Second, Cu^{II} ions should be able to approach each other and bridge. So, the effects of ligand molecular weight on the formation of Cu_2L_4 complexes are dual. Because long PSVP chain is in favor of attracting Cu^{II} ions and improving chain flexibility, chain length is conducive for the formation of dinuclear Cu^{II} complexes. When molecular weight of PSVP chains reaches a critical value, Cu_2L_4 complexes could be formed to a most degree. As a result, the reaction rate R_0 in oxidative coupling polymerization increased with ligand molecular weight and then leveled off when the $M_{n,\text{cr}}$ was reached (Fig. 3). On the other hand, the amount of PSVP does not affect

its flexibility and capacity of attracting Cu^{II} ions. Consequently, $M_{n,\text{cr}}$ is almost independent of N/Cu .

Although molar ratio of dinuclear Cu^{II} complexes to mononuclear Cu^{II} complexes was influenced as indicated by titration data, the catalytic selectivity is almost independent of the ligand MW as shown in Figure 4. The self-contradictory result could be explained by two reasons. First, dinuclear Cu^{II} complexes might also catalyze the C—C coupling of DMP in addition to mononuclear Cu^{II} complexes. If a neutral DMP molecule does not coordinate in bridging position of dinuclear Cu^{II} complex, but in its axial direction, it could experience one-electron transfer to produce a phenolic radical. As a result, to a certain degree, yield of DPQ increases with quantity of dinuclear Cu^{II} complexes. So, influence of ligand MW on catalytic selectivity is not simply equal to that of molar ratio of dinuclear Cu^{II} complexes to mononuclear Cu^{II} complexes. Second, the error of experimental data might be non-neglectable.

CONCLUSIONS

In this work, a set of styrene and *N*-vinyl pyridine copolymer (PSVP) samples were synthesized via RAFT polymerization. The well-defined copolymers were used as macromolecular ligand for the oxidative coupling polymerization of 2,6-dimethylphenol (DMP). The effects of the ligand molecular weight on the catalytic activity and selectivity were investigated. It was found that PSVP gives higher catalytic activity and higher selectivity than pyridine at the N/Cu ratios lower than 40. The activity increases with PSVP molecular weight but levels off above a critical molecular weight, $M_{n,\text{cr}}$. The $M_{n,\text{cr}}$ is about 5000 g/mol for PSVP with the vPy composition of 0.39, independent of the N/Cu ratio. The catalytic selectivity is independent of the molecular weight. Using PSVP and pyridine together further increases the catalytic activity at a comparable selectivity.

There are two kinds of catalytic species, dinuclear and mononuclear copper-amine complexes, which are mainly responsible for the C—O and C—C coupling reactions, respectively. From pH titration of the catalyst component, it is elucidated that a macromolecular ligand with high molecular weight and great chain flexibility facilitates the formation of dinuclear copper-amine complex. Therefore, the concentration of dinuclear copper-amine complexes increases with molecular weight at a given N/Cu ratio. When the molecular weight reaches a critical value, dinuclear copper-amine complexes are predominantly formed, resulting in high activity.

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