

Oxidative Polymerization of 2,6-Dimethylphenol in Water Using *bis*-Triazacyclononane Copper Catalyst

Kei Saito, Sweta Pant, Milton T. W. Hearn

Center for Green Chemistry, Monash University, Clayton, Victoria 3800, Australia

Received 14 June 2010; accepted 28 January 2011

DOI 10.1002/app.34322

Published online 15 June 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Water soluble 1,4,7-triazacyclononane derivatives were synthesized as the model of the tyrosinase binuclear active site and their copper (II) complexes have been employed as a catalyst for the oxidative polymerization of 2,6-dimethylphenol using water as the solvent. With this enzyme mimic catalytic system, the polymer, poly(2,6-dimethyl-1,4-phenylene oxide), was suc-

cessfully obtained from the polymerization with suppression of the formation of the quinone by-product, 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadienylidene)-2,6-dimethyl-2,5-cyclohexadien-one, during the polymerization process. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 2174–2180, 2011

Key words: poly(phenylene oxide); biomimic; synthesis

INTRODUCTION

Although the widespread use of synthetic polymers affords many quality-of-life advantages, their manufacture poses major energy demands and waste disposal problems.¹ This investigation was aimed to overcome some of these constraints in the production of one of the well known engineering plastics, poly(2,6-dimethyl-1,4-phenylene-oxide)(PPO), by developing a new, environmental friendly “green” process. This new green process uses water as the solvent, and takes advantage of metallo-complexes as the catalyst, thus reducing the use of toxic volatile organic solvents and the need for huge antiexplosive reactors in the manufacturing process. Traditionally, PPO has been prepared both industrially and in the laboratory by the oxidative polymerization of 2,6-dimethylphenol (DMP), based on the procedures discovered in 1959 by Hay and his GE group.² The polymerization is carried out at pressure using organic solvents like toluene under an oxygen atmosphere.

PPO synthesis in water is generally considered to be very difficult as the oxidation of DMP in water is known to predominantly give the by-product 4-(3,5-dimethyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,6-dimethyl-2,5-cyclohexadienone (diphenoquinone, DPQ). This by-product is formed by the C–C coupling of two monomeric phenol units.^{3,4} Recently, we

have succeeded in synthesizing PPO in water with suppression of the by-product DPQ using alkaline resistant water soluble catalysts including a copper complex of 1,4,7-tricarboxymethyl-1,4,7-triazacyclononane.^{5–8} To form PPO by the oxidative polymerization in alkaline water using copper amine catalysts, the catalysts needs to be stable and have the attribute of ready regeneration with oxygen. Although our initial studies with 1,4,7-tricarboxymethyl-1,4,7-triazacyclonone were encouraging, we have sought more optimal metal catalysts. In this regard, our approach has been motivated to take advantage of chemical mimics of biological systems which also can undergo oxidative processes.

Most chemical reactions in nature proceed *in vivo* in aqueous media through catalysis by enzymes.⁹ The catalytic properties of enzymes are known to depend on their three-dimensional structures. Assembly of the correct three-dimensional structure permits the active site(s) of the enzyme to function catalytically and control the structure and yield of the product(s). For example, oxidative polymerization is observed in nature as an important biosynthetic process catalyzed by metalloenzymes, proceeding smoothly in air at room temperature in aqueous media. Lignin, which composes 30% of wood tissue, is produced by the oxidative polymerization of coniferyl alcohol catalyzed by laccase, an enzyme containing a copper ion at the reactive center. The α -amino acid, tyrosine, can be oxidatively polymerized by tyrosinase (a copper enzyme) to melanin, the black pigment in animals. Recently, the active sites and three-dimensional structures of many enzymes have been investigated and enzyme mimetics as metallo-complexes have been synthesized.¹⁰ To produce PPO in water, the generation of

Correspondence to: K. Saito (Kei.Saito@monash.edu).

Contract grant sponsor: Australian Research Council; Monash University Faculty of Science Early Career Research Fund.

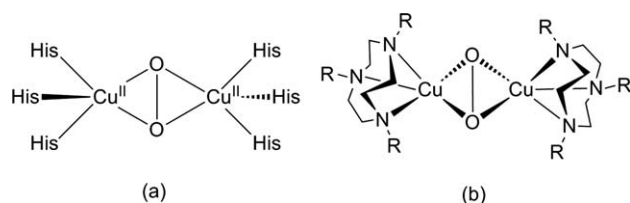


Figure 1 Structural representation of: (a) active site of tyrosinase and (b) dinuclear copper complex core formed by tacn.

appropriate chemical catalysts, which replicate these enzyme active sites or act as enzyme mimetics, was considered a key development. Recent studies on copper-O₂ chemistry have realized the prevalent formation of the [(Cu^{II})₂(μ-O)₂]²⁺ and [(Cu^{II})₂(μ-η²: η²-O₂)]²⁺ core with a variety of peralkylated diamine or triamine ligands.^{10–12} The active site of tyrosinase, the enzyme for oxidative polymerization in nature, has also recently been investigated. Its active site was found to involve a dinuclear copper species which was able to form a flexible *bis*-Cu(II) compound, [(Cu^{II})₂(μ-η²: η²-O₂)]²⁺, as the structural core during the catalysis, as evidenced by Sugiyama.¹⁰ (Fig. 1) To mimic this biological system, we focused on selecting macrocyclic structures which can form *bis*-metallo-compound structures similar to the active site of tyrosinase.

The mechanism for the formation of PPO remains unresolved even after years of extensive research.^{13–15} However, it is believed that formation of a dinuclear intermediate during the polymerization process is important.^{14,16} The use of *bis*-copper complexes as catalysts for the polymerization of DMP has been proposed to provide enhanced catalytic activity.¹⁵ This improved catalytic activity was believed to occur due to the ability of the complexes to easily form a dinuclear intermediate due to preorganization of the copper complex. In our earlier studies, the 1,4,7-triazacyclononane [tacn (1)] was shown to be able to also form a dinuclear copper complex, [(Cu^{II})₂(μ-η²: η²-O₂)]²⁺ core.^{12,16} (Fig. 1). Since tacn is able to form a dinuclear copper complex site similar to that found with the enzyme tyrosinase, its structural analogues could have the potential to be used as biomimetic catalysts for the oxidative polymerization of DMP. Various *bis*-copper complexes have been investigated for the oxidative polymerization of DMP in organic solvents in the past.^{14,16,17} However, *bis*-copper complexes of tacn have not been investigated for their potential use as catalysts, in both organic solvent and water, for the polymerization of DMP. We selected the copper complexes of the acetate derivatives of the *bis*-tacn ligand as a water soluble catalyst for the oxidative polymerization of DMP in water.

Here, we report the oxidative polymerization of DMP in alkaline water to form PPO using the water

soluble copper complexes of *bis*-tacn copper catalyst. 1,3-*bis*[4,7-*bis*(carboxymethyl)-1,4,7-triazacyclonon-1-yl]propane [*bis*(tacnta) (5)] was synthesized as a ligand and the polymerization of DMP to form PPO carried out using the copper complex of *bis*(tacnta) 5 as a catalyst in alkaline water. The polymerization using the copper complex of 1,4-*bis*(carboxymethyl)-1,4,7-triazacyclononane [tacnda (9)] was also carried out.

EXPERIMENTAL

Materials

All reagents and materials were purchased from Sigma-Aldrich Pty. Ltd. (Castle Hill, NSW, Australia) and used without further purification.

Synthesis of 1,3-*bis*[4,7-*bis*(carboxymethyl)-1,4,7-triazacyclonon-1-yl]propane [*bis*(tacnta) (5)]

Tacn was prepared following methods outline in the literature.^{18–21} A solution of tacn 1 (3.15 g, 0.0244 mol), dimethylformamide dimethyl acetal (3.00 g, 0.0252 mol) and toluene (130 mL) was refluxed at 140°C overnight. Then toluene was removed on the rotary evaporator to give 1,4,7-triazacyclo[5.2.1.0^{4,10}]decane 2 as a yellow oil. Yield: 89%. 1,3-Dibromopropane (2.19 g, 10.8 mmol) was added dropwise to a stirred solution of 2 (3.0 g, 21.5 mmol) in dry acetonitrile (20 mL) under nitrogen. The solution was stirred overnight under nitrogen. A pale white precipitate of 1,1'-(trimethylene)-*bis*(1-azoniatricyclo[2.2.2.1⁴]decane) dibromide 3 was obtained which was collected by filtration under vacuum, washed with cold acetonitrile and air dried. Yield: 47%. The salt 3 (1.3 g, 2.7 mmol) was dissolved in 24% hydrobromic acid (50 mL), the solution was refluxed at 140°C for 4 h then cooled to room temperature. This solution was then cooled to 6°C in a refrigerator to give a white precipitate of 1,2-*bis*(1,4,7-triazacyclonon-1-yl)propane hexabromide 4. The precipitate was collected under vacuum, washed with acetonitrile (2 × 10 mL) and ether (2 × 25 mL), then dried under vacuum. Yield: 77%. At last, bromoacetic acid (0.54 g, 3.89 mmol) was added with stirring to a solution 4 (0.50 g, 0.64 mmol) in water (4 mL) at 80°C. Sodium hydroxide pellets were added till the pH was ~ 11. To maintain the pH of solution at 11, 2M sodium hydroxide solution was added intermittently. After stirring at 80°C for 3 days, the pH of the solution remained constant at ~ 11 and the reaction was stopped. The yellow solution obtained contained the sodium salt of the ligand *bis*(tacnta) 5, excess sodium hydroxide, sodium bromide and sodium glycolate. IR, ¹H-NMR, ¹³C-NMR, and mass spectroscopic analyses were carried out on a portion of the solution evaporated to dryness and further dried over phosphorus pentoxide in a

vacuum oven for several days. Yield: 77%, $^1\text{H-NMR}$ (300 MHz, D_2O , ppm): δ 2.00 (2H, m, $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 3.00 (8H, s, tacn $\text{-CH}_2\text{-}$), 3.11 (20H, m, tacn $\text{-CH}_2\text{-}$ and $\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 3.57 (8H, s, acetate $\text{-CH}_2\text{-}$). $^{13}\text{C-NMR}$ (75 MHz, D_2O , ppm): δ 22.7 ($\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 50.4 ($\text{N-CH}_2\text{-CH}_2\text{-CH}_2\text{-N}$), 50.9, 51.3, 54.6 (tacn $\text{-CH}_2\text{-}$), 62.0 (acetate $\text{-CH}_2\text{-}$), 179.5 (acetate -CO_2). IR (KBr, cm^{-1}): 3427 s_b [$\nu_{\text{O-H}}$], 1589 s [$\nu_{\text{C=O}}$]. Mass spectrum (ESI): m/z 597.1 ($\text{M-Na} + 2\text{H}$) $^+$.

Synthesis of 1,4-bis(carboxymethyl)-1,4,7-triazacyclononane [tacnda (9)]

A solution of bromoethylacetate (2.44 g, 14.6 mmol) in acetonitrile (30 mL) was added to a solution of 2 (1.98 g, 14.2 mmol) and stirred overnight at room temperature. The resulting white product 6 was collected by filtration, washed with ether and air dried. Product 6 was then dissolved in water and heated to reflux for 4 h. After removal of water and drying, 7 was obtained as a dark-orange oil. Yield: 96%. 7 (1.82 g, 7.5 mmol) was dissolved in acetonitrile and solution of bromoethyleacetate (1.25 g, 7.5 mmol). Sodium carbonate (7.95 g, 7.5 mmol) was added and the mixture stirred overnight under reflux. The suspension was filtered to remove the insoluble salts and the solvent was removed from the filtrate under reduced pressure to yield a brown oil 8. Yield: 86%. This 8 (2.18 g, 6.6 mmol) was dissolved in aqueous 5M HCl (80 mL) and the solution refluxed for 2 days. The solution was reduced to dryness and redissolved in water (50 mL). The water was then removed and the residue taken up in 33% hydrobromic acid (10 mL) and glacial acetic acid (5 mL). The white precipitate that formed was filtrated, washed with acetone and dried under nitrogen to yield tacnda 9. Yield: 40%. $^1\text{H-NMR}$ (300 MHz, D_2O , ppm): δ 3.43 (4H, s, tacn $\text{-CH}_2\text{-}$), 3.58 (8H, m, tacn $\text{-CH}_2\text{-}$), 4.03 (4H, s, acetate $\text{-CH}_2\text{-}$). $^{13}\text{C-NMR}$ (75 MHz, D_2O , ppm): δ 42.9, 50.36, 50.98 (tacn $\text{-CH}_2\text{-}$) 56.46 (acetate $\text{-CH}_2\text{-}$), 172 (acetate -CO_2). IR (KBr, cm^{-1}): 1422 s [$\nu_{\text{C=O}}$]. Mass spectrum (ESI): m/z 246 (M+H) $^+$.

Oxidative polymerization of 2,6-dimethylphenol (DMP) using copper bis(tacnta) and tacnda catalyst

The following is a typical procedure for the polymerization. DMP (3.05 g, 25 mmol) and sodium *n*-dodecyl sulfate (0.73 g, 2.5 mmol) were dissolved in a solution of sodium hydroxide (1.00 g, 25 mmol) in water (25 mL). A solution of bis(tacnta) or tacnda copper complex, prepared *in situ* from the bis(tacnta) 5 or tacnda 6 (0.5 mmol, assuming quantitative yield), water (25 mL) and copper (II) chloride dihy-

drate (0.085 g, 0.5 mmol) was added. The solution was stirred with a mechanical stirrer (300 rpm) at 50°C under oxygen for 18 h. The product was salted out by addition of 1-dodecylpyridinium chloride hydrate (0.72 g, 2.5 mmol). The precipitate was collected by filtration under vacuum, washed with water, 10% HCl/methanol solution, methanol, and dried under vacuum. Yield: 70% (using copper bis(tacnta) catalyst), 99% (using copper tacnda catalyst), $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 2.09 (s, 6H, CH_3), 6.47 (s, 2H, Ar-CH CH). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ 16.8 (-CH_3), 114.8 (Ar-CH), 132.9 (Ar-CH), 145.8 (Ar-CH), 155.1 (Ar-CH). IR (KBr, cm^{-1}): 1188 s [$\nu_{\text{C-O-C}}$]. $M_w = 7.0 \times 10^3$, $M_w/M_n = 2.0$ (using copper bis(tacnta) catalyst), $M_w = 5.1 \times 10^3$, $M_w/M_n = 1.7$ (using copper tacnda catalyst).

Oxidative polymerization of 2,6-dimethylphenol (DMP) using copper ammonia catalyst

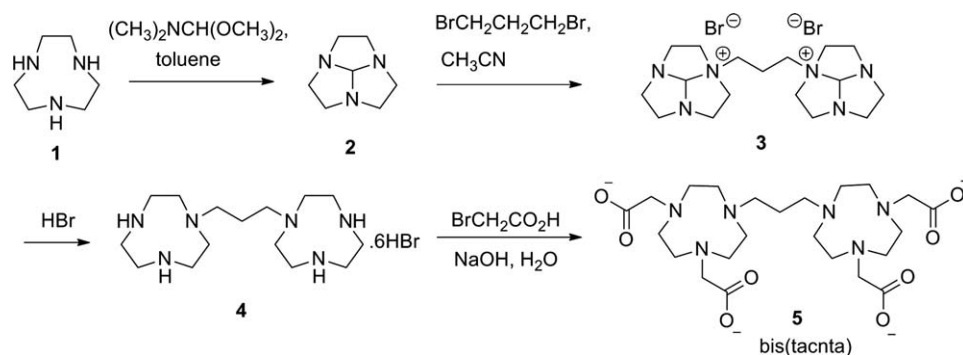
DMP (3.05 g, 25 mmol) was dissolved in water (25 mL) and, with oxygen bubbling through the solution, the surfactant sodium *n*-dodecyl sulfate (0.73 g, 2.5 mmol) was added. The solution was heated to 50°C and a dark blue solution of Cu-NH₃, prepared *in situ* from the ligand ammonia (25 mL) and copper (II) chloride dihydrate (0.31 g, 1.82 mmol), was added. The solution was stirred with a mechanical stirrer (3000 rpm) at 50°C under oxygen for 18 h. The procedure after this was the same as described above for Cu-tacnta. Yield: 60%. $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 2.09 (s, 6H, CH_3), 6.47 (s, 2H, Ar-CH CH). $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ 16.8 (-CH_3), 114.8 (Ar-CH), 132.9 (Ar-CH), 145.8 (Ar-CH), 155.1 (Ar-CH). IR (KBr, cm^{-1}): 1188 s [$\nu_{\text{C-O-C}}$]. $M_w = 4.3 \times 10^3$, $M_w/M_n = 1.5$.

Detection of DPQ by UV-Visible spectroscopy

The presence of DPQ in PPO was determined by analysis of a sample of the polymer in toluene using Ultraviolet-Visible (UV-Vis) spectroscopy. About 1.3 mg of the polymer was dissolved in 10 mL of toluene and the absorption at 421 nm in the spectra indicated the presence of DPQ. The molar extinction coefficient ϵ for a pure sample of DPQ (54,000 L mol $^{-1}$ cm $^{-1}$) in toluene was used to determine the percentage of DPQ in the polymer.⁶

Detection of the rate constant by UV-Vis spectroscopy

The rate constant of the polymerization was determined by analysis of the reaction solution at 1, 2, 3, 6, 10, 15, 30, 45, 60, and 90 min using UV-Vis spectroscopy during the polymerization under oxygen at 50°C in water; DMP 0.25 mol L $^{-1}$, sodium hydroxide



Scheme 1 Synthesis of *bis(tacnta)*.

0.25 mol L⁻¹, sodium *n*-dodecyl sulfate 0.025 mol L⁻¹ and *bis(tacnta)* copper catalyst 0.0025 mol L⁻¹. The absorption at 562 nm from the copper (I) complex of *bis(tacnta)* was measured at each time and used for the second order rate equation to determine the rate constant of the reaction

Characterization

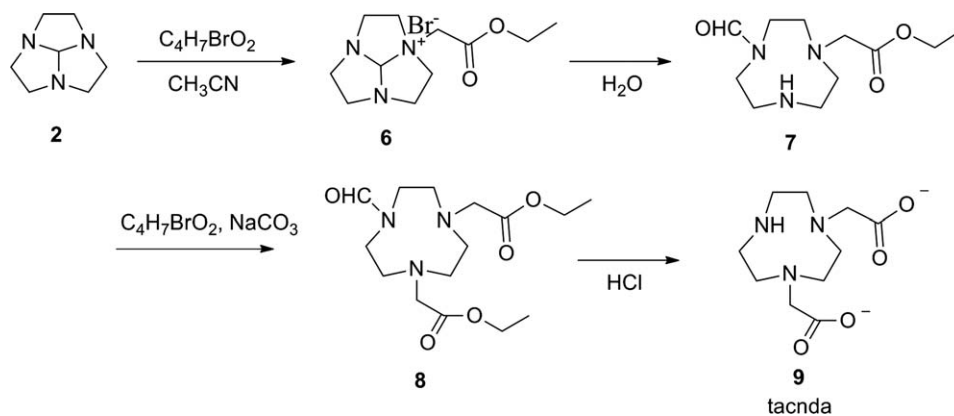
¹H and ¹³C-NMR spectra were recorded on a Bruker DPX-300 spectrometer. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum RX1 FTIR spectrophotometer as KBr pellets. UV-Vis spectra were recorded on a Cary 100Bio spectrophotometer as water or toluene solutions. Electrospray (ESI) mass spectroscopy was performed using a Waters Australia Platform II Quadrupole Mass Spectrometer with an electrospray source. Molecular weights of PPO were determined by GPC with a Tosoh high performance GPC system equipped with UV-8320 TSK GEL using SuperHZ2000 × 2, SuperHZ3000 × 1 and SuperHZM × 1 as the columns. Polystyrene standards, TSK standard polystyrene purchased from TOSOH, in chloroform were used to obtain calibration curves from the GPC. Thermal analysis of an accurately weighed sample (5–10 mg) of the polymer was performed using differential scanning calorimetry (DSC), which was carried out over a temperature range from 100 to 250°C with a TA DSC Q100 thermal analyzer at a heating rate of 10°C/min under nitrogen.

RESULTS AND DISCUSSION

In this study, water soluble catalysts based on the copper complexes of the *bis(tacnta)* 5 ligand and tacnda 9 were used for the oxidative polymerization in water of DMP. The *bis(tacnta)* 5 ligand was synthesized by bridging two tacn 1 molecules with a propyl linker and functionalized the four free NH group with pendant acetate arms. Tacn 1 was prepared following methods outline in the literature.^{18–21} The synthesis of *bis(tacnta)* 5 was a four-step process.

First, tacn 1 was refluxed with dimethylformamide dimethyl acetal in toluene to obtain the orthoamide 1,4,7-triazacyclo[5.2.1.0_{4,10}]decane 2 as an oil in 89% yield.^{18–22} Next, this orthoamide was converted to the *bis(amidinium)* salt, 1,1'-(trimethylene)-*bis*(1-azoniatricyclo[2.2.2.1.1,4]decane) dibromide 3, using 1,3-dibromopropane.^{20,23} This *bis(amidinium)* salt was obtained in 47% yield. Thirdly, the orthoamide bridge in this salt was cleaved by reaction with hydrobromic acid to give 1,2-*bis*(1,4,7-triazacyclonon-1-yl)propane hexabromide 4 in 77% yield.^{20,21} All the products were characterized with ¹H-NMR. In the case of 1,2-*bis*(1,4,7-triazacyclonon-1-yl)propane hexabromide the spectrum had signals at 1.91 and 3.08 ppm which were assignable to the methylene protons in the propyl bridge. Signals for the methylene protons of the tacn ring were observed between 3.08 and 3.61 ppm. Finally, the ligand *bis(tacnta)* 5 was synthesized by reacting 4 with bromoacetic acid in a sodium hydroxide solution for 3 days at 80°C to install the four pendant acetate groups (Scheme 1).

The ligand 5 was characterized by recording the ¹H-NMR and ¹³C-NMR spectra of a small portion of the ligand solution that was evaporated to dryness. The ¹H-NMR spectrum for *bis(tacnta)* 5 showed signals at 2.66 and 3.31 ppm which corresponded to protons on the methylene groups of the tacn ring and the acetate pendant arm, respectively, and there were also signals corresponding to the protons of the bridging propyl unit at 2.00 and 3.11 ppm. In the ¹³C-NMR spectrum for the ligand 5, signals corresponding to the methylene carbons of the tacn ring were observed at 50.9, 51.3, and 54.6 ppm and additional signals at δ 22.7 and 50.4 ppm observed for the methylene carbons of the propyl bridge. The methylene carbons on the acetate pendant arms and the carboxyl groups of the acetate arms were observed at δ 62.0 and 179.5 ppm, respectively. In the IR spectra of the ligands a peak was observed at 1589 cm⁻¹ for *bis(tacnta)* 5 which is characteristic of C=O stretching. Analysis of mass spectroscopy data for *bis(tacnta)* 5 revealed a peak at *m/z* 597 which was attributed to the fragment [M–Na + 2H]⁺,



Scheme 2 Synthesis of tacnda.

where M was the mass for the tetra sodium salt of *bis*(tacnta). From these analyses, it was found that the tri sodium salt of *bis*(tacnta) 5 was formed.

Solutions of the copper complexes of *bis*(tacnta) 5 were analyzed with UV-Vis spectroscopy. Infrared spectra of the complexes were also recorded. For the copper complexes of *bis*(tacnta) 5, $d-d$ transitions were observed at 664 nm. These transitions observed were comparable to those found for similar complexes in the literature.²⁴ In the IR spectra of the complexes the carbonyl stretching observed were within the stretching range expected for acetate groups ($-\text{CO}_2^-$), that is, 1610–1550 cm^{-1} .

Tacnda 9 was prepared by four steps from compound 2. First, 2 was converted to salt 6 by stirring in acetonitrile with ethyl-bromoacetate. The compound 6 was refluxed in water to yield compound 7 in 96% yield. Next, the synthesis of 8 was carried out in acetonitrile with ethylbromoacetate and sodium carbonate under reflux. The 8 was obtained as brown oil in 86% yield. A last, 8 was refluxed in HCl solution and taken up in HBr/glacial acetic acid solution to yield compound tacnda 9 in 40% yield (Scheme 2). The ligand tacnda 9 was characterized by recording the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra.

The copper (II) chloride complex formed with the synthesized *bis*(tacnta) 5 was used as a catalyst for the oxidative polymerization of DMP in water (Scheme 3). The complex was made *in situ* from copper (II) chloride dihydrate for the polymerization. An admixture of DMP and a small amount of the catalyst in alkaline water was vigorously stirred under oxygen with a surfactant (sodium *n*-dodecyl sulfate). Polymerization reactions using copper ammonia complex and the copper (II) chloride complex formed with the synthesized tacnda 9 as a catalyst was carried out as controls. The polymerization results are given in Table I.

The powder was obtained from the polymerization using *bis*(tacnta) copper catalyst in water after salting out with 1-dodecylpyridinium chloride hydrate. The

powder was identified as PPO with $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and IR spectroscopy and the molecular weight of the PPO polymer was determined using gel permeation chromatography (GPC).

As evident from these results, the PPO was successfully obtained from the polymerization in water using the *bis*(tacnta) copper catalyst. The molecular weight under aqueous condition was lower than the PPO that can be obtained in organic solvents using copper-pyridine complex as a catalyst (ca. $> 3.0 \times 10^4$),^{2,25} however, it was slightly higher than the PPO using copper ammonia complex. The polymerization using a *bis*(tacnta) copper catalyst showed similar results as the polymerization results tacnda copper catalyst and as previous results using 1,4,7-tricarboxymethyl-1,4,7-triazacyclononane.⁷ This result is of interest that it is indicating that the mono tacn copper complexes could be also forming the *bis*-copper complexes during the polymerization reaction. The results from different concentration of the catalyst in Table I indicate that there is a suitable concentration of catalyst to carried out this reaction to form high yield and the molecular weight.

To investigate the properties of PPO upon heating, the glass transition temperature (T_g) of the PPO polymer was determined using differential scanning calorimetry (DSC). The polymer synthesized using the *bis*(tacnta) copper catalyst in alkaline water was found to have a T_g value of 169°C. The glass transition temperatures for PPO produced using the *bis*(tacnta) copper catalyst was lower than that PPO produced using copper-pyridine complex in organic solvents ($\sim 210^\circ\text{C}$).²⁵ This was most likely due to the lower molecular weight of the polymers.

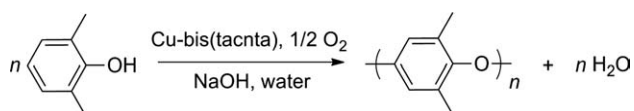
Scheme 3 Oxidative polymerization of DMP in alkaline water using *bis*(tacnta) copper catalyst.

TABLE I
Oxidative Polymerization of DMP to Produce the PPO Using *bis(tacnta)* Copper Catalyst^a

| Entry | Ligand | Catalyst (mmol L ⁻¹) | Yield (%) | M_w (M_w/M_n) ^b ($\times 10^3$) (-) | DPQ ^c (%) |
|-------|--------------------|----------------------------------|-----------|--|----------------------|
| 1 | NH ₃ | 50 | 60 | 4.3 (1.5) | 1.0 |
| 2 | Tacnda | 50 | 99 | 5.1 (1.7) | 0 |
| 3 | <i>bis(tacnta)</i> | 25 | 70 | 7.8 (2.0) | 0 |
| 4 | <i>bis(tacnta)</i> | 50 | 68 | 5.8 (1.9) | 0 |

^a All polymerizations were carried out under oxygen at 50°C in water; DMP 0.5 mol L⁻¹, sodium hydroxide 0.5 mol L⁻¹, and sodium *n*-dodecyl sulfate 0.05 mol L⁻¹; reaction time of 18 h.

^b Determined by gel permeation chromatography relative to polystyrene standards in chloroform.

^c Determined using UV-Vis spectroscopy of the sample in toluene.

The amount of DPQ in the polymers synthesized was determined using UV-Vis spectroscopy. For the polymers obtained using the *bis(tacnta)* copper catalyst in alkaline water, complete suppression of DPQ formation was observed within the limits of detection (Table I). It is known that the from the industrial method of polymerization of DMP in organic solvents using a copper-pyridine catalyst, less than 5% of DPQ is formed.² There was also DPQ detected in the polymer produced using copper ammonia as catalyst in water. DPQ has been reported to compromise properties of the polymer especially on processing at high temperatures. The use of *bis(tacnta)* and high pH environment (~ 13 – 14) by sodium hydroxide may have led to suppression of DPQ formation.

The molecular weight of the obtained PPO was also monitored during the polymerization with the *bis(tacn)* copper catalyst by taking small aliquots of the reaction solution at 0, 3, 6, 18, 24, 48, and 72 h. After immediate addition of acid to these aliquots to terminate the reaction, these solutions were analyzed by GPC to determine their molecular weight. Such time-course reactions were carried out for polymer-

izations using the *bis(tacnta)* copper catalyst. The results for these investigations are illustrated in Figure 2. From these studies, it is apparent that the molecular weight of PPO reached its maximum value at around 6500 for polymerizations using the copper complex of *bis(tacnta)* as a catalyst. The termination of the polymerization when the average molecular weight, M_w reached this value is most likely due to the insolubility of the polymer in the water solvent.^{8,26} The rate constant of the reaction was determined using the second order rate equation by measuring the conversion of copper (II) complex to copper (I) complex which is known as a rate-determining step of this polymerization. The conversion of copper (II) to copper (I) was analyzed with UV-Vis spectroscopy. It is known that the absorption of copper (II) complex (664 nm for the copper (II) complex of *bis(tacnta)*) decreases and the absorption of the copper (I) complex (562 nm for the copper (I) complex of *bis(tacnta)*) increases as a result of conversion of copper (II) to copper (I). From the UV-Vis results, the rate constant was determined as $k = 4.0 \times 10^{-4}$ for the polymerization under oxygen at 50°C in water; DMP 0.25 mol L⁻¹, sodium hydroxide 0.25 mol L⁻¹, sodium *n*-dodecyl sulfate 0.025 mol L⁻¹, and *bis(tacnta)* copper catalyst 0.0025 mol L⁻¹.

CONCLUSION

In this study, the oxidative polymerization of DMP in water to form PPO using a *bis(tacn)* copper catalyst has been demonstrated. This oxidative polymerization in water by with a water-soluble catalyst has the potential to be a green polymerization procedure.

We thank Prof. Roy Jackson, Dr. Tony Patti, Dr. Warwick Raverty, and Ms Eva Campi for fruitful discussions.

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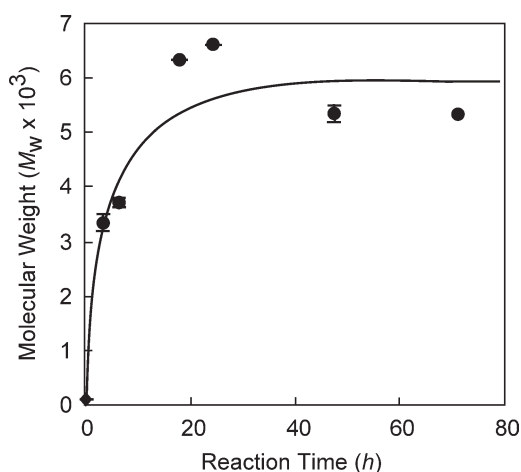


Figure 2 Reaction time-course of the molecular weight of PPO during the polymerization reaction using *bis(tacnta)* copper catalyst. The polymerization was carried out under oxygen at 50°C in aqueous sodium hydroxide; DMP 0.5 mol L⁻¹, sodium hydroxide 0.5 mol L⁻¹, sodium *n*-dodecyl sulfate 0.05 mol L⁻¹, and *bis(tacnta)* copper catalyst 0.005 mol L⁻¹.

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