

Effective Synthesis of Poly(2,6-Dimethyl-1,4-Phenylene Oxide) Derivatives by Oxidative Coupling Copolymerization of Alkoxyphenols with Copper(II) Catalyst

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Abstract: The oxidative coupling copolymerization between 2,6-dimethylphenol (DMP) and phenols having various alkoxy groups, such as methoxy (MOP), ethoxy, benzyloxy, butoxy, and 2-hydroxyethoxy groups, was carried out using a copper(II) catalyst under an O₂ atmosphere. The copolymerizations with alkoxyphenols effectively proceeded, and the unit ratios of the obtained copolymers were in good agreement with those in the feed. The coupling regioselectivity, such as oxyphenylene (CO) and phenylene (CC), of the alkoxyphenol unit constructed during the copolymerization was also estimated by the ¹H NMR analysis of the acetylated polymer. As an example, the copolymer with the unit ratios of DMP:*p*-MOP = 50:50 and CO:CC = 67:33, was obtained in 71% yield during the copolymerization with *p*-MOP (feed ratio, 50:50) in a mixed solvent of CH₂Cl₂ and methanol (7/1 (v/v)) for 24 h. The solubility and thermal property of the obtained copolymers were significantly affected by the structure of alkoxyphenol unit.

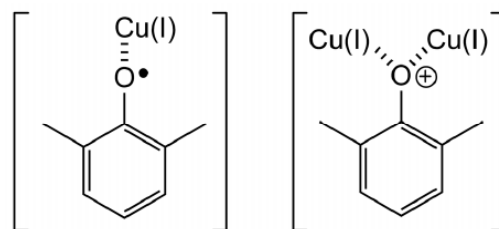
Keywords: Oxidative coupling, Copolymerization, Poly(phenylene oxide), Alkoxyphenol, Copper catalyst.

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is an important engineering plastic with good thermal, mechanical, and electrical insulating properties. Therefore, it can be found in many industrial applications, mainly used in blend forms with polystyrene. The PPO and its derivatives are prepared by a simple synthetic method, oxidative coupling polymerization (OCP), from 2,6-dimethylphenol (DMP) [1-3]. This polymerization system is also known to be environmentally benign and could contribute to green chemistry. This is due to the fact that the reaction proceeds under mild conditions with an abundant and clean oxidant, O₂, with only water produced as the by-product.

The mechanism of OCP with a Cu(II) catalyst involves coupling processes through phenoxy radical generated by one-electron oxidation of DMP and/or phenoxonium cation resulting from two-electron oxidation (Scheme 1) [3, 4]. Therefore, it is generally very difficult to control the reaction, for example, the coupling regio-chemistry [5-8] and copolymerization [9, 10]. The former restricts the monomer structure to a phenol with substituents at the 2- and 6-positions, such as DMP, in practice. The synthesis of the PPO with functional groups via the copolymerization has been also limited except for the use of some 2,6-

disubstituted phenols, such as 2-allyl-6-methylphenol and 2,6-diphenylphenol, as a comonomer [11-14].



Scheme 1: Active species for oxidative coupling polymerization of DMP.

We recently reported that the oxidative coupling copolymerization between DMP and 2-hydroxymethyl-6-methylphenol (HMMP) having a DMP skeleton proceeds to give a copolymer containing hydroxyl groups [15]. In addition, the obtained copolymers were used as additives for the fabrication of the polyurethane films, whose mechanical properties were significantly affected by the functional groups of the additives. However, the preparation of HMMP from *o*-cresol, which is still easy [16, 17], should be a bottleneck of this method. Accordingly, the copolymerization between DMP and the commercial phenolic compounds with functional groups is a significant concern [10].

During the course of our study for the synthesis of PPO derivatives, we found that the commercially-available alkoxyphenols can be effectively copolymerized using a copper(II) catalyst. There are only a few reports on the copolymerization of alkoxyphenol derivatives, which were derived from the corresponding

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phenols [18, 19]. Meanwhile, the oxidative coupling homo-polymerization of alkoxyphenols with enzymatic and metal catalysts has been reported [8, 20-24]. The polymers normally consist of a mixture of oxyphenylene (CO) and phenylene (CC) units, whereas the polymerization could proceed in a highly regiocontrolled manner under the enzymatic conditions [20-22]. In addition, the obtained polymer should be an interesting material because of its poly(hydroquinone) structure, which is a typical redox-active polymer, therefore, valuable for electronic and electrochemical applications [25].

In this study, the oxidative coupling copolymerization between DMP and the phenols bearing alkoxy groups, such as methoxy (MOP), ethoxy (EOP), benzyloxy (BnOP), butoxy (BOP), and 2-hydroxyethoxy groups (HEOP) (Scheme 2), using the copper(II)-diamine complex, such as di- μ -hydroxo-bis[*N,N,N',N'*-tetramethylethylenediamine]copper(II) chloride [CuCl(OH)-TMEDA], as the catalyst [26, 27] under an O₂ atmosphere was conducted, and their copolymerizability and coupling regio-chemistry (CO/CC) were investigated (Scheme 3).

EXPERIMENTAL

Materials

The monomers, DMP (Kanto), *p*-MOP (Kanto), *o*-MOP (Wako), *p*-EOP (Kanto), *o*-EOP (TCI), *p*-BnOP (TCI), *o*-BnOP (TCI), *p*-BOP (Wako), *o*-HEOP (Sigma-Aldrich), and the catalysts, CuCl(OH)-TMEDA (TCI),

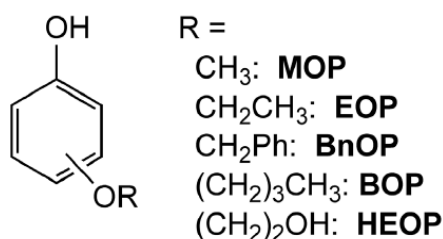
manganese(II) acetylacetonate [Mn(acac)₂, TCI], and *N,N'*-diethylethylenediamine (DEEDA, Wako), were used as received. The tetrahydroxybinaphthyl derivative, 3,3'-dihydroxy-2,2'-dimethoxy-1,1'-binaphthalene (THBN), was synthesized as previously reported [28, 29].

Measurements

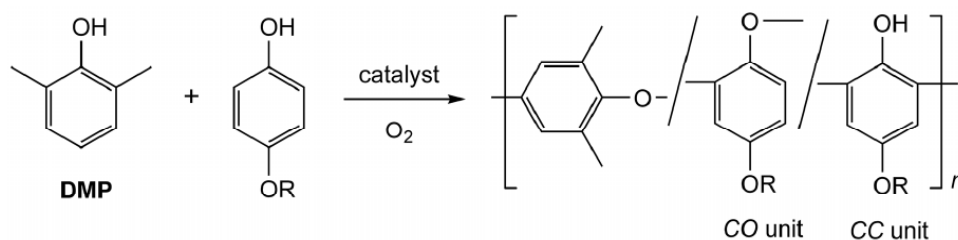
The ¹H NMR spectra were recorded by a JEOL JNM-ECS400 spectrometer at 400 MHz. The size exclusion chromatographic (SEC) analyses were performed using a Jasco PU-2080 Plus system equipped with a UV (Jasco UV-2075 Plus) detector and Shodex KF-803L and KF-806L columns for CHCl₃ or Tosoh TSK-G7000H and TSK-G3000H columns for tetrahydrofuran (THF) connected in series (temp. = 25 °C, flow rate = 0.8 mL/min). Calibration was carried out with polystyrene standards. The UV-vis absorption (UV) spectra were obtained using a Jasco V-360 spectrophotometer. The thermogravimetric (TG) analyses were conducted using a Rigaku Thermo-plus EVO2 instrument (heating rate: 10 °C/min, under air).

Typical Procedure for Oxidative Coupling Copolymerization of DMP and Alkoxyphenol [10, 15]

The copper(II) catalyst was added to a mixture of DMP and an alkoxyphenol ([monomers]/[Cu] = 10/1, monomers: 1 mmol) in a solvent (2 mL), then the mixture was stirred at 25 °C under an O₂ atmosphere. The product was isolated as the MeOH-insoluble part



Scheme 2: Monomers used for copolymerization.



Scheme 3: Oxidative coupling copolymerization between DMP and alkoxyphenols.

by centrifugation, then repeatedly washed with methanol, and finally dried *in vacuo* at 60 °C.

To estimate the unit structure of the alkoxyphenol (CO/CC), the acetylation reaction of the obtained copolymer was further carried out. 4-(Dimethylamino)pyridine (1.4 mg) was added to a mixture of a copolymer (20 mg), acetyl chloride (AcCl, 0.10 mL), and pyridine (0.15 mL) in dichloromethane (DCM) at 25 °C. The mixture was stirred for 24 h under N₂ and the product was isolated as the MeOH-H₂O (1/1, v/v) insoluble fraction by centrifugation, repeatedly washed, then dried *in vacuo*.

RESULTS AND DISCUSSION

The oxidative coupling homopolymerization of alkoxyphenols with the catalysts, such as CuCl(OH)-TMEDA [8, 24] and Mn(acac)₂-DEEDA [23], was previously reported. DMP and *p*-MOP were then copolymerized with these catalyst systems and the results are shown in Table 1. The copolymerizations (feed ratio 50:50) with Mn(acac)₂ for 48 h afforded methanol-insoluble copolymers, which were rich in the DMP unit (runs 1-3). These results indicate that DMP preferentially reacts during the copolymerization with the Mn(II) catalyst. In contrast, the unit ratio of the copolymer obtained during the copolymerization with the Cu(II) complex in a mixed solvent of DCM and MeOH was identical to that in the feed (run 4).

The copolymerizations in DCM were also performed for the indicated times of 2 and 24 h (runs 5 and 6). The monomer unit ratios of the obtained copolymers

were determined to be 55:45 and 50:50, respectively. Although the DMP unit ratio of the former polymer is slightly higher than that in the feed, they are approximately consistent with the feed ratio. In addition, the yield and the molecular weight increased with the increasing polymerization time. Accordingly, the copolymerization with CuCl(OH)-TMEDA effectively proceeds through the entire process.

The copolymerizations with various feed ratios were carried out (runs 7-9). In every case, the copolymer was obtained in a good yield, whose monomer unit ratio was in good agreement to that in the feed. These results again indicate that the copolymerization between DMP and *p*-MOP successfully takes place. The UV absorption spectra of poly-DMP/*p*-MOPs in CHCl₃ are shown in Figure 1. The onset values and the absorption intensities in the long wavelength region clearly increased with the increasing unit ratio of *p*-MOP, especially the increase in the phenylene (CC) unit introducing a higher extended π -conjugation into the polymer main chain should significantly contribute to this wavelength shift. The details of the *p*-MOP unit structure will be described later.

Table 2 summarizes the results of the copolymerization between DMP and the various alkoxyphenols with the Cu(II) catalyst. The phenol with a methoxy group at the *o*-position, *o*-MOP, also showed a good copolymerizability for DMP. The copolymerizations proceeded in good yields, and the produced polymers showed unit ratios, which were almost comparable to those in the feed (runs 1-5).

Table 1: Copolymerization between DMP (X) and *p*-MOP (Y)

Run	Catalyst	Feed Ratio X : Y	Solvent	Yield (%) ^{a)}	Unit Ratio ^{b)}		M _w × 10 ⁻³ (M _w /M _n) ^{c)}
					X : Y	CO : CC	
1	Mn(acac) ₂	50 : 50	DCM-MeOH	75	61 : 39	56 : 44	47 (21)
2	Mn(acac) ₂ -DEEDA	50 : 50	DCM-MeOH	57	63 : 37	51 : 49	4.7 (3.2)
3	Mn(acac) ₂ -DEEDA	50 : 50	DCM	49	74 : 26	56 : 44	4.1 (5.1)
4	CuCl(OH)-TMEDA	50 : 50	DCM-MeOH	71	50 : 50	67 : 33	7.3 (5.1)
5	CuCl(OH)-TMEDA	50 : 50	DCM	53	50 : 50	67 : 33	14 (4.6)
6 ^{d)}	CuCl(OH)-TMEDA	50 : 50	DCM	27	55 : 45	64 : 36	6.4 (2.1)
7	CuCl(OH)-TMEDA	70 : 30	DCM-MeOH	71	70 : 30	64 : 36	12 (3.6)
8	CuCl(OH)-TMEDA	80 : 20	DCM-MeOH	79	76 : 24	62 : 38	9.5 (3.6)
9	CuCl(OH)-TMEDA	90 : 10	DCM-MeOH	84	91 : 9	67 : 33	8.8 (2.5)

Conditions: [monomers]/[catalyst] = 10/1, time = 48 h for Mn-catalysts and 24 h for Cu-catalyst, temp. = r.t., O₂ atmosphere, DCM/MeOH = 7/1 (v/v).

a) MeOH-insoluble part.

b) Determined by ¹H NMR analysis after acetylation of the obtained polymer (CDCl₃, 50 °C).

c) Determined by SEC (CHCl₃, polystyrene standard).

d) Time = 2 h.

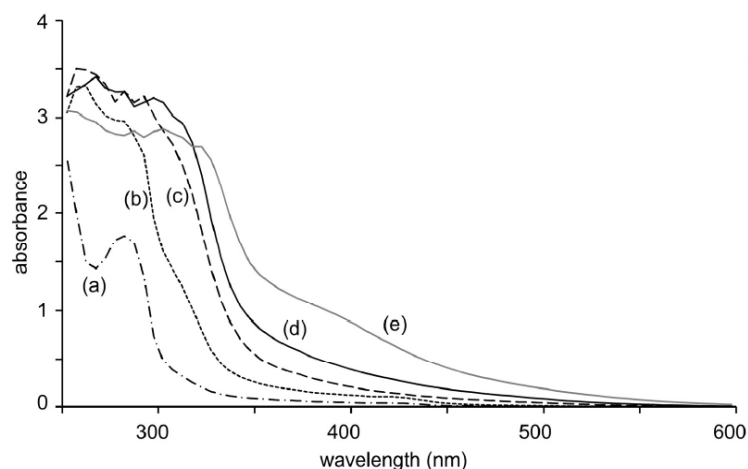


Figure 1: UV spectra of the obtained poly-DMP/*p*-MOP: (a) unit ratio DMP:*p*-MOP = 91:9, (b) 76:24, (c) 70:30, (d) 50:50, and (e) poly-*p*-MOP (CHCl₃, 2.0 × 10⁻³ M).

Table 2: Copolymerization between DMP (X) and Alkoxyphenols (Y) with CuCl(OH)-TMEDA

Run	Comonomer (Y)	Feed Ratio X : Y	Solvent	Yield (%) ^{a)}	Unit Ratio ^{b)}		<i>M_w</i> × 10 ⁻³ (<i>M_w</i> / <i>M_n</i>) ^{c)}
					X : Y	CO : CC	
1	<i>o</i> -MOP	50 : 50	DCM-MeOH	90	47 : 53	66 : 34	15 (2.5)
2	<i>o</i> -MOP	50 : 50	DCM	86	50 : 50	66 : 34	12 (4.4)
3	<i>o</i> -MOP	70 : 30	DCM-MeOH	87	69 : 31	69 : 31	22 (6.7)
4	<i>o</i> -MOP	80 : 20	DCM-MeOH	71	77 : 23	69 : 31	38 (5.4)
5	<i>o</i> -MOP	90 : 10	DCM-MeOH	89	86 : 14	69 : 31	57 (6.6)
6	<i>o</i> -EOP	50 : 50	DCM	>99	49 : 51	68 : 32	16 (4.9)
7	<i>p</i> -EOP	50 : 50	DCM	74	50 : 50	67 : 33	11 (4.5)
8	<i>o</i> -BnOP	50 : 50	DCM	>99	52 : 48	67 : 33	17 (4.5)
9	<i>p</i> -BnOP	50 : 50	DCM	87	48 : 52	69 : 31	14 (8.8)
10	<i>p</i> -BOP	50 : 50	DCM	79	60 : 40	68 : 32	11 (2.9)
11	<i>o</i> -HEOP	50 : 50	DCM	73	43 : 57 ^{d)}	69 : 31	--- ^{e)}
12	<i>o</i> -HEOP	70 : 30	DCM	75	72 : 38	68 : 32	14 (2.5)

Conditions: [monomers]/[Cu] = 10/1, time = 24 h, temp. = r.t., O₂ atmosphere, DCM/MeOH = 7/1 (v/v).

a) MeOH-insoluble part.

b) Determined by ¹H NMR analysis after acetylation of the obtained polymer (CDCl₃, 50 °C).

c) Determined by SEC (polystyrene standard).

d) Determined by ¹H NMR analysis (DMSO-*d*₆, 80 °C).

e) Insoluble in THF and CHCl₃.

The alkoxyphenols, such as *o*-EOP, *p*-EOP, *o*-BnOP, *p*-BnOP, and *o*-HEOP, were again successfully copolymerized with DMP (runs 6-9, 11, and 12), while the product having a higher DMP unit ratio (60%) than that in the feed (50%) was obtained during the copolymerization with *p*-BOP (run 10). Although details are not clear at present, this may be due to the steric effect of the butoxy group.

As mentioned above, the OCP of the mono-substituted phenols can form two types of unit structures, oxyphenylene (CO) and phenylene (CC), during the oxidative coupling. With regard to the

homopolymer, the ratio could not be estimated from the ¹H NMR analysis, because the peaks of the aromatic and hydroxyl protons were broad and overlapped, as reported in previous studies. Therefore, it was evaluated by titration of the H₂ volume generated during the reaction of the phenolic hydroxyl group with LiAlH₄ in THF [8, 20-23]. In addition, to the best of our knowledge, there is no study regarding the coupling regioselectivity for the copolymer.

The acetylation of the copolymer obtained from *o*-MOP, poly-DMP/*o*-MOP, with the unit ratio of DMP:*o*-MOP = 47:53 (Table 2, run 1), using an excess amount

of AcCl and pyridine was carried out. Through this process, the phenolic hydroxyl group of the CC unit could be acetylated. The ^1H NMR spectrum of the acetylated product is depicted in Figure 2, together with that of the original copolymer. The peaks are assigned as shown in the figure, and the detailed unit composition, DMP:*o*-MOP(CO):*o*-MOP(CC), was determined to be 47:35:18 (CO:CC = 66:34). On the other hand, the titration using LiAlH_4 for the same copolymer was conducted twice according to a previously reported procedure [23], and the unit ratio was estimated to be 47:34:19 and 47:35:18, respectively. These values are very consistent with that determined by ^1H NMR analysis of the acetylated copolymer. In this study, the former acetylation method for determination of the unit ratio was adopted.

The evaluated coupling selectivities (CO:CC) are also listed in Tables 1 and 2. The catalyst system significantly affected the regiochemistry. The Mn(II) catalysts showed almost no selectivity (Table 1, runs 1-3), whereas the copolymers rich in the CO unit were obtained during the polymerization with the Cu(II) catalyst. It was reported that the homopolymerization of *p*-MOP with $\text{CuCl}(\text{OH})\text{-TMEDA}$ in DCM afforded a polymer with a very similar unit composition, CO:CC = 68:32 [8]. Therefore, during the copolymerization, the coupling reaction of alkoxyphenols should proceed in a similar manner to that for the homopolymerization. However, the structure of the alkoxy groups showed

little effect on the selectivity during the copolymerization with the Cu(II) complex.

The tetrahydroxybinaphthyl derivative, THBN, is an interesting monomer for the OCP leading to an optically-active polymer with a rigid main chain constructed from continuous binaphthol units [28, 29]. This monomer has a phenol framework with a methoxy group at the *o*-position, therefore, could be copolymerized with DMP. The copolymerization between DMP and the racemic THBN (80:20 feed ratio) with $\text{CuCl}(\text{OH})\text{-TMEDA}$ in THF for 24 h was conducted (Scheme 4), and a methanol-insoluble fraction was isolated after phenylacetylation using an excess amount of phenylacetyl chloride and pyridine according to the previously reported procedure [10]. The product was obtained in 63% yield ($M_w = 8.9 \times 10^3$, $M_w/M_n = 1.7$), whose unit ratio was determined to be DMP:THBN = 84:16 by ^1H NMR analysis. The copolymer could be again effectively produced from the 2-naphthol derivative.

The obtained copolymers containing methoxy groups, poly-DMP/*o*-MOP and poly-DMP/*p*-MOP, with the unit ratio of 50:50 are totally soluble in THF, CHCl_3 , and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP), whereas poly-DMP/*o*-HEOP (43:57 unit ratio) is insoluble in these solvents. By contrast, all of these copolymers have a solubility in aqueous alkaline HFP [HFP/0.1 M NaOH aq., 10/1 (v/v)]. The structure of the alkoxy groups significantly affected the polymer solubility [10].

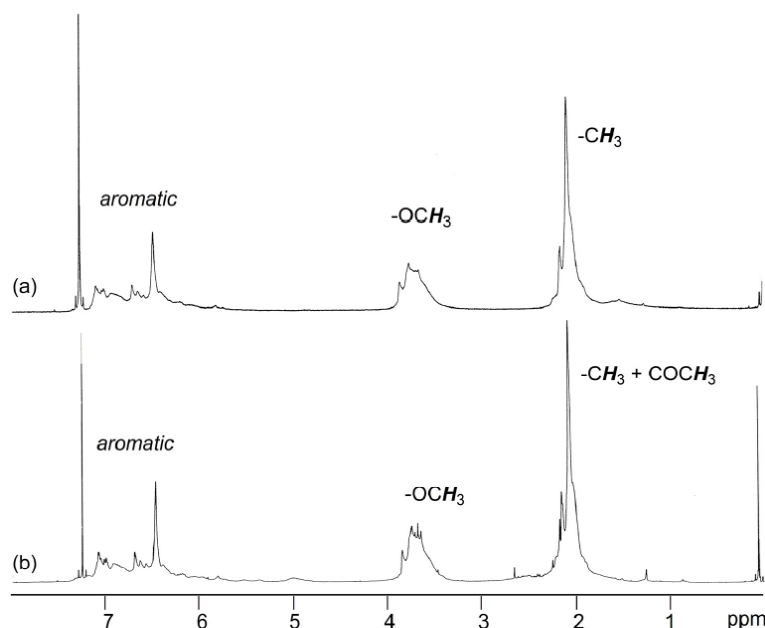
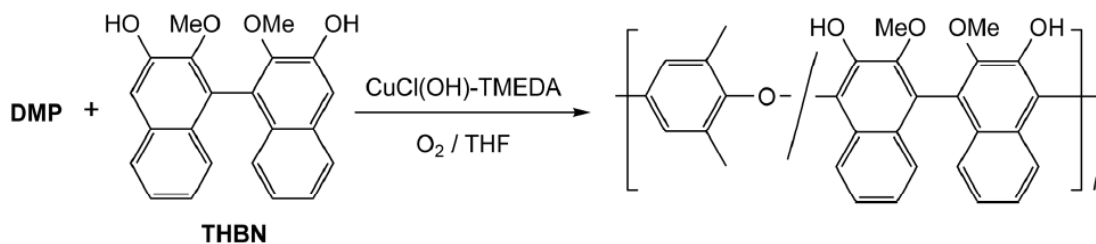


Figure 2: ^1H NMR spectra of (a) poly-DMP/*o*-MOP (Table 2, run 1) and (b) acetylated poly-DMP/*o*-MOP (CDCl_3 , 50 °C).



Scheme 4: Oxidative coupling copolymerization between DMP and THBN.

The thermal stability of the obtained copolymers, poly-DMP/MOP and poly-DMP/EOP, was measured by TG (Figure 3) and the observed 5 and 10% weight-loss temperatures (T_5 and T_{10}) are listed in Table 3. It was reported that the T_5 estimated for poly-DMP (PPO) prepared using the CuCl(OH)-TMEDA catalyst ($M_w = 7.4 \times 10^4$, $M_w/M_n = 4.9$) was 382 °C [10]. Much lower T_5 values were observed for the copolymers containing 50% of the alkoxyphenol unit (runs 1, 2, 5 and 6). However, the observed TG profiles were quite different between the copolymers containing *o*- and *p*-alkoxyphenol units, and the former showed higher thermal stability than that for the latter. The thermal stability significantly increased to $T_5 = 408$ °C when the copolymer has a 23% of the *o*-MOP unit (run 4). Therefore, introduction of the appropriate amount of the *o*-MOP unit into the PPO chain may be effective for controlling the thermal property, although details are not clear at present.

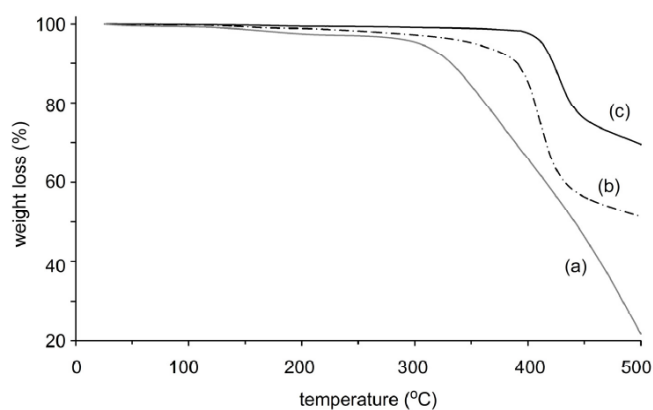


Figure 3: TG traces of the obtained copolymers: (a) poly-DMP/*p*-MOP (unit ratio DMP:*p*-MOP = 50:50), (b) poly-DMP/*o*-MOP (unit ratio DMP:*o*-MOP = 50:50), and (c) poly-DMP/*o*-MOP (unit ratio DMP:*o*-MOP = 77:23).

CONCLUSIONS

The oxidative coupling copolymerization between DMP and alkoxyphenols with the Cu(II) catalyst was performed, and the copolymers with the unit ratio,

which almost corresponds with that in the feed, were successfully provided. In addition, the coupling regioselectivity of the alkoxyphenol unit of the copolymers was also determined by the acetylation of the obtained copolymer. The simple and efficient synthesis of PPO with functional groups via the copolymerization was accomplished, especially due to the fact that the phenylene unit can introduce the phenolic hydroxyl as well as the ether functions. The

Table 3: 5 and 10% Weight-Loss Temperature of the Obtained Copolymers

Run	Copolymer	Unit Ratio X : Y ^{a)}	T_5 ^{b)} (°C)	T_{10} ^{c)} (°C)
1	poly-DMP/ <i>p</i> -MOP	50 : 50	305	335
2	poly-DMP/ <i>o</i> -MOP	50 : 50	369	396
3	poly-DMP/ <i>o</i> -MOP	69 : 31	405	418
4	poly-DMP/ <i>o</i> -MOP	77 : 23	408	417
5	poly-DMP/ <i>p</i> -EOP	50 : 50	309	331
6	poly-DMP/ <i>o</i> -EOP	49 : 51	370	385

a) Determined by ¹H NMR analysis (CDCl₃, 50 °C).

b) Five percent weight-loss temperature.

c) Ten percent weight-loss temperature.

solubility and thermal property of the obtained PPO derivatives were significantly affected by the introduced alkoxyphenol unit.

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