

## Research Article

# Oxidative Coupling Copolymerization of 2,6-Dimethylphenol and Dihydroxynaphthalene Affording Poly(phenylene oxide) Derivatives

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The oxidative coupling copolymerization between 2,6-dimethylphenol (DMP) and dihydroxynaphthalenes, such as the 2,3- and 2,6-dihydroxynaphthalenes (2,3- and 2,6-DHN), was carried out using a Cu catalyst under an O<sub>2</sub> atmosphere. The polymerization was significantly affected by the structure of the comonomer, and the copolymers were efficiently obtained during the copolymerization of DMP and 2,6-DHN. The obtained copolymers containing hydroxyl groups of the DHN unit were further transformed into polymers containing ester and urethane groups. The obtained copolymers containing various functional groups showed a very different solubility from that of the homopolymer of DMP.

## 1. Introduction

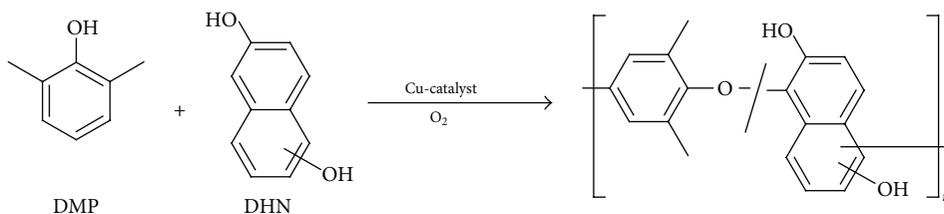
Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is one of the most widely accepted engineering plastics because of its good thermal, mechanical, and electrical characteristics. In addition, the method used for synthesizing PPO, the oxidative coupling polymerization (OCP) of 2,6-dimethylphenol (DMP), is known to be an environmentally benign system due to the fact that the reaction proceeds under mild conditions to produce only water as the by-product. Meanwhile, the OCP mediates the free radical coupling process between highly active phenoxy radicals; consequently, it is very difficult to control the reaction; for instance, the copolymerization leading to PPO derivatives is restricted to some extent [1–3]. Although a typical strategy for the functionalization of PPO should be the use of polymer reactions, such as the bromination of methyl side groups and further transformations of bromosubstituted polymers [3–5], there are few reports about the copolymerization between DMP and other phenolic compounds.

Recently, we reported that the oxidative coupling copolymerization between DMP and 2-hydroxymethyl-6-methylphenol, having a DMP framework with a hydroxyl

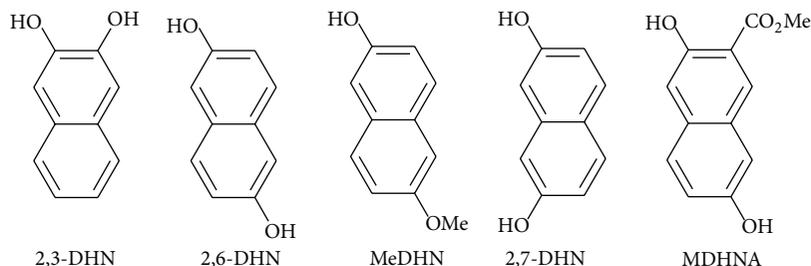
group, efficiently proceeds to afford a copolymer containing hydroxyl groups [6]. Although this could offer a secure method leading to the functionalized PPO, it is imperative that the comonomer be prepared from *o*-cresol [7, 8]. Accordingly, the copolymerization between DMP and commercially available phenolic compounds with functional groups is a very attractive topic. On the other hand, the polymers with a rigid backbone often show poor solubility and difficulty in processing, which have been improved by introducing novel segments into the main chain [9–12].

It is known that the OCP of dihydroxynaphthalenes, such as the 2,3- and 2,6-dihydroxynaphthalenes (DHNs), produces polymers, that is, poly(2,3-dihydroxy-1,4-naphthylene) [13–15] and poly(2,6-dihydroxy-1,5-naphthylene) [16–19], respectively. The reaction process is based on the catalytic oxidative coupling of 2-naphthols, which is one of the most facile methods for constructing a 1,1'-bi-2-naphthol structure [20–22].

In this study, the copolymerization of DMP with the commercial dihydroxynaphthalenes, 2,3-DHN and 2,6-DHN, using a copper catalyst in an O<sub>2</sub> atmosphere was investigated (Scheme 1).



SCHEME 1: Oxidative coupling copolymerization between DMP and DHN.



SCHEME 2: DHN monomers used for copolymerization.

## 2. Experimental

**2.1. General.** The  $^1\text{H}$  NMR spectra were taken by a JEOL JNM-ECS400 (400 MHz for  $^1\text{H}$ ) spectrometer. The infrared (IR) spectra were recorded using a Shimadzu FTIR-8700 spectrometer. The size exclusion chromatographic (SEC) analyses were conducted using a Jasco PU-2080 Plus system equipped with a UV (Jasco UV-2075 Plus) detector and Shodex KF-803L and KF-806L columns for  $\text{CHCl}_3$  or Tosoh TSK-G7000H and TSK-G3000H columns for tetrahydrofuran (THF) connected in series (temp. =  $25^\circ\text{C}$ , flow rate = 0.8 mL/min). Calibration was carried out with polystyrene standards. The UV-vis absorption (UV) spectra were recorded by a V-630 spectrophotometer (Jasco). The thermogravimetric (TG) analyses were performed using a Rigaku Thermo-plus EVO2 apparatus (heating rate:  $10^\circ\text{C}/\text{min}$ ).

**2.2. Material.** The monomers DMP (Kanto), 2,3-DHN (Aldrich), 2,6-DHN (Wako), and 2,7-DHN (Wako), the copper catalyst di- $\mu$ -hydroxo-bis[( $N,N,N',N'$ -tetramethylethylenediamine)copper(II)] chloride [ $\text{CuCl}(\text{OH})$ -TMEDA, TCI] [23, 24], and the ligand bipyridyl (BPy, Wako) were used as received. The dihydroxynaphthalene derivative, methyl 2,3-dihydroxynaphthalene-2-carboxylate (MDHNA), was prepared from the commercially available acid (TCI) by esterification with methanol and sulfuric acid (Scheme 2) [15]. For further transformation of the obtained PPO copolymer, phenylacetyl chloride (Wako) and butyl isocyanate (TCI) [6] were employed.

**2.3. Typical Procedure for Oxidative Coupling Copolymerization of DMP [6].** The copper catalyst was added to a mixture of DMP and a comonomer ( $[\text{monomers}]/[\text{Cu}] = 10/1$ , total amounts of the monomers: 0.8 mmol,  $\text{CuCl}(\text{OH})$ -TMEDA: 18 mg) in THF (2 mL), and the mixture was stirred at  $25^\circ\text{C}$  for 24 h in an  $\text{O}_2$  atmosphere. The solvent was evaporated,

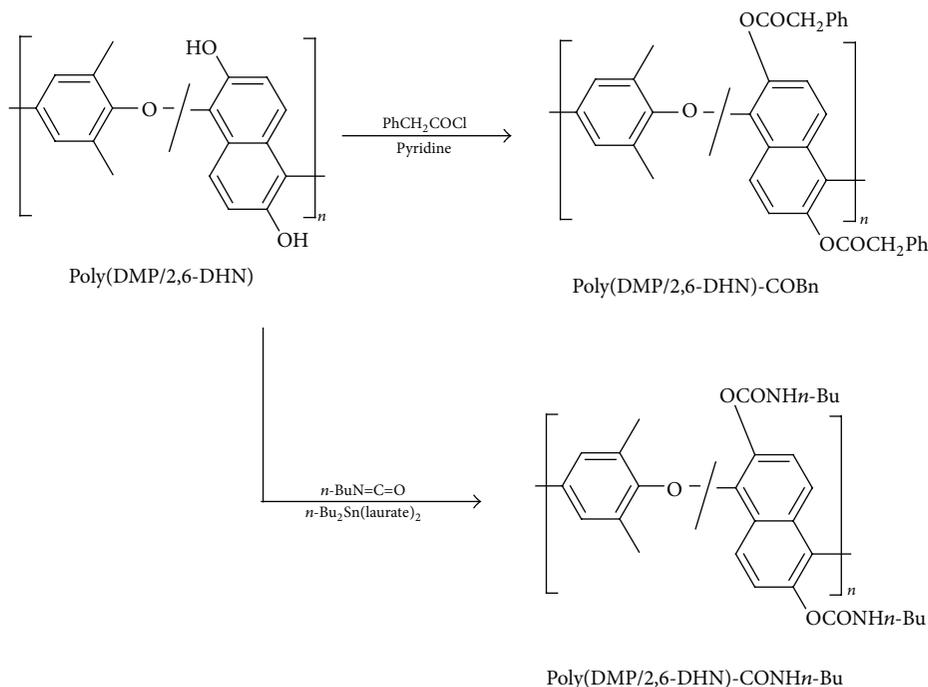
and dichloromethane (DCM, 2 mL) and excess amounts of phenylacetyl chloride (approximately 6 equivalent of the comonomer used) and pyridine were added. After stirring under an  $\text{N}_2$  atmosphere for 24 h, the reaction was quenched with a mixture of MeOH-aqueous 2 mol/L of HCl (9/1, v/v, 50 mL). The polymer was isolated as the MeOH-insoluble fraction by centrifugation, then repeatedly washed with methanol, and finally dried *in vacuo*.

## 3. Results and Discussion

The phenolic compounds, DMP, and the 2,3- and 2,6-DHNs, were homopolymerized with two types of conventional copper catalysts, such as  $\text{CuCl}(\text{OH})$ -TMEDA and  $\text{CuCl}$ -BPy, in a DCM-MeOH (7/1, v/v) mixed solvent [6] under an oxygen atmosphere. To isolate the products as the MeOH-insoluble part for polymerization of the dihydroxynaphthalenes, the polymer was further acetylated using acetyl chloride and pyridine, as previously reported [9–11]. The results are summarized in Table 1.

The polymerization of DMP gave a polymer in a good yield (runs 1 and 2), whereas the catalyst system affected the polymer yield during the polymerization of the dihydroxynaphthalenes. The methanol-insoluble polymer was almost quantitatively obtained in 97% yield by the polymerization of 2,3-DHN with the TMEDA catalyst (run 4). The polymerization of 2,6-DHN with  $\text{CuCl}$ -BPy afforded a polymer, which is insoluble in the common organic solvents, such as THF and  $\text{CHCl}_3$ , in the high yield of 88% (run 5).

Table 2 lists the results of the copolymerization between DMP and the dihydroxynaphthalenes in THF under various conditions. The unit ratio of the obtained polymer was determined from the  $^1\text{H}$  NMR spectra of the peak intensity ratio of the methyl protons around 2 ppm for the DMP unit and methylene protons of phenylacetyl group around 3.5 ppm for DHN unit. The BPy catalyst again resulted in a poor



SCHEME 3: Transformations of the obtained copolymer.

TABLE 1: Homopolymerization of DMP or DHNs.

Run	Monomer	Catalyst	Yield (%) <sup>a</sup>	$M_w \times 10^{-3}$ ( $M_w/M_n$ ) <sup>b</sup>
1	DMP	CuCl-BPy <sup>c,d</sup>	70	19.1 (2.5)
2	DMP	CuCl(OH)-TMEDA	77	72.6 (4.9)
3	2,3-DHN	CuCl-BPy <sup>c</sup>	28 <sup>e</sup>	17.0 (1.3)
4	2,3-DHN	CuCl(OH)-TMEDA	97 <sup>e</sup>	6.4 (1.6)
5	2,6-DHN	CuCl-BPy <sup>c,d</sup>	88 <sup>e</sup>	— <sup>f</sup>
6	2,6-DHN	CuCl(OH)-TMEDA <sup>d</sup>	33 <sup>e</sup>	— <sup>f</sup>

Conditions: [monomer]/[Cu] = 10/1, solvent = DCM-MeOH (7/1, v/v), time = 48 h, temp. = r.t., and O<sub>2</sub> atmosphere.

<sup>a</sup>MeOH-insoluble part.

<sup>b</sup>Determined by SEC (THF or CHCl<sub>3</sub>, polystyrene standard).

<sup>c</sup>[Monomer]/[Cu] = 5/1.

<sup>d</sup>Polymerization time = 24 h.

<sup>e</sup>MeOH-insoluble fraction of acetylated products.

<sup>f</sup>Insoluble in THF and CHCl<sub>3</sub>.

yield during the polymerization of 2,3-DHN (run 1). During the copolymerization with 2,3-DHN of various feed ratios, the copolymers, which mainly consisted of the DHN unit, were produced in low yields (runs 1–4). The polymer yields increased with an increase in the feed ratio of 2,3-DHN. Although the polymer was obtained in 54% yield during the copolymerization with the feed ratio of 30 : 70 (DMP : 2,3-DHN), the unit ratio was estimated to be 2 : 98 (run 4).

The copolymerization with 2,6-DHN (50 : 50, feed ratio) and the BPy catalyst afforded a polymer mainly consisting of the DHN unit (DMP : DHN = 17 : 83) (run 5); in contrast, the TMEDA catalyst system produced a copolymer in the

high yield of 91% with the unit ratio of DMP : DHN = 46 : 54 (run 8). The obtained polymer was fully soluble in THF and CHCl<sub>3</sub>. The catalyst system significantly affected the copolymerization with the dihydroxynaphthalenes.

The copolymerizations (50 : 50 feed ratio) with CuCl(OH)-TMEDA were performed for the indicated times of 3 and 18 h (runs 6 and 7). The obtained polymers again showed unit ratios, whose values are almost consistent with that observed for the copolymer prepared by the 24 h polymerization. In addition, the yield and the molecular weight increased with the increasing polymerization time. Accordingly, the copolymerization effectively proceeds through the entire process. Furthermore, the copolymerizations with various feed ratios were conducted, and the observed unit ratios of the obtained copolymers were in good agreement with those in the feed (runs 9 and 10). These results again indicate that the copolymerization successfully takes place during the polymerization using the monomers, DMP and 2,6-DHN, and the catalyst of CuCl(OH)-TMEDA.

Table 3 summarizes the results of the copolymerization between DMP and various 2-naphthol derivatives with the CuCl(OH)-TMEDA catalyst. The monomer, 6-methoxy-2-naphthol (MeDHN) (Scheme 2), which was prepared from 2,6-DHN by the monomethylation with MeI and K<sub>2</sub>CO<sub>3</sub>, was copolymerized with DMP (runs 1 and 2). The copolymerizations resulted in poor yields, and the methanol-insoluble part obtained by the reaction with the feed ratio of 70 : 30 (DMP : MeDHN) was mainly composed of the DMP unit (96 : 4). This result suggests that both β-hydroxyl groups of 2,6-DHN should contribute to bond formation during the OCP. The copolymerization with 2,7-DHN (50 : 50 feed ratio) was carried out to produce a polymer in a low yield

TABLE 2: Copolymerization between DMP and DHNs.

Run	Comonomer	Catalyst	Feed ratio		Yield (%) <sup>a</sup>	Unit ratio		$M_w \times 10^{-3}$ ( $M_w/M_n$ ) <sup>c</sup>
			DMP : DHN			DMP : DHN <sup>b</sup>		
1	2,3-DHN	CuCl-BPy	50 : 50		11	9 : 91	3.6 (1.2)	
2	2,3-DHN	CuCl(OH)-TMEDA	50 : 50		38	5 : 95	4.5 (1.3)	
3	2,3-DHN	CuCl(OH)-TMEDA	70 : 30		48	12 : 88	9.5 (1.3)	
4	2,3-DHN	CuCl(OH)-TMEDA	30 : 70		54	2 : 98	9.9 (1.3)	
5	2,6-DHN	CuCl-BPy	50 : 50		66	17 : 83	4.7 (1.3)	
6	2,6-DHN	CuCl(OH)-TMEDA <sup>d</sup>	50 : 50		29	47 : 53	9.0 (1.3)	
7	2,6-DHN	CuCl(OH)-TMEDA <sup>e</sup>	50 : 50		50	50 : 50	10.3 (1.3)	
8	2,6-DHN	CuCl(OH)-TMEDA	50 : 50		91	46 : 54	15.2 (2.4)	
9	2,6-DHN	CuCl(OH)-TMEDA	70 : 30		50	68 : 32	10.4 (1.2)	
10	2,6-DHN	CuCl(OH)-TMEDA	30 : 70		68	31 : 69	8.8 (1.2)	

Conditions: [monomers]/[Cu] = 10/1, solvent = THF, time = 24 h, temp. = r.t., and O<sub>2</sub> atmosphere.

<sup>a</sup>MeOH-insoluble part of the products after phenylacetylation.

<sup>b</sup>Determined by <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>).

<sup>c</sup>Determined by SEC (THF, polystyrene standard).

<sup>d</sup>Polymerization time = 3 h.

<sup>e</sup>Polymerization time = 18 h.

with the DMP unit of 87% (run 3). The ester having a 2,6-DHN structure, MDHNA, afforded a polymer in 96% yield during the copolymerization, and the unit ratio was evaluated to be 58 : 42 when the feed ratio was 70 : 30 (run 4). Although the details of the copolymer structure are not clear at present, the framework of 2,6-DHN plays an important role in constructing the PPO derivatives during the OCP.

Transformations of the naphthol groups of poly(DMP/2,6-DHN) were carried out (Scheme 3). The unprotected poly(DMP/2,6-DHN) was prepared by the copolymerization with CuCl(OH)-TMEDA with the feed ratio of DMP : 2,6-DHN = 90 : 10, and after washing with methanol, the polymer was collected in 50% yield. The copolymer was treated with an excess amount of phenylacetyl chloride and pyridine [poly(DMP/2,6-DHN)-COBn] or an excess amount of butyl isocyanate in the presence of the catalyst, dibutyltin dilaurate, at room temperature for 24 h [poly(DMP/2,6-DHN)-CONH*n*-Bu] [6]. The former was isolated by washing with MeOH, and the unit ratio was determined to be 86 : 14 ( $M_w = 3.95 \times 10^4$ ,  $M_w/M_n = 3.1$ ). The latter was collected as the hexane-insoluble part, because it was soluble in MeOH. The <sup>1</sup>H NMR spectrum of the obtained polymer is shown in Figure 1. The peaks are assigned as shown in the figure, and the unit ratio was estimated to be 87 : 13 ( $M_w = 4.07 \times 10^4$ ,  $M_w/M_n = 2.0$ ), which is identical to the value for the former.

Figure 2 depicts the IR spectra of poly(DMP) (PPO) and poly(DMP/2,6-DHN)-COBn (Table 2, run 9). The absorption for the introduced carbonyl group clearly appeared at 1751 cm<sup>-1</sup>. The TG analyses were also conducted for these polymers. The thermal stability of the copolymer (the latter) significantly decreased in comparison with that of the homopolymer (the former), and the 5% weight-loss temperature was estimated to be 382 for the former and 237°C for the latter.

The UV absorption spectra of poly(DMP) and poly(DMP/2,6-DHN)s in CHCl<sub>3</sub> are shown in Figure 3. The onset

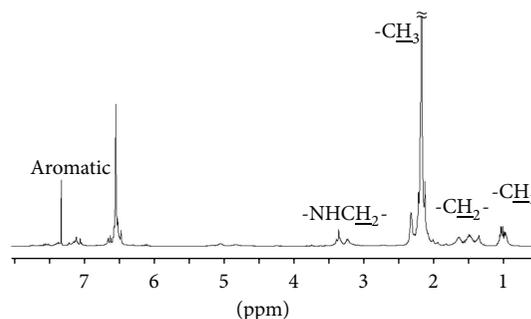


FIGURE 1: <sup>1</sup>H NMR spectrum of poly(DMP/2,6-DHN)-CONH*n*-Bu (CDCl<sub>3</sub>, 50°C).

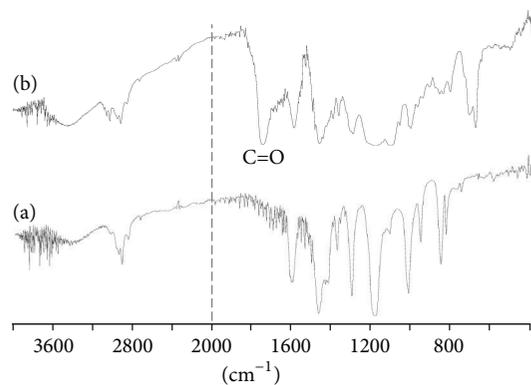


FIGURE 2: IR spectra of (a) poly(DMP) and (b) poly(DMP/2,6-DHN)-COBn (KBr).

positions of the copolymers are at a much longer wavelength than that of the homopolymer of DMP, indicating that the copolymers have a higher extended  $\pi$ -conjugation than

TABLE 3: Copolymerization between DMP and DHNs with CuCl(OH)-TMEDA.

Run	Comonomer	Feed ratio DMP : DHN derivative	Yield (%) <sup>a</sup>	Unit ratio DMP : DHN <sup>b</sup>	$M_w \times 10^{-3}$ ( $M_w/M_n$ ) <sup>c</sup>
1	MeDHN	50 : 50	6	—	—
2	MeDHN	70 : 30	11	96 : 4	—
3	2,7-DHN	50 : 50	34	87 : 13	10.0 (2.0)
4	MDHNA <sup>d</sup>	70 : 30	96	58 : 42	10.8 (1.6)

Conditions: [monomers]/[Cu] = 10/1, solvent = THF, time = 24 h, temp. = r.t., and O<sub>2</sub> atmosphere.

<sup>a</sup>MeOH-insoluble part of the products after phenylacetylation.

<sup>b</sup>Determined by <sup>1</sup>H NMR analysis (CDCl<sub>3</sub>).

<sup>c</sup>Determined by SEC (THF, polystyrene standard).

<sup>d</sup>Solvent = DCM-MeOH (7/1, v/v).

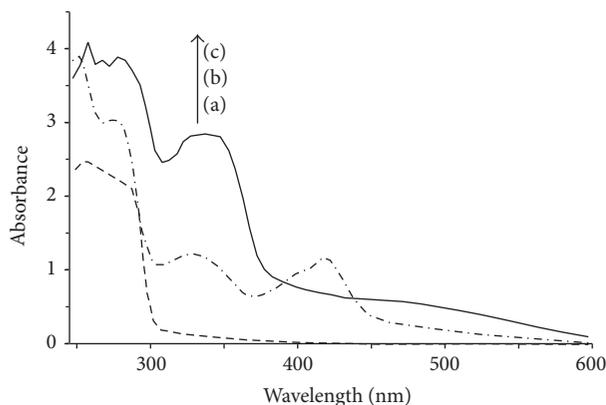


FIGURE 3: UV spectra of the obtained polymers: (a) poly(DMP) ( $C = 5.0 \times 10^{-3}$  M), (b) poly(DMP/2,6-DHN) (unit ratio, DMP : 2,6-DHN = 84 : 16) ( $C = 1.3 \times 10^{-3}$  M), and (c) poly(DMP/2,6-DHN) (unit ratio, DMP : 2,6-DHN = 60 : 40) ( $C = 1.4 \times 10^{-3}$  M) (CHCl<sub>3</sub>).

TABLE 4: Solubility of the obtained copolymers.

Solvent	Poly(DMP/2,6-DHN)			Poly(DMP) <sup>b</sup>
	(-OH) <sup>a</sup>	(-OCOBn)	(-OCONHn-Bu)	
THF	S	S	S	I
CHCl <sub>3</sub>	S	S	S	S
MeOH	I	I	S	I
HFIP	S	—	—	I
EtOH + NaOH aq. <sup>c</sup>	S	—	—	I

I: insoluble; S: soluble.

<sup>a</sup>DMP unit : DHN unit = 51 : 49. <sup>b</sup> $M_w = 7.26 \times 10^4$ ,  $M_w/M_n = 4.9$  (measured by SEC).

<sup>c</sup>EtOH/0.1 M NaOH aq. = 10/1.

PPO. In addition, the 2,6-DHN unit ratio in the copolymer significantly affected the  $\pi$ -conjugation.

The solubility of the obtained polymers was examined and the results are summarized in Table 4. The DMP homopolymer, PPO, is soluble in chloroform, whereas the copolymer with 2,6-DHN and the functionalized ones, poly(DMP/2,6-DHN)-COBn and poly(DMP/2,6-DHN)-CONHn-Bu, are soluble in THF as well as chloroform. In addition, poly(DMP/2,6-DHN)-CONHn-Bu has a solubility in

methanol, as already mentioned. The copolymer bearing naphthol groups, poly(DMP/2,6-DHN), showed a solubility in aqueous alkaline ethanol. The copolymer and its derivatives demonstrated quite different solubilities from that of poly(DMP) [9, 12].

## 4. Conclusion

The oxidative coupling copolymerization of DMP and dihydroxynaphthalenes was carried out, and the preparation of PPO with functional groups was successfully achieved. The copolymerization was affected by the catalyst and the comonomer structure and produced the copolymer, especially, by using 2,6-dihydroxynaphthalene in an effective manner. The PPO derivatives obtained by the copolymerization and further transformations showed significantly different characteristics in solubility from that of the original PPO.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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