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Synthesis, structures and thermal properties of new class epoxide-terminated telechelic poly(2,6-dimethyl-1,4-phenylene oxide)s

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Abstract

Dihydroxyl telechelic poly(2,6-dimethyl-1,4-phenylene oxide)s (**1**) with regiocontrolled end-group structures have been synthesized by oxidative polymerization of 2,6-dimethylphenol with various aromatic diols in the presence of CuBr/dibutylamine catalysts. The novel one- or two-armed telechelic derivatives based on aromatic diols as core and **1** as arms were subsequently epoxidized with epichlorohydrin and a series of new epoxidized poly(2,6-dimethyl-1,4-phenylene oxide)s (**2**) were accessible with number average molecular weight ranged from 3500 to 14,000. The end-group structures and regioselectivity of polymers were controlled by the CuBr/dibutylamine catalysts under different reaction conditions, and the structures and properties were studied by nuclear magnetic resonance spectroscopy, gel permeation chromatography, thermogravimetric analysis and differential scanning calorimetry. Upon heating in the presence of oxygen, the one-armed dihydroxyl telechelic polymer was converted via intermolecular coupling and redistribution reaction to the two-armed derivative with significant increase in its molecular weight and elimination of diol monomer. Treatment of dihydroxyl telechelic derivatives with epichlorohydrin and NaOH afforded the epoxide-terminated telechelic derivatives in 77–94% yields.

Keywords: Poly(2,6-dimethyl-1,4-phenylene oxide); Telechelic; Regioselectivity

1. Introduction

Poly(phenylene oxide) (PPO), also known as poly(phenylene ether) (PPE), is a well-known synthetic polymeric material widely used in electrical or electronic equipments, vehicle parts and business machines due to its balanced mechanical properties, low moisture absorption, excellent electrical insulation property and dimension stability [1]. PPO is one of the potential materials to satisfy the demand for high frequency substrates in electronics industry; however, the low resistance to non-polar solvents and non-curable nature militate against its use for printed circuit board matrix materials. Attempts to blend PPO into epoxy-made copper clad laminate substrates to improve the thermal and electrical properties of epoxy resins often result in phase separation due to the chemical structure differences and the lack of compatibility between the two compounds [2–6]. Recently, curable PPO resins prepared by introducing functional groups to polymer side chains were investigated to improve the inferior compatibility and phase separation between PPO and epoxy resins. Such modifications include acidifications [7], aminations [8], allylations [9] and epoxidations [10]. As part of our continuing research in developing high T_g and low D_k materials for electronic applications, we report herein the synthesis of new telechelic PPO terminating with glycidyl ether groups and explore the structures and properties of these thermosetting materials.

Telechelic PPOs are polymers consisting of poly(2,6-dimethyl-1,4-phenylene oxides) as backbone bearing reactive functional groups on both chain ends. A great interest has been

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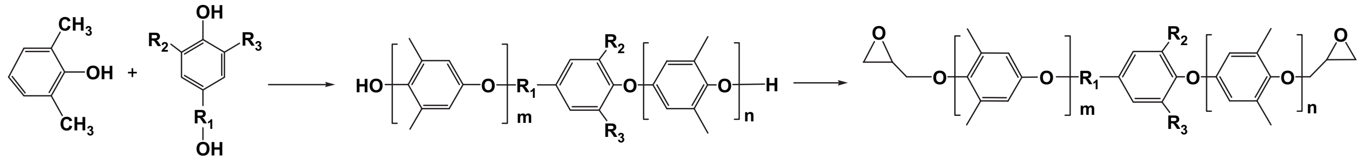
developed over the past decades in the telechelic polymers or macromonomers since they provide a facile route to design sophisticated polymer structures including block, graft, and network copolymers [11–22]. In contrast with the conventional PPO which possesses high molecular weight and low functionality, the telechelic PPOs can be viewed as a linear macromonomer or prepolymer with a molecular weight of 10^3–10^4 and functionality of about 2. Hydroxyl-terminated telechelic PPO is generally prepared via redistribution or depolymerization of high molecular weight PPO with various phenolic derivatives in the presence or absence of radical initiators [23,24]. Alternatively, the telechelics can be prepared from coupling reactions of PPO with either 3,3′,5,5′-tetramethyl-4,4′-diphenoquinone [25] or tetramethyl bisphenol-A in the presence of dimethylaminopyridine [26]. Another method employing aromatic nucleophilic substitution reaction of 4-bromo-2,6-dimethylphenol has also been proved satisfactory for the formation of telechelic PPO using a phase-transfer catalyst [27]. The redistribution reactions of high molecular weight PPO often encounter problems such as bimodal molecular weight distribution, incorporation of radical initiators into polymer chains and difficulty in controlling the exact molecular structure of telechelics. Thus, the aim of our work is to develop a convenient method for preparation of bi-functionalized polymers consisting of PPO as backbone with unimodal molecular weight distribution and well-defined end-group structures.

2. Experimental

*2.1. Outline of preparative procedures for epoxy-terminated telechelic poly(2,6-dimethyl-1,4-phenylene oxide)s (**2**)*

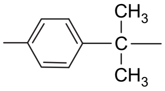
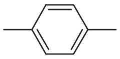
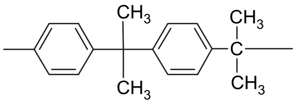
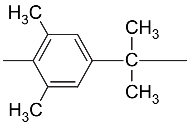
Epoxide-terminated telechelic poly(2,6-dimethyl-1,4-phenylene oxide) **2** was synthesized from epoxidation reactions of the corresponding dihydroxyl-terminated polymer **1** using epichlorohydrin and NaOH as outlined in Table 1. The synthesis involves a two-step reaction. The first step is to prepare the dihydroxyl-terminated PPO containing well-defined end-group structure. Unlike the methods published previously [25,26], the 2,6-DMP is copolymerized with the corresponding aromatic diols using CuBr/dibutylamine as catalyst in the presence of oxygen. As a result, a variety of bis(phenol) or biphenol moieties are incorporated into PPO backbone either internally or at terminal position. In the second step, an excess of epichlorohydrin is used for epoxidation in the presence of NaOH to afford the epoxidized telechelics **2** with controlled molecular structure in 77–94% yields.

Table 1
Synthesis and analysis of the telechelic PPO polymers



1

2

Entry	R_1	R_2	R_3	**1**				**2**			
				Yield (%)	M_n	M_w	T_g (°C)	Yield (%)	M_n	M_w	T_g (°C)
a		H	H	70[a]	4599	8041	188	77	9005	13,273	178
b		H	H	70[b]	5257	9437	193	78	14,288	19,300	181
c		H	H	50[a]	3631	7545	183	80	7399	9157	205
d		H	H	73[a]	3742	8315	189	82	3539	9510	207
e		CH_3	CH_3	76[b]	5028	8479	183	94	6403	11,215	182

All T_g values were obtained after the second heating scan.

[a] One-armed product was predominantly obtained, $m = 0$, $n \neq 0$.

[b] Two-armed product was predominantly obtained, m, $n \neq 0$.

2.2. Materials

All reagents and solvents were reagent-grade purchasing from commercial companies and used as received. 2,6-Dimethylphenol (2,6-DMP) was obtained from Acros. Methanol was obtained from Mallinckrodt. Toluene and chloroform were from Medla. Ethylenediaminetetraacetic acid (EDTA) was purchased from Scharlau Chemie. 4,4′-Biphenol and tetramethyl bisphenol-A (TMBPA) were purchased from Tokyo Kasei Kogyo Co., Ltd. Cuprous bromide was supplied from Alfa Aesar. 4,4′-Isopropylidene bisphenol (bisphenol-A) was from Showa. Sodium hydroxide, 4,4′-(1,4-phenylenediisopropylidene) bisphenol (bisphenol-P) and dibutylamine were received from Aldrich. Epichlorohydrin and 2-methoxyethanol were obtained from Fluka.

2.3. Characterization

^{1}H and ^{13}C NMR spectra were recorded on a 300 and 75 MHz Varian Mercury$^+$ 300 spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The molecular weight of the polymers was determined by gel permeation chromatography (GPC), which was carried out with polymer solutions in tetrahydrofuran (THF). Samples were prepared at nominally 1 mg/mL in THF and injected by Waters 717 autosampler. GPC system (Waters 515 high performance liquid chromatography pump, 1 mL/min, 40 °C) was equipped with Waters Styragel HR0.5, HR4E and HR5 and a Waters model 2410 refractive-index detector. The molecular weights and polydispersity of the products were calibrated with polystyrene molecular weight standards (molecular weight = 500–370,000, SM-105, Shodex Japan). Differential scanning calorimetry (DSC) measurements were performed on a DSC Q10 differential scanning calorimeter (TA Instruments). The instrument was calibrated with high purity indium as a standard. Samples of about 5 mg were weighed in aluminum pans (diameter = 5 mm; TA Instruments), which were hermetically sealed for standard DSC analysis. The sample was heated at a rate of 10 °C/min to 300 °C, cooled to 40 °C and heated again. The nitrogen gas flow was 50 mL/min.

Thermogravimetric analysis (TGA) was performed with a TGA Q50 (TA Instruments) thermogravimetric analyzer under a nitrogen atmosphere. Samples (10–15 mg) were placed in platinum pans and put in an oven at 30 °C. Heating scans were carried out from 30 to 800 °C at 10 °C/min. Nickel was used for calibration. The temperatures of 5 wt% weight loss were determined. Pyrolysis-gas chromatograph/mass spectra (Py-GC/MS) were recorded on a Frontier Lab double-shot pyrolyzer PY-2020D and a Hewlett-Packard HP 6890 GC equipped with a HP 5973 mass selective detector. The volatile products were analyzed with an Ultra Alloy Column UA-5 (5% diphenyl) capillary column (30 m × 0.25 mm; film thickness, 0.25 μm). Samples of 0.5–1.0 mg were weighted and loaded into micro-furnace preheated at 300 °C. The temperature of column oven was first set at 40 °C. After the pyrolysis process had finished, the column was heated at 40 °C for 5 min; 40–300 °C at 20 °C/min. Mass spectrum measurements were obtained using the electron impact ionization technique (electron energy 70 eV; scan range 50–650 amu).

2.4. General procedure for the preparation of hydroxyl-terminated telechelic poly(2,6-dimethyl-1,4-phenylene oxide)s (***1***)

To a stirred solution of cuprous bromide (0.114 g, 0.0008 mol) in 42 mL of toluene and 10 mL of methanol at 25 °C was added 7.32 g (0.057 mol) of dibutylamine. The mixture was bubbled with oxygen for 10 min and subsequently was added slowly with 2,6-DMP (1.954 g, 0.016 mol) and bisphenol-A (0.7296 g, 0.0032 mol). The reaction temperature was kept at 25 °C with a continuous oxygen flow through the reaction mixture for 3 h. The resulting mixture was washed twice with 50 mL portion of 0.02 N EDTA and repeated twice with 70 mL portion of deionized water. The polymer was precipitated by dropwise addition into a 10-fold excess of stirred methanol. The white precipitate was purified by dissolving in minimum amount of THF and reprecipitated in methanol. The precipitated polymer was collected by filtration, washed with methanol and dried *in vacuo* overnight. Compound **1a**: 1.88 g, yield = 70%. The similar procedure was used for all of the polymers **1b**–**1e**, except for **1b**, that 2 mL of methanol was added and for 1**c**, that 10 mL of methanol was added while keeping the temperature at 0 °C.

2.4.1. Compound ***1a***

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.18 (d, 2H, Ar-*H* of bisphenol-A, $J = 9.18$ Hz), 6.93 (d, 2H, Ar-*H* of bisphenol-A, $J = 9.15$ Hz), 6.84 (d, 2H, Ar-*H* of bisphenol-A, $J = 9.18$ Hz), 6.84 (d, 2H, Ar-*H* of bisphenol-A, $J = 9.18$ Hz,), 6.74 (s, Ar-*H* of PPO next to the aromatic ring of bisphenol-A), 6.47 (s, Ar-*H* of internal PPO), 6.41 (s, Ar-*H* of terminal PPO), 2.08 (s, Ar-CH_3 of PPO), 1.651 (s, Ar-C(CH_3)$_2$- of bisphenol-A). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 155.4, 154.7, 153.5, 147.0, 146.3, 145.4, 132.5, 127.9, 124.3, 119.2, 117.8, 114.4, 41.8, 31.0, 16.8.

2.4.2. Compound ***1b***

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.55 (d, 2H Ar-*H* of biphenol, $J = 8.4$ Hz), 7.10 (d, 2H, Ar-*H* of biphenol, $J = 8.7$ Hz), 6.81 (s, Ar-*H* of PPO next to the aromatic ring of biphenol), 6.47 (s, Ar-*H* of internal PPO), 6.34 (s, Ar-*H* of terminal PPO), 2.08 (s, Ar-CH_3 of PPO).

2.4.3. Compound ***1c***

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.50 (d, 2H, Ar-*H* of biphenol, $J = 9.1$ Hz), 7.44 (d, 2H, Ar-*H* of biphenol, $J = 8.8$ Hz), 7.07 (d, 2H, Ar-*H* of biphenol, $J = 9.1$ Hz), 6.89 (d, 2H, Ar-*H* of biphenol, $J = 9.1$ Hz), 6.79 (s, Ar-*H* of PPO next to the aromatic ring of biphenol), 6.47 (s, Ar-*H* of internal PPO), 6.37 (s, Ar-*H* of terminal PPO), 2.08 (s, Ar-CH_3 of PPO).

2.4.4. Compound **1d**

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.19 (d, 2H, Ar-*H* of bisphenol-P, $J = 8.0$ Hz), 7.12 (s, 4H, Ar-C(CH$_3$)$_2$-*Ar*-C(CH$_3$)$_2$-Ar, central Ar-*H* of bisphenol-P), 7.11 (d, 2H, Ar-*H* of bisphenol-P, $J = 8.0$ Hz), 6.92 (d, 2H, Ar-*H* of bisphenol-P, $J = 8.0$ Hz), 6.72 (d, 2H, Ar-*H* of bisphenol-P, $J = 8.0$ Hz), 6.77 (s, Ar-*H* of PPO next to the aromatic ring of bisphenol-P), 6.47 (s, Ar-*H* of internal PPO), 6.37 (s, Ar-*H* of terminal PPO), 2.08 (s, Ar-C*H*$_3$ of PPO), 1.66 (s, 6H, Ar-C(C*H*$_3$)$_2$- of bisphenol-P), 1.63 (s, 6H, Ar-C(C*H*$_3$)$_2$- of bisphenol-P). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 155.34, 154.70, 153.52, 147.71, 146.99, 145.42, 132.53, 128.02, 127.89, 126.23, 119.15, 117.75, 114.44, 42.07, 30.90, 16.65.

2.4.5. Compound **1e**

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 6.96 (s, 4H, Ar-*H* of TMBPA), 6.47 (s, Ar-*H* of PPO), 6.36 (s, Ar-*H* of terminal PPO), 2.08 (s, Ar-C*H*$_3$ of PPO), 1.69 (s, 6H, Ar-C(C*H*$_3$)$_2$- of TMBPA).

2.5. General procedure for the preparation of epoxy-terminated telechelic poly(2,6-dimethyl-1,4-phenylene oxide)s (**2**)

To a three-neck round-bottomed flask, equipped with magnetic stirrer, reflux condenser, and thermometer were added epichlorohydrin (10 g, 0.11 mol), 2-methoxyethanol (0.8 g) and telechelic PPO (**1a**, 0.6 g). Under vigorous agitation, the mixture was heated to 55–60 °C, and a 10% aqueous sodium hydroxide solution (0.125 g) dissolved in 0.8 g of 2-methoxyethanol was added separately over a period of 1 h while maintaining the reaction temperature at 60 °C. Upon completion of the addition, the reaction temperature was kept at 60 °C for another 2 h. The reaction mixture was washed with deionized water to remove salts and the organic phase was separated and the volatiles were removed under vacuum with a gradual temperature rise over 1 h to 120 °C. A pale brown solid residue was obtained. The polymer was purified by dissolving in THF and reprecipitated in methanol solution. The precipitated polymer was collected by filtration, washed with methanol and dried *in vacuo* overnight. Recovery yield: 0.47 g (77%). The similar procedure was used for all of the polymers **2b**–**2e**, except that the quantity of NaOH was 0.27 g, 0.14 g, 0.15 g, and 0.15 g for **2b**–**2e**, respectively.

2.5.1. Compound **2a**

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.18 (d, 2H, Ar-*H* of bisphenol-A, $J = 8.7$ Hz), 7.15 (d, 2H, Ar-*H* of bisphenol-A, $J = 8.7$ Hz), 6.91 (d, 2H, Ar-*H* of bisphenol-A, $J = 8.7$ Hz), 6.83 (d, 2H, Ar-*H* of bisphenol-A, $J = 8.7$ Hz), 6.76 (s, 2H, Ar-*H* of PPO next to the aromatic ring of bisphenol-A), 6.47 (s, 2H, Ar-*H* of internal PPO), 6.36 (s, Ar-*H* of terminal PPO), 4.16–4.17, 3.96–3.97, 3.62–3.80, 3.34, 2.73–2.91 (m, glycidyl ether protons), 2.08 (s, Ar-C*H*$_3$ of PPO), 1.68 (s, Ar-C(C*H*$_3$)$_2$- of bisphenol-A). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 156.38, 154.71, 153.53, 145.87, 145.41, 143.42, 132.53, 131.52, 128.95, 119.11, 117.81, 114.43, 73.22, 68.73, 50.17, 44.75, 41.87, 31.00, 16.77.

2.5.2. Compound **2b**

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.55 (d, 2H, Ar-*H* of biphenol, $J = 9.3$ Hz), 7.10 (d, 2H, Ar-*H* of biphenol, $J = 9.2$ Hz), 6.81 (s, Ar-*H* of PPO next to the aromatic ring of biphenol), 6.47 (s, Ar-*H* of internal PPO), 3.97–3.96, 3.76–3.72, 3.32, 2.91–2.67 (m, glycidyl ether protons), 2.08 (s, Ar-C*H*$_3$ of PPO). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 73.21, 50.57, 44.55 (for glycidyl ether carbons).

2.5.3. Compound **2c**

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.52 (d, 2H, Ar-*H* of biphenol, $J = 8.3$ Hz), 7.50 (d, 2H, Ar-*H* of biphenol, $J = 8.3$ Hz), 7.08 (d, 2H, Ar-*H* of biphenol, $J = 8.3$ Hz), 6.99 (d, 2H, Ar-*H* of biphenol, $J = 8.3$ Hz), 6.80 (s, Ar-*H* of PPO next to the aromatic ring of biphenol), 6.47 (s, Ar-*H* of internal PPO), 4.24–4.27, 3.97–4.03, 3.69–3.96, 3.22–3.44, 2.62–2.96 (m, glycidyl ether protons), 2.08 (s, Ar-C*H*$_3$ of PPO). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 73.70, 69.31, 50.92, 50.52, 45.06, 44.86 (for glycidyl ether carbons).

2.5.4. Compound **2d**

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 7.06–7.23 (m, 8H, Ar-*H* of biphenol), 6.92 (d, 2H, Ar-*H* of bisphenol-P, $J = 8.5$ Hz), 6.83 (d, 2H, Ar-*H* of bisphenol-P, $J = 8.6$ Hz), 6.77 (s, Ar-*H* of PPO next to the aromatic ring of bisphenol-P), 6.47 (s, Ar-*H* of internal PPO), 4.12–4.26, 3.97–4.03, 3.65–3.77, 3.27–3.44, 2.68–2.98 (m, glycidyl ether protons), 2.08 (s, Ar-C*H*$_3$ of PPO), 1.67 (s, 6H, Ar-C(C*H*$_3$)$_2$- of bisphenol-P), 1.64 (s, 6H, Ar-C(C*H*$_3$)$_2$- of bisphenol-P). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 156.28, 154.70, 153.25, 147.709, 146.97, 145.41, 132.53, 128.02, 127.81, 126.23, 119.15, 117.73, 114.42, 73.21, 68.69, 50.56, 50.17, 44.75, 42.06, 30.90, 16.76.

2.5.5. Compound **2e**

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 6.97 (s, 4H, Ar-*H* of TMBPA), 6.47 (s, Ar-*H* of PPO), 6.34 (s, Ar-*H* of terminal PPO), 3.969–4.02, 3.67–3.82, 3.28–3.42, 2.81–2.95, 2.66–2.77 (m, glycidyl ether protons), 2.08 (s, Ar-C*H*$_3$ of PPO), 1.640 (s, 6H, Ar-C(C*H*$_3$)$_2$- of TMBPA). ^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 73.20, 50.57, 44.55 (for glycidyl ether carbons).

2.6. General procedure for the conversion of one-armed telechelic PPO to two-armed derivatives

To a three-neck round-bottomed flask, equipped with magnetic stirrer, reflux condenser, and oxygen inlet were added 1.0 g of **1c** and 50 mL of chloroform. After 30 min of stirring, a small flow of oxygen was bubbled through the mixture and the solution was heated at 60 °C with a continuous flow of oxygen for 48 h. The resulting solution mixture was added to a 10-fold excess of methanol to precipitate the polymer. After filtration and washing with methanol, the precipitated polymer was dried *in vacuo*. Recovery yield: 0.85 g (85%). The filtrate was evaporated *in vacuo* and residue was subjected to pyrolysis-gas chromatograph/mass spectral analysis.

3. Results and discussion

3.1. Hydroxyl-terminated telechelic poly(2,6-dimethyl-1,4-phenylene oxide)s (*1*)

All compounds **1** and **2** were isolated as white or light yellow powders and the structures were characterized by ^{1}H NMR, ^{13}C NMR, GPC, DSC and TGA. The carbon–oxygen coupling reaction between diol monomers and 2,6-DMP could proceed either on one end (one-armed) or both ends (two-armed) of aromatic diol depending on the diol structure and reaction conditions. For example, the use of bisphenol-A led to the formation of one-armed telechelics (**1a**) whereas a predominantly two-armed product (**1e**) was obtained when TMBPA was employed as co-monomer under similar reaction conditions. In the case of biphenol, under a lower reaction temperature (0 °C) and higher methanol content solvent system (ca. 20 vol%), the polymerization proceeded less favorably and resulted in the formation of one-armed telechelics (**1c**) as major product and two-armed telechelic (**1b**) as the minor product; however, by increasing the reaction temperature and decreasing the methanol fraction (ca. 5 vol%) of solvent system, majority of two-armed telechelic structure was obtained (**1b**). It is inferred that the lower reaction temperature made the polymerization process kinetically unfavorable and the increase of methanol (which is a non-solvent for PPO polymer) content might have deferred the C–O coupling and afforded the predominantly one-armed product [28].

Evidence for end-group structure was accounted by the ^{1}H NMR chemical shifts that appeared from $\delta = 6.5$–7.5 ppm, which could be assigned to the aromatic protons of PPO and the corresponding diols. Typical ^{1}H NMR spectra for assignations of one-armed or two-armed structure are shown in Fig. 1 using the biphenol case. The ^{1}H NMR spectrum of the two-armed PPO telechelics disclosed two typical signals for the aromatic protons of biphenol at $\delta = 7.55$ and 7.10 ppm (denoted as b′ and a′ in Fig. 1) as two doublets representing a symmetrical biphenol structure with a typical value (ca. 9 Hz) for ortho-coupling constant. On the other hand, the four doublet signals appeared at $\delta = 7.50$, 7.45, 7.08, and 6.89 ppm (denoted as c, b, d and a, respectively in Fig. 1) with same coupling constants were assigned to the aromatic protons of biphenol on the terminal side of PPO telechelics (**1c**). A minor portion (approximately 22.8%, based on integration intensities) of **1b** was also formed in **1c** and attempts at purification were unsuccessful due to their similar polarities. Other signals such as the methyl protons at $\delta = 2.1$ ppm (Ar-CH_3) and the aromatic protons at $\delta = 6.47$ ppm of internal PPO repeat unit (Ar-*H*, denoted as d′ in **1b** and f in **1c**), $\delta = 6.35$ ppm for aromatic protons of terminal PPO (Ar-*H*, e′ in **1b** and g in **1c**) and $\delta = 6.8$ ppm for aromatic protons of PPO next to the biphenyl ring (Ar-*H*, c′ in **1b** and e in **1c**), also agreed with the structure. We subsequently found that polymer **1c** would convert to **1b** when dissolving in polar solvents such as THF or $CHCl_3$ after heating at 60 °C for 106 h. Fig. 2 illustrates typical plot of data for the transformation of **1c** to **1b** monitored by ^{1}H NMR spectroscopy. Despite the slight change of chemical shift positions, the disappearance of the four doublet peaks at $\delta = 7.50$, 7.45, 7.08, and 6.89 ppm (c, b, d, and a of **1c**) along with the concomitant appearance of two new doublet peaks for biphenol protons at $\delta = 7.55$ and 7.10 ppm (b′ and a′ of **1b**) indicated that the transformation proceeded completely. Such transformation was also noted for **1a** wherein a symmetrical bisphenol-A structure with two new doublet peaks at $\delta = 7.26$ and 6.93 ppm was observed, after heating at 60 °C for 144 h. It was also found, when bisphenol-P was employed as copolymerizing monomers, that predominantly one-armed polymer was observed. Presumably the *ortho*-methyl-substituted bis(phenol)s are more reactive due to the electron-donating methyl groups and thus allow oxidative polymerization to take place on both ends affording the two-armed telechelics, whereas the *ortho*-unsubstituted phenol derivatives, bearing

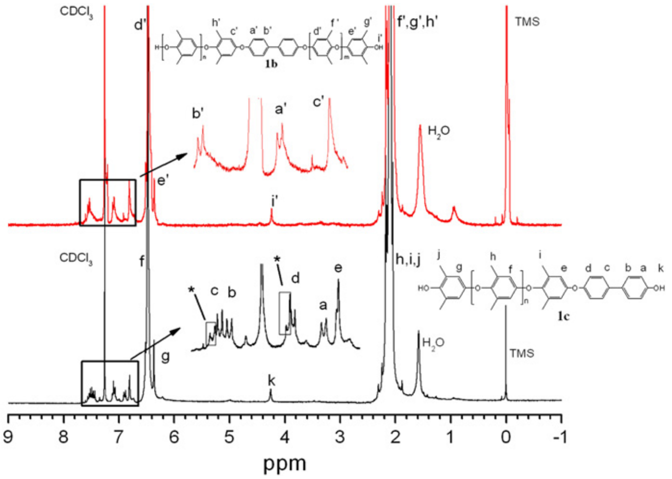


Fig. 1. A representative ^{1}H NMR spectra of two-armed telechelic PPO (**1b**, top) and its corresponding one-armed derivative of biphenol (**1c**, bottom). Note: "*" means peaks originate from a′ and b′ resonances of two-armed derivative **1b**.

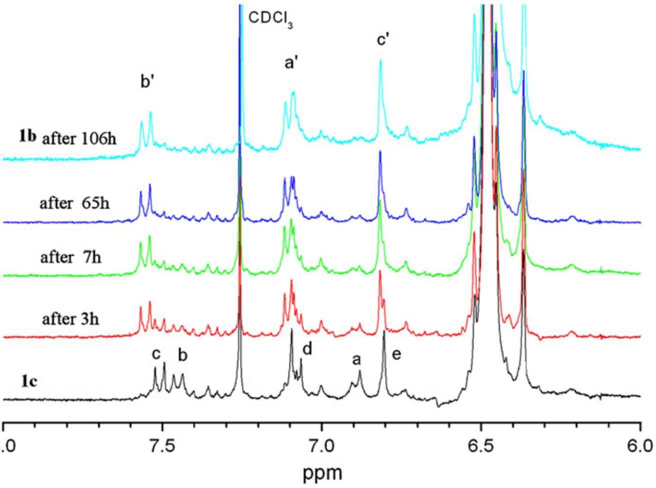


Fig. 2. ^{1}H NMR spectral evidence of structural transformation of **1c** to **1b** (60 °C in $CDCl_3$).

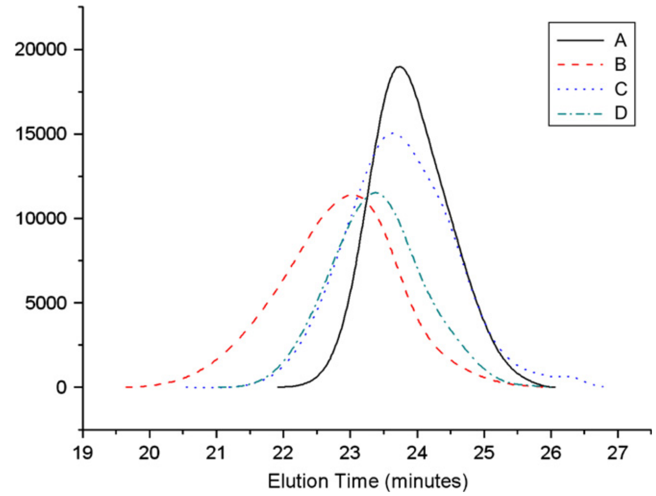


Fig. 3. GPC charts of polymers for transformation experiments (temperature = 60 °C, time = 48 h, solvent – chloroform). A: biphenol one-armed dihydroxyl telechelics, $M_n = 4994$, $M_w = 6480$. B: the two-armed product converted from A, $M_n = 10,939$, $M_w = 19,585$. C: bisphenol-A one-armed dihydroxyl telechelics $M_n = 4599$, $M_w = 9005$. D: the two-armed product converted from C, $M_n = 7297$, $M_w = 10,538$.

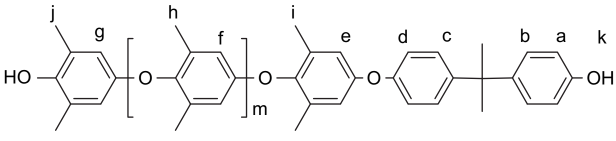
higher oxidation potential [29], are prone to incorporating as a tail end in PPO under the mild reaction conditions. This is consistent with the findings that when tetrachloro- and tetrabromobisphenol-A are employed as co-monomers under similar conditions, only pure PPO is formed.

3.2. Proposed mechanism for structure transformation of one-armed dihydroxyl telechelic PPOs

Although many PPO derivatives with various pendant groups instead of methyl groups have been synthesized [28], it is the first time, to the best of our knowledge, that the biphenol-type monomers can be directly incorporated into PPO backbone through oxidative polymerization using the method reported above. Furthermore, in contrast to the conventional catalysts which exhibited poor regioselectivity for *ortho*-unsubstituted phenols [28,30,31], no extensive crosslinking or highly branched products was observed in this study. It is thought that the aryloxy radicals formed initially by the oxidation of corresponding phenols are coordinated to copper–amine complex [32], which in turn block the *ortho* positions from attack due to the bulky dibutylamine ligands, and consequently result in the regiocontrolled selectivity at *para* positions. Interestingly, both the two-armed derivatives converted from **1a** and **1c** demonstrated a significant increase of the molecular mass (Fig. 3), which implied that the conversion from the one-armed to two-armed product might be a consequence of intermolecular redistribution of two one-armed compounds. It was further found that when the transformation reaction was carried out under nitrogen, no spectral change (^{1}H NMR) was observed after 72 h, indicating that molecular oxygen might serve as a radical initiator or hydrogen abstractor during the course of transformation reaction. In the transformation experiments, the polymers were heated at 60 °C in chloroform for 2 days under oxygen and the reaction mixtures were added to a 10-fold excess of methanol to precipitate the products. Decanting and removal of solvent left a small amount of brown residue, which was submitted to pyrolysis-gas chromatograph/mass spectra-selected ion monitoring (Py-GC/MS-SIM) spectral analysis. For selected ion identification, SIM mass spectral data of 186 *m*/*z* with similar fragmentation patterns of biphenol was detected, revealing the elimination of biphenol moieties during the transformation reaction of **1c**. Likewise, use of **1a** under identical conditions provided the bisphenol-A as the eliminated side products. The SIM spectral results are available in Supplementary data.

Although numerous articles have been published on the reaction mechanism of oxidative coupling reactions of dialkylphenols, the reaction mechanism for C–O coupling of phenoxy radicals is still not well recognized because of radical instability and reactivity. However, it is generally accepted that phenoxy radicals are involved in chain extension mechanism and coupling of two phenoxy radicals gives rise to the quinone–ketal intermediates [32]. Considering the role of oxygen and the elimination of diol co-monomer as side product in transformation experiments, the mechanism could be described as a series of steps of phenol oxidations, quinone–ketal coupling and redistribution processes as illustrated in Fig. 4. Initially, aryloxy radicals **I** and **II** were presumably generated by oxidation of **1c** with oxygen radicals (step 1). Compound **II** might form 2,6-dimethyl cyclohexadienone radical and reacted with **I** via C–O coupling reaction to give the quinine-ketal intermediate **III**, which, in turn, dissociated to a new radical pair, **IV** and **V** through redistribution process (step 2). The higher molecular weight compound **IV** could further react with another aryloxy radical and incorporated 2,6-dimethylphenol moieties using a similar sequence of quinone–ketal formation and dissociation and ultimately, led to the formation of higher molecular weight two-armed product with elimination of biphenol moiety (step 3).

Provided that polymers **1** and **2** are linear, the number average molecular weight can be also calculated from ^{1}H NMR spectra according to the intensity ratio of chemical shifts between methyl groups of PPO and the aromatic protons of the corresponding diols. For example, the calculated average molecular weight ($M_{n,\ \mathrm{H\ NMR}}$) of **1a** can be estimated using the following formula:



$$n\,(\mathrm{NMR}) = \frac{(h+i+j)/6}{(a+b+c+d)/8} \tag{1}$$

$$M_{n,\ \mathrm{H\text{-}NMR}} = n * (M_{wt}\,(\mathrm{DMP})\text{-}2) + M_{wt}\,(\text{bis-A})\text{-}2 + 2 * (M_{wt}\,(\text{end group}))$$

where n is the average degree of polymerization and M_{wt}(DMP) and M_{wt}(bis-A) are molecular weights of 2,6-dimethylphenol and bisphenol-A, and M_{wt}(end group) represents the corresponding end groups (H or glycidyl ether). Table 2

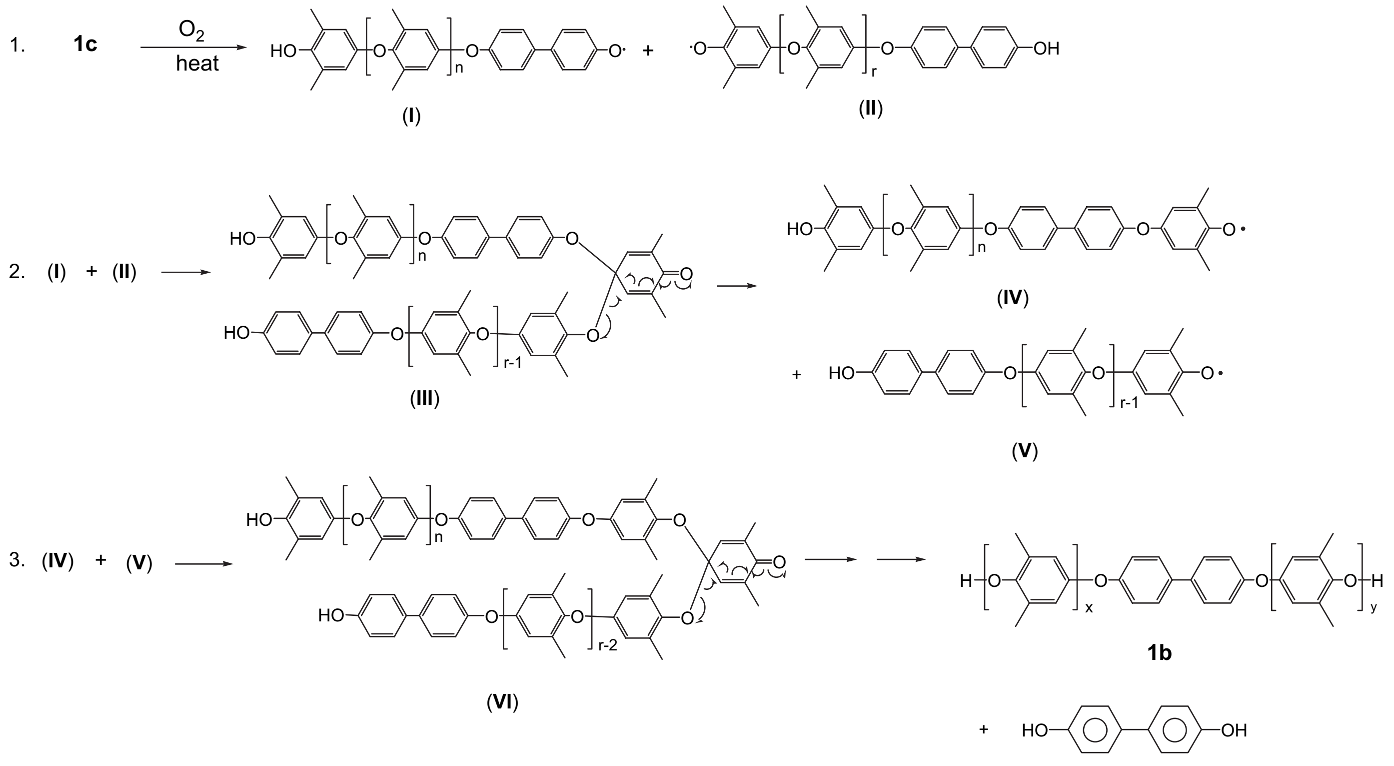


Fig. 4. Proposed mechanism for transformation from one-armed to two-armed products.

lists the M_n data by calculation using formula (1), and all the calculated values are within the range of 3200–11,000, which are in reasonable agreement with GPC measurements, although some deviations may arise from the difference of hydrodynamic volume calibrated from polystyrene standards.

3.3. Preparation and thermal properties of epoxide-terminated telechelic poly(2,6-dimethyl-1,4-phenylene oxide)s (2)

The epoxidations of **1** were carried out at 60 °C in epichlorohydrin and 2-methoxyethanol for 3 h using NaOH as catalyst and the resulting epoxidized polymers were investigated by ^{1}H, ^{13}C NMR, GPC, DSC and TGA. Fig. 5 illustrates representative ^{1}H NMR spectrum of two-armed epoxidized PPO derived from TMBPA (**2e**). The disappearance of phenolic chemical shifts (Ar-OH) at $\delta = 4.3$ ppm (denoted as h′ in **1e**) and the appearance of glycidyl terminal group at $\delta = 3.98$, 3.69, 3.35, 2.88, and 2.70 ppm which were assigned to methylene protons in the $-CH_2O$ group attached to PPO (denoted as e in **2e**), methyne proton of the epoxy group (f in **2e**) and the methylene protons of the epoxy group (g in **2e**), respectively indicated that complete epoxidation had occurred. Further structural verification of **2e** was confirmed by its ^{13}C NMR spectrum wherein three glycidyl ether carbon resonances at $\delta = 73.2$ ppm (methyleneoxy group between the phenolic and the epoxy group), 50.5 ppm (the methyne carbon of the epoxy group), and 44.5 ppm (the methylene carbon of the epoxy group) were observed. Also present in the ^{13}C NMR spectrum were three aliphatic carbon resonances

Table 2
Calculated average molecular weight and thermal analysis data for polymers **1** and **2**

Entry	1			2		
	$M_{n,\ H\ NMR}$	$T_{d,5\%}$ (°C)	$Y_{char}\%$ (800 °C)	$M_{n,\ H\ NMR}$	$T_{d,5\%}$ (°C)	$Y_{char}\%$ (800 °C)
a	4866	403.1	24.4	5095	355.1	39.3
b	3264	405.1	41.5	10,740	407.9	34.2
c	4122	419.7	26.8	4086	392.1	36.6
d	3609	435.1	26.1	3392	432.1	33.4
e	4910	394.8	28.6	4096	367.4	24.3

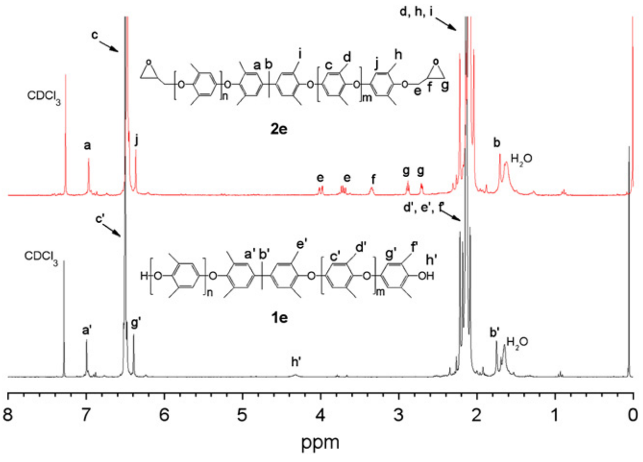


Fig. 5. A representative ^{1}H NMR spectra of two-armed hydroxyl telechelic PPO (**1e**, bottom) and its corresponding epoxide derivative of TMBPA (**2e**, top).

(at $\delta = 42.0$, 31.0, and 16.5 ppm) and other aromatic carbon resonances of TMBPA and PPO, which were in agreement with structure assignments of **2e**. The diglycidyl end-capped polymers generally displayed higher molecular weights than their hydroxyl precursors, which revealed certain extents of chain extension of epoxy resins with hydroxyl-telechelics during the course of reaction. The GPC chromatographs of all hydroxyl- and epoxide-terminated PPO polymers showed unimodal peaks of M_n ranged from 3500 to 14,000 with relatively low polydispersity of 1.2–2.7, which revealed a well-controlled polymerization process.

The glass transition behaviors of polymers **1** and **2** were examined with differential scanning calorimetry and the results are shown in Table 1. All of the hydroxyl and epoxy PPO telechelics exhibited a single glass transition temperature with good solubility and low viscosity in common organic solvents. No evidence for melting transitions was found, which suggested that all polymer derivatives are amorphous. The values of T_g for polymer **1** ranging from 181 to 193 °C are higher than those of conventional low molecular grades of PPO resins (PPO® SA120, $T_g = 163$ °C; $M_n = 2350$, $M_w = 6300$) indicating a decrement of free volume, probably because of the interactions induced by hydroxyl groups in telechelics structure. Another possible explanation for the increment of T_g could be the slightly higher molecular weight of polymers **1**. As compounds **2** generally possessed higher molecular weight than compounds **1**, a higher T_g would be expected for compounds **2** due to the fewer chain ends and a lower free volume. On the other hand, the loss of hydroxyl group in compounds **2** appeared to render up the intermolecular interactions between polar functional groups, which led to a decrease of T_g value. These two influences counteracted in different extents and might be explained for the random order in the comparison of T_g values between compounds **1** and **2**. Thermal stabilities of polymers **1** and **2** were examined by thermogravimetric analysis (TGA) with the 5 wt% decomposition temperature, $T_{d,5\%}$ and the results are listed in Table 2. The order of thermostability of polymers **1** and **2** is analogous to that of diol monomers in which the $T_{d,5\%}$ for bisphenol-P, bisphenol-A, biphenol and TMBPA descended at 252, 231, 230 and 215 °C, respectively. Presumably, the $-C_6H_4-C(CH_3)_2-C_6H_4-C(CH_3)_2-$ group of **1d**, which is very bulky, has a predominant effect in restricting skeletal torsional motion and chain conformation of the polymer. The biphenol polymers generally showed a better thermal stability than that of bisphenol-A system probably because of the rigid rod structure. Both polymers **1** and **2** displayed essentially a single degradation step and the degradation temperatures between 290 and 350 °C for polymer **2** could be ascribed to the decomposition of glycidyl ether group [33]. The blending and curing modifications of polymers **1** and **2** with novolac-type epoxy resins are ongoing and will be reported later.

4. Conclusions

Telechelic polymers with good thermal and chemical stabilities have attracted much attention for the potentials in the preparation of well-defined block and graft copolymers. In this study, we have successfully synthesized a new class of thermal crosslinkable polymer consisting of poly(2,6-dimethyl-1,4-phenylene oxide) as backbone with hydroxyl or glycidyl ether functional groups attached to both ends. Under the mild conditions, a variety of aromatic diols can be incorporated into the PPO structure by reacting with 2,6-DMP through oxidative polymerization with good yields and regioselectivity. The formation of novel one- or two-armed telechelic derivatives is principally related to the inductive effect of *ortho*-substituted groups of the co-monomers whereas the steric hindrance of dibutylamine ligands in catalyst system may preclude the *ortho*-unsubstituted phenols from branching or cross-linking reactions. Thermal analysis results indicate that the values of T_g for polymers **1** are generally higher than those of conventional low molecular grades of PPO and the incorporation of bulky or rigid rod structure enhanced the thermal stability of resulting polymers.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.polymer.2006.12.010.

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