Synthesis of poly(2,6-dimethyl-1,4-phenylene oxide) derivatives containing hydroxyl and amino groups by oxidative coupling copolymerization

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ABSTRACT

Oxidative coupling copolymerization between 2,6-dimethylphenol (DMP) and functional monomers containing hydroxyl and amino groups, 2-hydroxymethyl-6-methylphenol and 2-(4-methylphenylamino)methyl-6-methylphenol, was carried out with a Cu catalyst under an O_2 atmosphere. The polymerization was significantly affected by the polymerization solvent used, and the copolymers were effectively obtained by polymerization in polar solvents, such as a mixed solvent system containing methanol. The obtained copolymer containing hydroxyl groups was further transformed into polymers containing ester and urethane groups, which were used as additives for the fabrication of polyurethane films. The tensile properties of the films containing the obtained copolymers were significantly improved compared to those of films prepared without an additive, as well as films containing the homo-polymer of DMP.

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1. Introduction

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is one of the most commonly used engineering plastics due its good thermal and electrical characteristics. In addition, the method used to synthesize PPO, oxidative coupling polymerization (OCP), is known to be environmentally friendly because the reaction proceeds under mild conditions in an oxygen atmosphere, producing only water as the by-product. Moreover, OCP mediates a radical coupling process involving highly active phenoxy radicals, which are very difficult to control. Therefore, few types of phenolic monomers, such as 2,6-dimethylphenol (DMP), have been used in practice, and the copolymerization leading to PPO derivatives is also restricted to some extent [1–3]. Although a typical strategy for the functionalization of PPO is the use of polymer reactions, such as the bromination of methyl side groups and further transformations of bromo-substituted polymers [3–8], there are few reports on the copolymerization of DMP derivatives, with the exception of 2-allyl-6-methylphenol, in which the limitation of the monomer source may also be a bottleneck [9–12].

In this study, the copolymerization of DMP with DMP derivatives containing hydroxyl and amino groups, 2-hydroxymethyl-6-methylphenol (HMMP) and 2-(4-methylphenylamino)methyl-6-methylphenol (TAMP) (Scheme 1), was examined, and the obtained polymers, functionalized PPOs, were used as an additive for the formation of polyurethane (PU) films. The DMP derivatives HMMP and TAMP can be easily synthesized from o-cresol via 2-hydroxy-3-methylbenzaldehyde [13–16], however, to the best of our knowledge, there is no report on the OCP of these compounds.

Polyurethanes are an important class of material extensively used in various applications, such as in coatings, fibers, foams, and elastomers requiring high performance [17–21]. For example, PUs can be found in basements, absorption materials, and biomedical devices, such as artificial heart valves and catheters, due to their good mechanical and biocompatible properties [22–27]. However, PUs exhibit poor thermal stability and susceptibility to the in vivo environment. Therefore, the physical stability of PUs must be improved. It is known that the inter-hydrogen bonding between the urethane groups of PUs, as well as the micro-phase structure of the hard and soft segments, significantly affects the macroscopic properties of the final materials. The incorporation of PPO containing functional groups that interact with the urethane groups of PU chains may control the properties of PU to
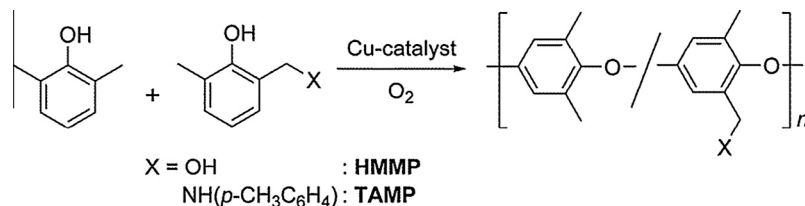
Scheme 1. Oxidative coupling copolymerization between DMP and the DMP derivatives.

2. Experimental

2.1. General

^{1}H NMR spectra were obtained using a JEOL JNM-ECS400 (400 MHz for ^{1}H) spectrometer. Size exclusion chromatographic (SEC) analyses were performed on a Jasco PU-2080 Plus system equipped with a UV (Jasco UV-2075 Plus) detector using Shodex KF-803L and KF-806L columns for CHCl₃ or Tosoh TSK-G7000H and TSK-G3000H columns for THF connected in series (temp. = 25 °C, flow rate = 0.8 mL/min). Calibration was carried out with polystyrene standards. Tensile tests were performed using a Shimadzu EZ-L(500N) apparatus with dumbbell-shaped test pieces [film width = 5 mm, stress rate = 300 mm/min, 25 °C].

2.2. Material

The monomer DMP (Kanto) and the copper catalyst di-μ-hydroxo-bis[(N,N,N′,N′-tetramethylethylenediamine)copper(II)] chloride [CuCl(OH)-TMEDA, TCI] [32–35] were used as received. The functional monomers HMMP and TAMP were synthesized from o-cresol as reported in the literature [13–16]. Poly(tetramethylene oxide) 650 (molecular weight = 600–710, PTMO, Wako), methylenediphenyl 4,4′-diisocyanate (MDI, Wako), 1,4-butanediol (Kanto), dibutyltin dilaurate (Wako), phenyl isocyanate (Wako), 4-methoxyphenyl isocyanate (TCI), and butyl isocyanate (TCI) were employed for PU synthesis [20] and the further transformation of the obtained PPO copolymer without further purification.

2.3. Typical procedure for oxidative coupling copolymerization of DMP

The catalyst was added to a mixture of DMP and a comonomer ([monomers]/[Cu] = 20/1, monomers: 1 mmol) in a solvent (2 mL), and the mixture was stirred at approximately 25 °C for 24 h under an O₂ atmosphere. The product was isolated as the MeOH-2 mol/L HCl (5/1 (v/v))-insoluble part by centrifugation, then repeatedly washed with methanol, and finally freeze-dried from the benzene solution.

2.4. Acetylation of the obtained copolymer

Pyridine (0.1 mL) was introduced into a mixture of copolymer (51 mg) and AcCl (0.1 mL) in CH₂Cl₂ (2 mL) at 25 °C; the mixture was stirred for 24 h. The product was isolated (55 mg) as the MeOH-2 mol/L HCl (4/1 (v/v))-insoluble fraction by centrifugation, washing with methanol, and freeze-dried from the benzene solution.

2.5. Transformation of the obtained copolymer with isocyanates

A mixture of copolymer (50 mg), RNCO (0.1 mL), and dibutyltin dilaurate (0.01 mL) in N,N-dimethylformamide (DMF, 2 mL) was stirred at 60 °C for 24 h. The methanol-insoluble products (R = Ph: 50 mg; 4-MeOC₆H₄: 56 mg; n-Bu: 60 mg) were obtained by washing with MeOH-2 mol/L HCl (4/1 (v/v)) and with methanol, and then freeze-dried from the benzene solution.

2.6. PU film formation

To a solution of PTMO (3.3 g) and MDI in tetrahydrofuran (THF: 10 mL) a Sn(IV) catalyst was added. After stirring at 50 °C for 2 h under a N₂ atmosphere, a THF solution of 1,4-butanediol was introduced ([PTMO]/[MDI]/[1,4-butanediol]/[Sn] = 1/2/1/0.02). The stirring was continued at 25 °C for 1 h to yield a THF solution of PU [13 wt%, MeOH-insoluble part: 89%, number-average molecular weight (M_n): 7.4×10^4, weight-average molecular weight (M_w): 1.9×10^5].

Film formation was carried out using a mixture of the above-described THF solution of PU (4 g) and a solution of poly(DMP/HMMP) derivatives (2.5 mg, 0.5 wt% to PU) in THF (1 mL) using a Petri dish (45 mm⌀). Films were prepared by drying at 45 °C for 24 h, and the obtained films were further dried at 80 °C for 3 h under vacuum.

3. Results and discussion

DMP and the DMP derivatives (50:50 feed ratio) were copolymerized with the CuCl(OH)-TMEDA catalyst in various solvents under an oxygen atmosphere (Scheme 1). The results are summarized in Table 1. The homo-polymerization of HMMP with the CuCl-pyridine catalyst (5 mol%) in the presence of Na₂SO₄ in toluene at room temperature for 2 h did not afford a product, whereas a methanol-insoluble polymer was obtained in 50% yield by the polymerization of DMP under the same conditions [36]. Copolymerization with HMMP as the comonomer in toluene afforded a polymer in a low yield of 23%, whose unit ratio (DMP:HMMP) was determined to be 91:9 by ^{1}H NMR analysis (run 1). The solvents, CHCl₃ and THF, significantly improved both the yield and unit ratio, whose values were 76% and 67:33 in the latter case (run 3), respectively. Therefore, it is concluded that the polarity of the solvent affects the copolymerizability of HMMP.

The plausible active intermediate of the HMMP unit's ω-end is illustrated in Scheme 2, in which copper(II) is intra-molecularly coordinated by the hydroxyl group. A stable six-membered chelation ring may inhibit further coupling [2], whereas polar solvents, such as THF, should activate the copper(II) intermediate to induce polymerization, although the details of this process are not currently clear. To support this scheme, the copolymerization in methanol was examined (runs 4–6), although methanol has often been used for the oxidative coupling reaction and OCP, mainly because methanol easily dissolves the catalyst [37–41]. Actually, it was observed that the mixed solvent with methanol significantly

Table 1
Copolymerization of DMP (1:1 feed ratio).[a]

| Run	Comonomer	Solvent	Yield (%)[b]	Unit ratio[c] DMP:comonomer	$M_w \times 10^{-3}$ (M_w/M_n)[d]
1	HMMP	Toluene	23	91:9	13.3 (2.5)
2	HMMP	CHCl₃	51	81:19	9.1 (1.7)
3	HMMP	THF	76	67:33	3.1 (1.3)
4	HMMP	Toluene–MeOH[e]	31	82:18	7.0 (1.5)
5	HMMP	Toluene–MeOH[f]	24	54:46	6.0 (2.1)
6	HMMP	CHCl₃–MeOH[e]	39	76:24	4.4 (1.3)
7	TAMP	CHCl₃	57	72:28	10.5 (2.0)
8	TAMP	CHCl₃–MeOH[e]	69	73:27	6.4 (1.7)

[a] Conditions: catalyst = CuCl(OH)-TMEDA, temp. = r.t., time = 24 h, O₂ atmosphere.
[b] MeOH-insoluble part.
[c] Determined by ¹H NMR analysis.
[d] Determined by SEC (eluent: CHCl₃).
[e] 7/1 (v/v).
[f] 3/1 (v/v).
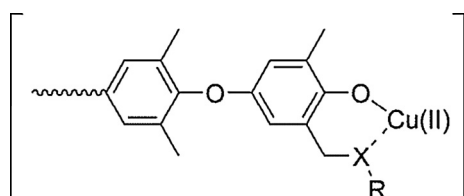
Scheme 2. Plausible intermediate for the oxidative coupling copolymerization with the Cu(II) catalyst.

affected the unit ratio of the obtained polymers. For example, the polymerization in toluene–methanol (3/1, v/v) afforded a polymer with a unit composition of 54:46 in low yield.

The copolymerization of DMP with TAMP in CHCl₃ also afforded a copolymer in 57% yield with a unit ratio of DMP:TAMP = 72:28 (run 7). However, a similar value of the unit ratio was observed for the mixed solvent system containing methanol, whereas the polymer yield increased to 69% (run 8). Figs. 1(b) and 2(b) demonstrate the ¹H NMR spectra of the obtained copolymers, poly(DMP/HMMP) (run 3) and poly(DMP/TAMP) (run 7), together with those of the comonomers HMMP and TAMP (Figs. 1(a) and 2(a)), respectively. The peaks are assigned as shown in the figures.

Table 2 lists the results of the copolymerization between DMP and HMMP in various feed ratios. During the polymerization in toluene or CHCl₃, the copolymers, which mainly consisted of the DMP unit, were produced (runs 1–4). The copolymerization in the toluene–methanol mixed solvent clearly affected the polymerizability of HMMP, leading to a copolymer with an HMMP unit ratio higher than the unit ratios observed for the polymers obtained in toluene (runs 5–7).

Further transformations of the side-chain hydroxyl groups of poly(DMP/HMMP) were carried out to use the products as an additive for PU film formation (Scheme 3). The copolymer (Table 1, run 3) was treated with an excess amount of acetyl chloride and pyridine (poly-**1**) or an excess amount of isocyanate esters in the presence of the catalyst, dibutyltin dilaurate, (poly-**2**−poly-**4**) at room temperature for 24 h. After washing with methanol and freeze-drying from the benzene solution, the products were nearly obtained in quantitative yield. The ¹H NMR spectrum of the acetylated polymer, poly-**1**, is shown in Fig. 1(c). A shift in the methylene proton peak from 4.5 ppm for the original polymer to 5.0 ppm was clearly observed, and the unit ratio of DMP: YMMP was estimated to be 67:33, whose value is identical to the original one. The ¹H NMR spectrum of the polymer possessing the urethane group poly-**4** is demonstrated in Fig. 1(d). The unit ratio was evaluated to be 68:32, which again is in good agreement with the original value. These results indicated that the transformation of the
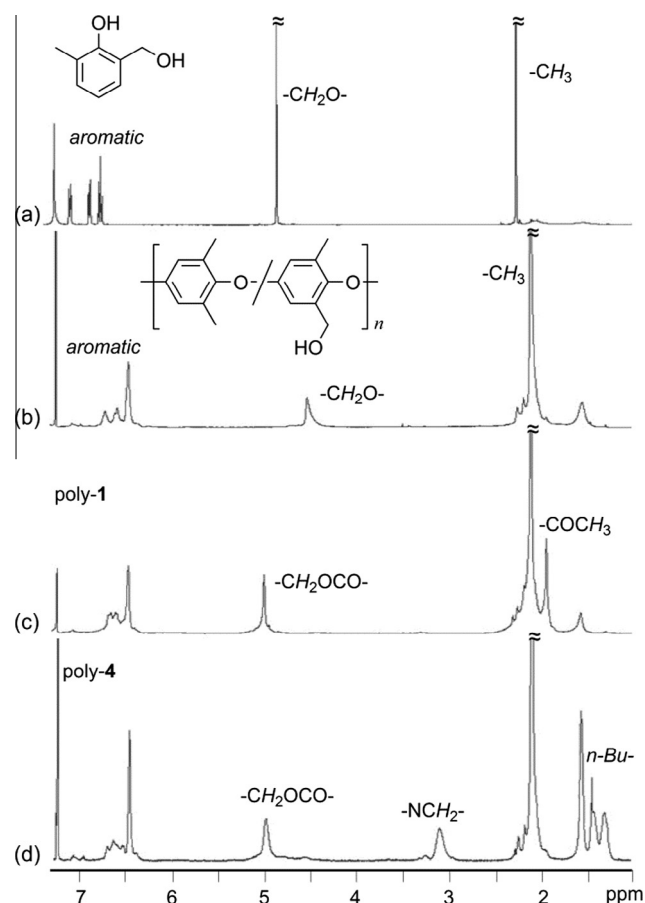
Fig. 1. ¹H NMR spectra of (a) HMMP, (b) poly(DMP/HMMP) (Table 1, run 3), (c) poly-**1**, and (d) poly-**4** (400 MHz, CDCl₃).

hydroxyl groups introduced by the copolymerization of HMMP was successfully attained. Moreover, the SEC analyses in CHCl₃ revealed an M_w value of 8.5×10^4 ($M_w/M_n = 1.7$) for poly-**1** but were unsuccessful for poly-**2**−poly-**4**, most likely because significant aggregation should occur in the eluent.

A PU solution in THF was prepared using PTMO, MDI, and 1,4-butanediol as the extender (1:2:1) in the presence of the Sn(IV) catalyst [18]. In addition, poly(DMP) was synthesized by polymerization with CuCl(OH)-TMEDA in CHCl₃ at room temperature under an O₂ atmosphere (methanol-insoluble part: 76%, $M_w = 1.1 \times 10^4$, $M_w/M_n = 5.1$). The polymers poly(DMP), poly(DMP/HMMP) (Table 1, run 3), and poly-**1**−poly-**4** were used as an additive (0.5 wt%) for PU film formation.
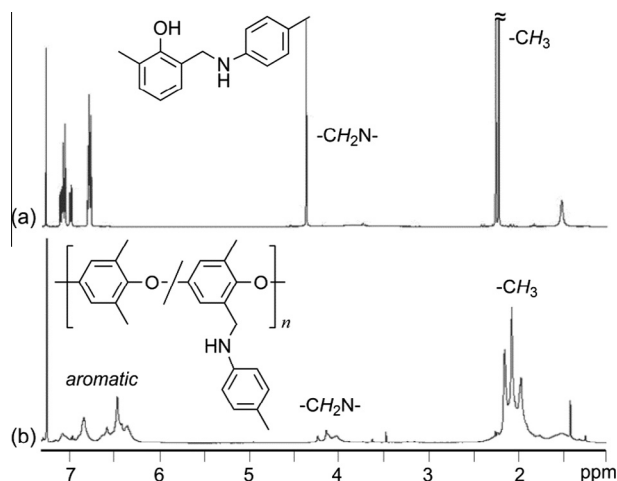
Fig. 2. ^{1}H NMR spectra of (a) TAMP and (b) poly(DMP/TAMP) (Table 1, run 7) (400 MHz, CDCl$_3$).

Table 3
Properties of PU films containing poly(DMP/HMMP) derivatives.

Run	Additive (0.5 wt%)	Thickness (μm)	Elastic modulus (N/mm^2)
1	None	185.1	2.88
2	Poly(DMP)[a]	184.3	1.92
3	Poly(DMP/HMMP)[b]	193.0	2.83
4	Poly-1	181.9	3.17
5	Poly-2	187.2	3.04
6	Poly-3	180.5	3.22
7	Poly-4	182.6	3.05

[a] $M_w = 1.1 \times 10^4$, $M_w/M_n = 5.1$.
[b] Table 1, run 3.

the latter, the structure of the urethane group also affected the PU film properties (runs 5–7). These results suggest that the hydrogen-bond interaction between PU and PPO should play an important part in controlling the properties of the PU films.

A PU containing isocyanate end groups was then prepared using PTMO, MDI, and 1,4-butanediol in a ratio of 1:2:0.8, and the obtained THF solution was used for film formation by adding poly(DMP/HMMP) (Table 1, run 3) (0.5 wt%). During the film formation process, the isocyanate of PU should react with the hydroxyl group of PPO to form a covalent bond [42]. The PU films obtained with and without poly(DMP/HMMP) were again colorless and clear; the thicknesses of the films were 174 and 157 μm, respectively. The former, which contained the additive, showed an elastic modulus of 3.80 N/mm^2, whereas a value of 3.30 N/mm^2 was observed for the latter. Thus, poly(DMP/HMMP) is significantly effective in controlling PU film properties as an additive; in addition, the values obtained are quite different from those observed for the films prepared using the normal PU (Table 3, runs 1 and 3).

Colorless and clear films were obtained; their properties are summarized in Table 3. The average thickness was approximately 180 μm. When poly(DMP) was used as an additive, the elastic modulus of the resulting film was significantly reduced to 1.92 N/mm^2 (run 2) compared to that observed for the film prepared without an additive (run 1). In contrast, the PU films containing PPO with the functional groups showed values that were comparable or greater than the value measure for the original PU film. In particular, a value of approximately 3.2 N/mm^2 was observed for the films prepared with poly-1 and poly-3, which contained ester and urethane groups, respectively (runs 4 and 6). In

Table 2
Copolymerization of DMP and HMMP[a].

Run	Solvent	Feed ratio DMP:HMMP	Yield (%)[b]	Unit ratio[c] DMP:HMMP	$M_w \times 10^{-4}$ (M_w/M_n)[d]
1	Toluene	3:1	72	96:4	3.9 (3.8)
2	Toluene	2:1	49	94:6	5.6 (1.8)
3	Toluene[e]	3:1	78	89:11	2.6 (23)
4	CHCl$_3$	3:1	79	92:8	17.8 (14)
5	Toluene–MeOH[f]	3:1	66	93:7	6.5 (5.8)
6	Toluene–MeOH[f]	2:1	48	81:19	5.6 (1.8)
7	Toluene–MeOH[f]	1:3	49	30:70	7.1 (2.1)[g]

[a] Conditions: catalyst = CuCl(OH)–TMEDA, temp. = r.t., time = 24 h, O$_2$ atmosphere.
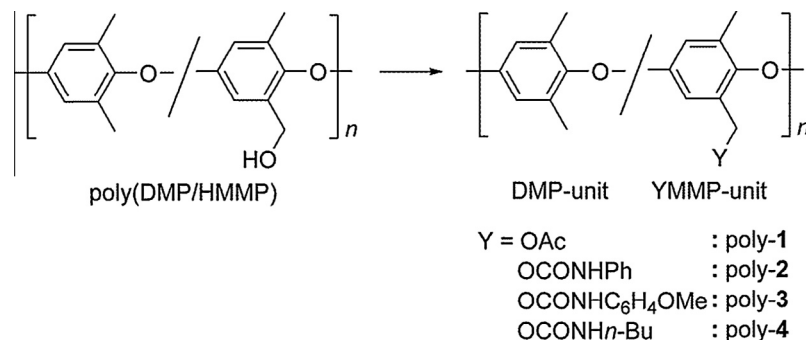[b] MeOH-insoluble part.
[c] Determined by ^{1}H NMR analysis.
[d] Determined by SEC (eluent: CHCl$_3$).
[e] Catalyst = CuCl + 2 pyridine.
[f] 7/1 (v/v).
[g] Determined after acetylation of the original polymer with an excess amount of AcCl and pyridine in CHCl$_3$.

Scheme 3. Transformations of poly(DMP/HMMP) into polymers possessing ester (poly-1) and urethane groups (poly-2–poly-4).
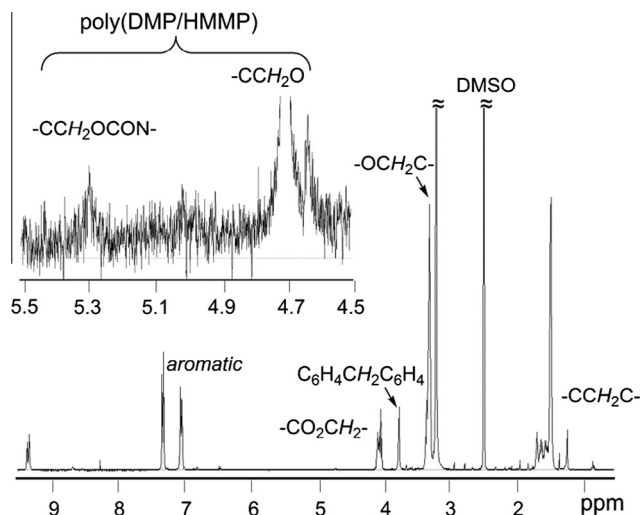
Fig. 3. ^{1}H NMR spectra of the PU containing poly(DMP/HMMP) (0.5 wt%) (400 MHz, DMSO-d_6).

The film obtained using the poly(DMP/HMMP) additive was dissolved in DMSO-d_6 and a submitted to ^{1}H NMR analysis (Fig. 3). The peaks based on the PU are assigned as shown in the figures. The expanded spectrum shows a region of methylene protons of poly(DMP/HMMP). The peaks at approximately 4.7 ppm correspond to those of the original polymer, whereas the small absorption peak at 5.3 ppm must be attributed to the methylene protons of the neighboring urethane group. Therefore, some of the hydroxyl groups reacted with the isocyanate terminal of PU, and the integral ratio of these two peaks was estimated to be 9:1. These results suggest that urethane bond formation between PU and PPO significantly affects the properties of the resulting films.

4. Conclusion

The copolymerization of DMP and DMP derivatives containing hydroxyl and amino groups was carried out, and the preparation of PPO with functional groups was successfully achieved. The copolymerization was affected by the polymerization solvent used, and the polar solvent, a mixed system containing methanol, yielded the copolymer in an effective manner. The obtained PPO derivatives were used as an additive for PU film formation, and the formation of intermolecular hydrogen and covalent bonds was observed significantly improve the tensile properties of the resulting films.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.reactfunctpolym.2014.07.009.

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