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2,2',3,3',5,5'-Hexaphenyl-[1,1'-biphenyl]-4,4'-diols as Monomer Units for Redox Polymers: Synthesis and Polymerization Strategies

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2,2′,3,3′,5,5′-HEXAPHENYL-[1,1′-BIPHENYL]-4,4′-DIOLS AS MONOMER UNITS FOR REDOX POLYMERS: SYNTHESIS AND POLYMERIZATION STRATEGIES

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ABSTRACT

2,2′,3,3′,5,5′-Hexaphenyl-[1,1′,-biphenyl]-4,4′-diol (**Ib**), which is prepared by the oxidative coupling of 2,3,6-triphenylphenol, and its oxidized form (**IIIb**) constitute a powerful oxidation–reduction system. The oxidative coupling reaction is carried out in the presence of molecular oxygen with copper(I) chloride as a catalyst and butyronitrile as ligand and solvent. An approach to the incorporation of such biphenols into an oxidation–reduction polymer is presented.

INTRODUCTION

Highly hindered biphenols such as **Ia** and their oxidized forms constitute powerful oxidation–reduction systems (Scheme 1). In the oxidized form these compounds exist as intensely colored diphenoquinones **IIa** [1a] or biphenoxy radicals **IIIa** [1b, 1c] and are effective oxidizing agents, such as in the oxidative coupling of 2,6-disubstituted phenols to yield biphenols of type **Ia** and the conversion of diphenyl-methane into 1,1′,2,2′-tetraphenylethane [2]. Diphenoquinones, such as **IIa** (R = H), are formed as the C—C coupled by-product in the oxidative polymerization of 2,6-diarylphenols [3a] in the presence of molecular oxygen and a copper/amine catalyst, but they can be prepared as the principal product if the oxidation reaction is performed at 100°C using butyronitrile or benzonitrile as the ligand and solvent [3b]. The diphenoquinone **IIa** is very insoluble and precipitates out of the

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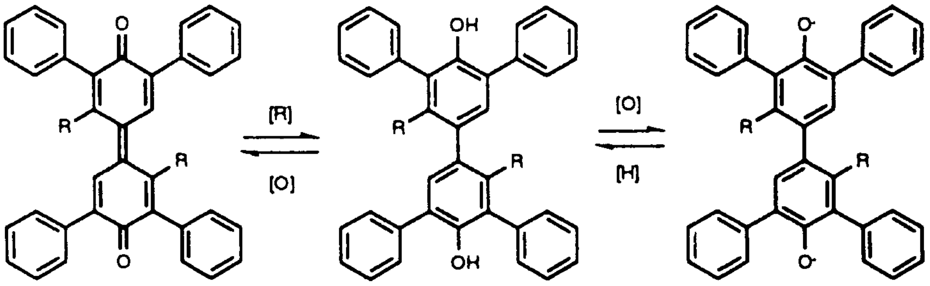

IIa R=H
IIb R=Ph

Ia R=H
Ib R=Ph

IIIa R=H
IIIb R=Ph
IIIc R=4-MeOPh

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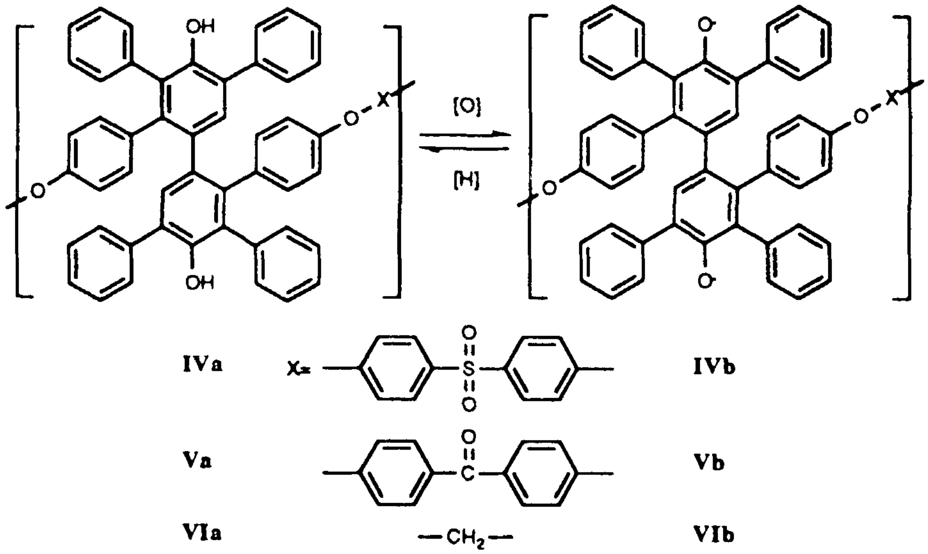
solution during the reaction as a very dark green solid which in solution is orange colored. The same oxidative coupling reaction conditions can be successfully applied for the conversion of 2,3,6-triphenylphenol into 2,2′,3,3′,5,5′-hexaphenyl-[1,1′-biphenyl]-4,4′-diol **Ib** [4]. In contrast to the diphenoquinones, the oxidized form of **Ib** is very soluble and because of the phenyl groups in the 2,2′-positions, which would not allow the central rings to be coplanar, it probably exists as the biphenoxy radical **IIIb** rather than the diphenoquinone **IIb**. Biphenoxy radicals of this type are more powerful oxidizing agents than the diphenoquinones, and they are presently under active study in our laboratory. In addition to good solubility, **Ib** would be expected to show high thermal and oxidative stability since it is completely aromatic. With these properties, highly sterically hindered biphenols such as **Ib** should be interesting redox monomer units for the preparation of oxidation-reduction polymers. Redox resins containing hydroquinone or other redox systems have been prepared [5a], but despite patents describing their applications, these polymers have seen little commercial utility, probably because the materials that have been synthesized are not very thermally stable and have relatively low redox potentials [5b].

A polymer containing these highly hindered aromatic biphenols as repeating units linked by diphenylsulfone or benzophenone moieties or a methylene bridge (Scheme 2) should have high stability and should be usable at elevated temperatures and be chemically stable. The preparation of a redox polymer of this type is the object of the investigations we report in this paper. The synthesis of a functionalized 2,2′,3,3′,5,5′-hexaphenyl-[1,1′-biphenyl]-4,4′-diol and its polymerization to polymers **IVa**, **Va**, and **VIa** is described.

EXPERIMENTAL

General Procedures

Toluene and NMP were distilled before use from calcium hydride. K_2CO_3 was dried in an oven at 130°C. 4,4′-Dichlorodiphenylsulfone and 4-methoxycinnamaldehyde were obtained from commercial suppliers. Melting points were determined



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in a Fisher John's melting point apparatus and are uncorrected. Infrared spectra were recorded as solutions in $CHCl_3$ on an Analet AQS-60 IRFT spectrometer. UV spectra were obtained on an Unicam-SP-800 instrument. ^{1}H-NMR and ^{13}C-NMR spectra were determined on either a 200 MHz or a 300 MHz XL Varian NMR spectrophotometer using chloroform-*d* as a solvent containing tetramethylsilane as the internal standard. Chemical shifts are reported in parts per million from tetramethylsilane on the δ scale. Microanalyses were done at Guelph Chemical Laboratories Ltd., Ontario, Canada. Mass spectra were recorded on a Du Pont 21-492 B mass spectrometer. HPLC analysis was performed on a Milton Roy CM 4000 instrument. Molecular weights were determined by gel permeation chromatography using polystyrene as a standard with chloroform as solvent on a Waters 510 GPC with a UV detector and with four μ-Styragel columns (500, 10^4, 10^5, and 100 Å) in series. Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Seiko SSC5200 thermal analysis system (TG/DTA 220 and DSC 220) with heating rate 10 or 20°C per minute.

2,2′,3,3′,5,5′-Hexaphenyl-[1,1′-biphenyl]-4,4′-diyloxy (IIIb)

A suspension of 2,2′,3,3′,5,5′-hexaphenyl-[1,1′-biphenyl]-4,4′-diol (**Ib**, 0.75 g, 1.2 mmol) and Ag_2O (1.12 g, 0.048 mol) in chlorobenzene (50 mL) was placed in a 100-mL screw-cap flask protected from light, and the mixture was shaken in a Vibrax apparatus for 20 hours. The resulting purple suspension was filtered under vacuum through a thin layer of Celite. The chlorobenzene was evaporated and the residue was then collected and dried under reduced pressure to give **IIIb**; mp 212–214°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.90–7.37 (m, 32 H, PhH); UV-Vis (C_6H_5Cl) λ_{max} 294, 508 nm (ϵ 13,600, 49,300). MS (EI) *m/e* 638 (M^+).

Analysis. Calculated for $C_{48}H_{32}O_2$: C, 90.28; H, 5.02%. Found: C, 89.80, H 5.10%.

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The purple solid could not be recrystallized since it is extremely soluble in most organic solvents in which it gives intensely colored purple solutions. This is in strong contrast to 3,3′,5,5′-tetraphenyldiphenoquinone obtained from 2,6-diphenylphenol which is extremely insoluble in most solvents.

3-(4-Methoxyphenyl)-2,6-diphenylcyclo-2-hexenone (**IXb**)

trans-4-Methoxycinnamaldehyde (**VIIb**, 25.00 g, 0.142 mol), 1,3-diphenylacetone (**VIII**, 29.90 g, 0.142 mol), and diethylamine (20 mL) were stirred magnetically in a 250-mL round-bottom flask under a nitrogen atmosphere. The reaction proceeded exothermically to form a thick melt which then solidified to form a yellow solid. The solid was triturated with ethanol and then filtered. The resulting solid was magnetically stirred in hot ethanol for 3 hours. After cooling, the solid was filtered and dried in a vacuum oven to yield an approximately equimolar mixture of two isomeric compounds (48.1 g, 0.136 mol, 96% yield). The mixture was used without separation of the isomers for the next step. Recrystallization from ethyl acetate–petroleum ether yielded a single isomer **IXb**: mp 168–170°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.87–2.97 (m, 2 H), 3.60–3.80 (m, 2 H), 3.74 (s, 3 H), 4.05 (dd, J = 1.5, 12 Hz, 1 H), 6.70–6.75 (d, 2 H), 7.00–7.55 (m, 12 H). IR ($CDCl_3$) 1674 (C=O), 1611 (conjugated C=C), 1250 cm^{-1} (CH_3O); MS (EI) *m/e* 354 (M^+).

Analysis. Calculated for $C_{25}H_{15}O_2$: C, 85.29; H, 5.68%. Found: C, 84.98; H, 6.02%.

3-(4-Methoxyphenyl)-2,6-diphenylphenol (**Xb**)

In a three-neck round-bottom flask equipped with a condenser, a thermometer, and a nitrogen inlet were placed **IXb** (20.00 g, 56 mmol) and 1.30 g of 5% Pd on charcoal. This mixture was melted and heated up to 250–260°C for 40 minutes while it was stirred magnetically. After 1 hour the temperature was brought down to room temperature and approximately 300 mL hot ethyl acetate was added. This mixture was stirred magnetically to ensure that all the product was dissolved and then filtered while hot. The catalyst collected on the filter was washed several times with small portions of hot ethyl acetate. The solutions were combined and evaporated, and the residual solid was recrystallized to form a light pink solid. Drying in the vacuum oven for several hours yielded **Xb** (16.30 g, 46 mmol, 82% yield): mp 173–175°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 3 H, CH_3O), 5.32 (s, 1H, OH), 6.70 (d, J = 8.8 Hz, 2 H), 7.02 (d, J = 8.8 Hz, 2 H), 7.05–7.60 (m, 12 H, ArH); IR ($CDCl_3$) 3536 cm^{-1} (OH, free) 1247 cm^{-1}. MS (EI) *m/e* calculated 352.1463, found 352.1479; 352 (M^+).

Analysis. Calculated for $C_{25}H_{20}O_2$: C, 85.29; H, 5.68%. Found: C, 84.94; H, 6.02%.

2,2′-Bis(4-methoxyphenyl)-3,3′,5,5′-tetraphenyl-[1,1′-biphenyl]-4,4′-diol (**XIa**)

The phenol **Xb** (16.00 g, 46 mmol), butyronitrile (200 mL), and CuCl (1.60 g, 14 mmol) were placed in a 500-mL three-neck flask equipped with condenser and mechanical stirrer. This mixture was heated up to 100°C and stirred vigorously while O_2 was bubbled into the flask. The solution gradually changed to a deep violet color. After 5 hours the mixture was allowed to cool down to room temperature and filtered. The solid was dissolved in hot chloroform and filtered while hot. The catalyst collected was washed with hot chloroform several times. The solvent was evaporated in a Rotavap and the residue was recrystallized from a mixture of methanol and chloroform. The violet product was a mixture of biphenoxy radical **IIIb** and biphenol **Ib**. The resulting product was reduced with a small amount of hydrazine in chloroform at reflux for 6 hours. The solvent was evaporated and the solid was recrystallized from $CHCl_3$-MeOH to give **XIa** (73% yield); mp 305-307°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 6 H CH_3O), 5.05 (s, 2 H, OH), 6.50-7.50 (m, 30 H, ArH); ^{13}C (300 MHz, $CDCl_3$) δ 58.34, 115.54, 128.91, 130.13, 130.38, 131.31, 131.41, 131.75, 132.50, 134.24, 135.03, 135.57, 136.11, 136.77, 138.84, 140.88, 143.14, 151.10, 160.34; IR ($CDCl_3$) 3534 cm^{-1} (free OH), 1245 cm^{-1} (CH_3O). MS (EI) *m/e* 702 (M^+).

Analysis. Calculated for $C_{50}H_{38}O_4$: C, 85.47; H, 5.47%. Found: C, 84.90; H, 5.49%.

2,2′-Bis(4-methoxyphenyl)-3,3′,5,5′-tetraphenyl-[1,1′-biphenyl]-4,4′-diyloxy (IIIc)

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A suspension of biphenol **XIa** (0.50 g, 0.71 mmol) and Ag_2O (0.65 g, 2.94 mmol) in chlorobenzene (50 mL) was shaken in a screw-cap 100-mL flask protected from light in an Ika-Vibrax-VXR apparatus for 24 hours. The resulting purple suspension was filtered through a thin layer of Celite and the solvent evaporated under reduced pressure. The solid recovered was dried under reduced pressure to give the oxidized form of **XI** (**IIIc**) as a dark purple crystalline powder; mp 200-202°C, ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.84 (s, 6 H, CH_3O), 6.90-7.28 (m, 30 H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 55.35, 114.09, 131.81, 134.16, 135.46, 135.38, 136.30, 141.28, 144.11, 147.44, 127.02, 127.40, 127.73, 128.44, 129.45, 130.60, 132.3, 159.35, 184.02; UV-Vis (C_6H_5Cl) λ_{max} 292, 528 nm (ϵ 31,500, 27,800); IR ($CDCl_3$) 1250 cm^{-1} (OCH_3). MS (EI) *m/e* 700 (M^+).

Analysis. Calculated for $C_{50}H_{36}O_4$: C, 85.71; H, 5.14%. Found: C 85.78; H, 5.49%.

2,2′-Bis(4-hydroxyphenyl)-3,3′,5,5′-tetraphenyl-[1,1′-biphenyl]-4,4′-diol (XIb)

In a round-bottom flask equipped with a drying tube was placed the biphenol **XIa** (11.65 g, 17 mmol) and methylene chloride (20 mL). The suspension formed was stirred at 0°C under a nitrogen atmosphere while a 1 M solution of BBr_3 (85 mL, 85 mmol, 5.7 equiv) was injected into the reaction mixture through a septum. The reaction was allowed to warm up to room temperature after 40 minutes. The mixture, which turned into a thick gel, was poured into ice and stirred magnetically. An additional amount of methylene chloride was added to facilitate phase separation. The partially emulsified organic phase was filtered and the recovered solid was washed on the filter with methylene chloride. The recovered product (10.20 g, 15 mmol, 88% yield) was 95% pure HPLC. Recrystallization from ethyl acetate-hexane and extensive drying yielded **XIb** (82.0%), mp 309-311°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 4.82 (s, 2 H, OH, unhindered), 5.12 (s, 2 H, OH, hindered), 6.43 (d, 8 H), 7.05-7.56 (m, 22 H, ArH); IR $CDCl_3$), 3533-3593, 3600, 3628 cm^{-1}, intermolecular bonded OH (unhindered), free OH (hindered). MS (EI) *m/e* calculated for $C_{48}H_{34}O_4$: 674.2457. Found: 674.2460.

2,2′-Bis(4-acetoxyphenyl)-3,3′,5,5′-tetraphenyl-[1,1′-biphenyl]-4,4′-diol Diacetate (**XIc**)

The tetraphenol **XIb** (2.69 g, 4 mmol) and potassium acetate (1.70 g, 18 mmol) were refluxed in acetic anhydride (30 mL) for approximately 4 hours. The mixture was first cooled under a tap and further cooled by the addition of some ice, and was then poured into a beaker containing 450 mL water and stirred for approximately 30 minutes. The precipitate which formed was recovered and then washed several times with water and dried for several hours to give the tetraacetate **XIc** (2.80 g, 3.32 mol, 83%), which could be recrystallized from toluene-hexane; mp 310–313°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.61 (s, 3 H, $OCOCH_3$ hindered), 2.20 (2, 3 H, $OCOCH_3$, unhindered), 6.50–6.85 (m, 8 H), 6.90–7.70 (m, 22 H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 20.21 ($OCOCH_3$, unhindered), 21.11 ($OCOCH_3$, hindered), 119.18, 126.51, 127.08, 127.53, 128.29, 128.92, 130.50, 132.50, 133.68, 133.95, 135.34, 135.58, 136.27, 137.31, 138.56, 139.75, 145.0, 148.77, 168.91; IR ($CDCl_3$) 1758 cm^{-1} (C=O, four acetates overlapped). MS (EI) *m/e* calculated for $C_{56}H_{42}O_8$: 842.2879. Found: 842.2878.

2,2′-Bis(4-hydroxyphenyl)-3,3′,5,5′-tetraphenyl-[1,1′-biphenyl]-4,4′-diol Diacetate (**XII**)

To a 250-mL round-bottom flask containing a magnetic stirring bar was added tetraacetate **XIc** (15.00 g, 17.8 mmol), chloroform (150 mL), methanol (50 mL), and piperidine (15 mL) to allow selective deprotection of the less hindered acetate groups. The mixture was stirred for 4 hours at reflux. After cooling, an additional 100 mL chloroform was added and the mixture was extracted with 100 mL water containing a small portion of hydrochloric acid, washed with water (2 × 100 mL), and dried over magnesium sulfate. The solvent was evaporated and the solid recrystallized from chloroform-hexane (90% yield): **XII**, mp 295–297°C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.50 (s, 6 H, $OCOCH_3$, hindered), 5.12 (s, 2 H, biphenol), 6.09–7.42 (m, 30 H, ArH); ^{13}C NMR (300 MHz, $CDCl_3$) δ 20.09 ($-OCOCH_3$), 144.48 ($C-OCOCH_3$), 156.39 (C—OH), 171.08 ($-OCOCH_3$); IR ($CDCl_3$) 1756 cm^{-1} (C=O, acetates), 3532 cm^{-1} (OH, biphenol); MS (EI) *m/e* 759 (M^+).

Analysis. Calculated for $C_{52}H_{38}O_2$: C, 82.30; H, 5.28%. Found: C, 82.04; H, 5.28%.

Polymer Preparation

Poly(ether Sulfone) (**IVa**) and Poly(ether Ketone) (**Va**)

The diacetoxybiphenol **XII** (3.00 g, 3.95 mmol), 4,4′-difluorodiphenylsulfone (1.01 g, 3.95 mmol), NMP (16 mL), and toluene (10 mL) were placed in a 50-mL three-neck flask fitted with a Dean-Stark trap. While the reaction mixture was kept under nitrogen atmosphere at elevated temperature, potassium carbonate (0.71 g, 5.14 mmol) was added and the reaction was allowed to reflux. The water was removed at the azeotrope temperature and the reaction was continued for 10 hours.

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After cooling, chlorobenzene (10 mL) was added and the solution was filtered through a thin layer of Celite. The filtrate was precipitated in methanol (300 mL) and water (50 mL) containing a small portion of hydrochloric acid, and the solid was collected by filtration. The polymer was dissolved in chloroform (20 mL) and reprecipitated in methanol (300 mL). The polymer was separated and dried in a vacuum oven at 120°C for 12 hours (85% yield). The polymer contains both the protected acetate groups and the deprotected acetate groups which were characterized by NMR: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.64 (s, 6 H, $-OCOCH_3$), 5.14 (s, 2 H, $-OH$), 6.45–7.79 (m, 38 H, PhH).

The resulting polymer (1.50 g) was dissolved in a 50-mL round-bottom flask in dioxane (25 mL) and treated with an excess of hydrazine under nitrogen. The mixture was stirred at room temperature for 24 hours. The solution was extracted with chloroform and washed with water (3 × 100 mL) containing hydrochloric acid to give **IVa**. The solution was precipitated in methanol (200 mL), filtered, and dried at 120°C for 20 hours under vacuum. ^{1}H NMR (200 MHz, $CDCl_3$) δ 5.16 (s, 2 H, $-OH$), 6.41–7.80 (m, 38 H, PhH).

Va was prepared in an identical fashion.

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Polyformal VIa

Into a 100-mL round-bottom flask equipped with a magnetic stirrer and condenser were charged diacetatebiphenol **XII** (2.00 g, 2.64 mmol), dibromomethane (1.10 g, 6.33 mmol), and NMP (6 mL). The reaction was carried out under nitrogen atmosphere. After the solution became a homogeneous solution, potassium hydroxide (0.32 g, 5.77 mmol) was added and the reaction was gradually heated up to 95°C and kept there for 7 hours. The mixture was allowed to cool to room temperature and filtered through Celite. The filtrate was precipitated in methanol (200 mL) and water (50 mL) containing hydrochloric acid. The polymer was dissolved in chloroform and reprecipitated in methanol. The resulting polymer was removed by filtration and dried at 120°C in a vacuum oven. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.63 (s, 12 H, overlapped $-OCOCH_3$ and $C(CH_3)_2$), 5.31 (s, 2 H, CH_2), 6.45–7.81 (m, 34 H, PhH).

The reduction reaction was carried out with 1.00 g of the resulting polymer, an excess of hydrazine, and 15 mL of dioxane at room temperature for 24 hours under nitrogen atmosphere. The mixture was extracted with chloroform and washed with water (3 × 100 mL) containing a small portion of HCl. The polymer **VIa** was extracted and precipitated in methanol and dried at 120°C for 24 hours in a vacuum oven (89% yield). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.63 (s, 6 H, $C(CH_3)_2$), 5.12 (s, 2 H, $-OH$), 5.35 (s, 2 H, CH_2), 6.42–7.79 (m, 34 H, PhH).

Oxidation of Polymers

IVa dissolved in chlorobenzene was oxidized with fresh Ag_2O (8 mmol/g of polymeric material) in a sealed bottle protected from light by shaking in a Vibrax apparatus for 24 hours. The purple suspension was filtered through Celite and concentrated before precipitating in MeOH. The precipitate was left to coagulate for a few hours and then collected. The oxidized polymer **IVb** was recovered in quantitative yield. UV-Vis (THF) λ_{max} 290, 530 nm (ϵ 30,600, 6360). ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.50–7.80 (ArH).

RESULTS AND DISCUSSION

Preparation of Monomers and Polymers

The preparation of 2,3,6-triphenyphenol (**Xa**), the starting material for the preparation of **Ib**, has been previously described [6, 7]. It consists of the condensation of 1,3-dibenzylketone (**VIII**) with cinnamaldehyde (**VIIa**) in the presence of diethylamine to give the intermediate cyclohexenone followed by a dehydrogenation reaction (Scheme 3). This same strategy would also be convenient for the preparation of a 3-(4-methoxyphenyl) 2,6-diphenylphenol (**Xb**) which could then be dimerized by oxidative coupling to give the biphenol **XIa**. A 4-methoxy substituent seemed an appropriate choice since the methoxy group would most likely be stable to the conditions of the subsequent C—C coupling reaction and could be easily removed prior to the polymerization reaction.

The condensation reaction of *trans*-4-methoxycinnamaldehyde (**VIIb**) with 1,3-dibenzylketone (**VIII**) in the presence of diethylamine afforded a mixture of two compounds with very close retention times formed in approximately equal amounts (HPLC) in an overall yield of 96%. One isomer was obtained pure by fractional recrystallization (Scheme 3). The mixture of isomers **IXb** was aromatized by heating at 250-260°C with (5%) Pd on charcoal to give 2,6-diphenyl-3(4-methoxy)phenylphenol (**Xb**) in approximately 83% yield after recrystallization from ethyl acetate.

The oxidative coupling of **Xb** gave **XIa** in 73% yield (Scheme 4). The reaction was catalyzed by CuCl(I) in butyronitrile heated at 95°C under vigorous stirring with O_2 bubbling through the reaction mixture. As the reaction proceeded, the mixture became purple due to the formation of the biphenoxy radical which was formed along with **XIa**. Addition of hydrazine at the end of the reaction converted

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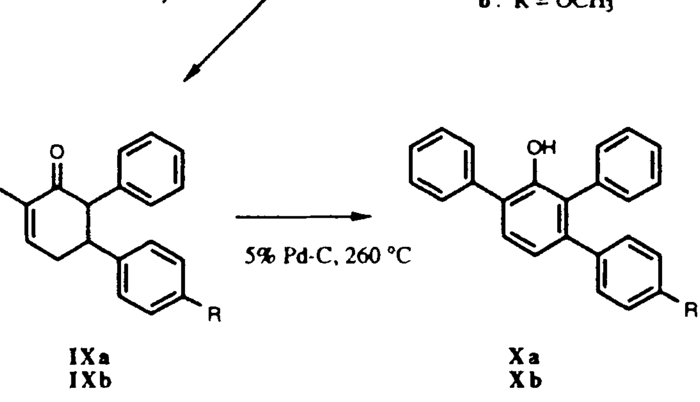

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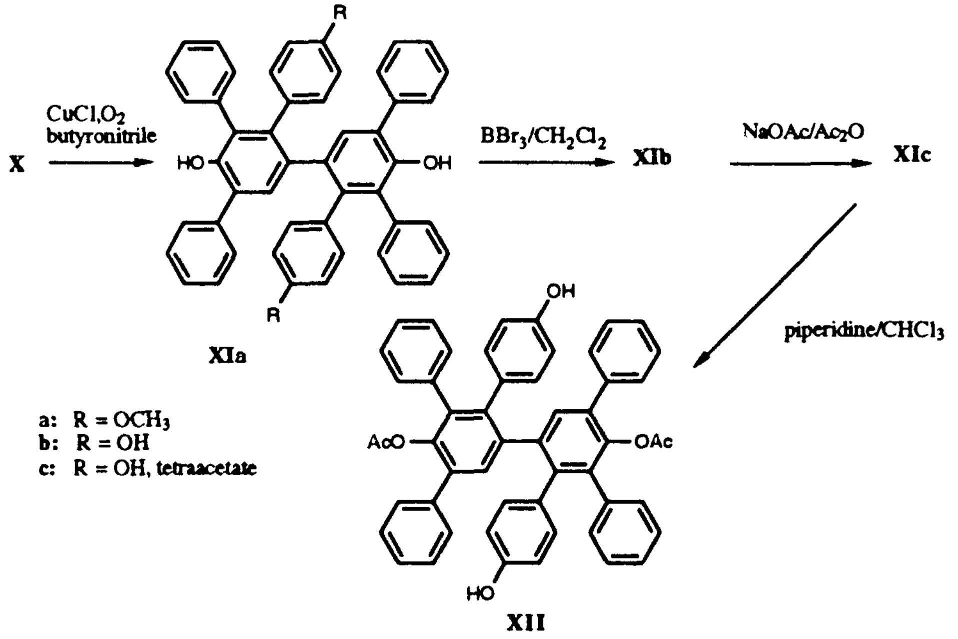

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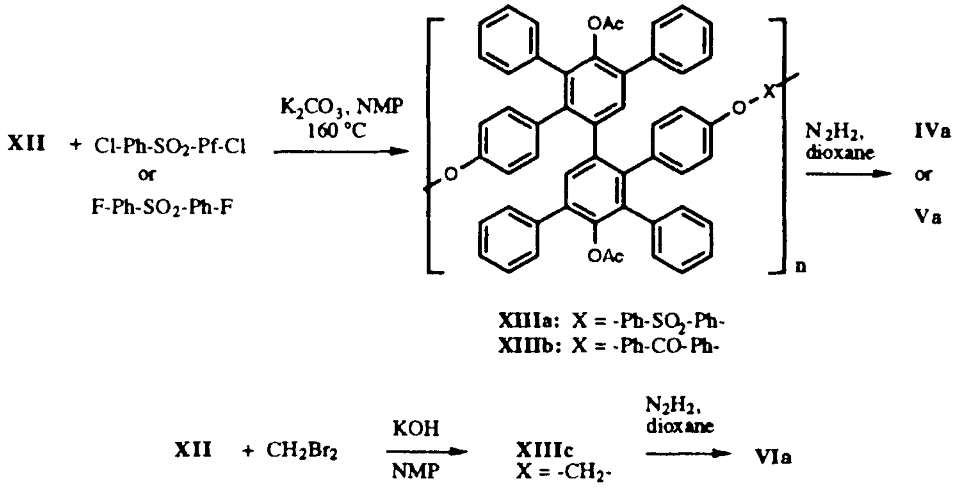
the oxidized form into the biphenol **XIa**. Cleavage of the methoxy group of **XIa** was performed with 5.7 mol BBr_3 in CH_2Cl_2, the stirred mixture was kept at 0°C for 30 minutes, and then for 30 minutes at room temperature to obtain **XIb**. There was some difficulty in achieving a complete reaction even when up to 6.50 mol BBr_3 were used. Similar difficulty has been found in removing this functionality from polymers in which it has been used to protect phenolic groups [8]. Protection of tetraphenol **XIb** with acetic anhydride in the presence of potassium acetate afforded the tetraacetoxyhexaphenylbiphenol **XIc** in 82% yield after recrystallization from ethyl acetate. The less hindered acetate groups of the tetraacetate derivative **XIc** could be selectively deprotected by using piperidine as a base. The resulting diacetate **XII** was obtained in 90% yield. The separated ^1H and ^{13}C chemical shifts of the unhindered phenolic groups and hindered acetate groups are clearly shown. The unhindered phenolic hydroxyl signals appeared at 5.12 ppm while the signal due to unhindered acetate groups disappeared and the hindered acetate signal remained at 1.50 ppm.

We attempted to polymerize the tetraphenol **XIb** directly by reaction with 4,4′-difluorodiphenylsulfone or 4,4′-difluorobenzophenone in NMP with potassium carbonate to give the poly(aryl ether) or by the reaction with methylene bromide to give the polyformal. Although the unhindered phenolic groups are considerably more reactive than the hindered phenolic groups, there is still enough reactivity so that branching and eventually crosslinking occurs, so that we were not successful in making high molecular weight linear polymers. We recently demonstrated the synthesis of poly(aryl ether)s using masked biphenols in which the phenolic groups are protected as acetates or carbamates which are hydrolyzed during the reaction to generate the phenoxide ions *in situ* [9]. Direct polymerization of the tetraacetate **XIc** under these conditions on the expectation that the unhindered acetate groups



SCHEME 5.

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would be selectively deprotected was partially successful; however, high molecular weight polymers were not obtained. The polymerization of the selectively protected diacetate **XII** with 4,4′-difluorodiphenylsulfone or 4,4′-difluorobenzophenone carried out in NMP with potassium carbonate at 165°C for 30 hours (Scheme 5) was much more successful. During the reaction the acetate groups were partially deprotected. The resulting polymers **XIIIa** and **XIIIb** were completely deprotected with hydrazine to give polymers (85% yield) **IVa** and **Va**.

The polyformal **XIIIc** was prepared from **XII** with an excess of CH_2Br_2 and potassium hydroxide in NMP at 95°C for 7 hours. In this case, deprotection of the acetate groups did not occur during the polymerization reaction.

Properties of the polymers **IVa**, **Va**, and **VIa** are listed in Table 1. The polymers have excellent solubility at room temperature in organic solvents such as methylene chloride, NMP, and DMSO. Inherent viscosities and weight-average molecular weights determined by GPC vs polystyrene standards are 0.11–0.23 dL/g and 10,000–56,800, respectively. The biphenoxy radicals and the polymeric radicals are intensely colored materials. The UV-Visible absorptions of reduced (**IIIb**, **XIa**), and oxidized (**IIIb**, **XI**) monomers and the reduced (**IVa**, **Va**) and oxidized (**IVb**, **Vb**)

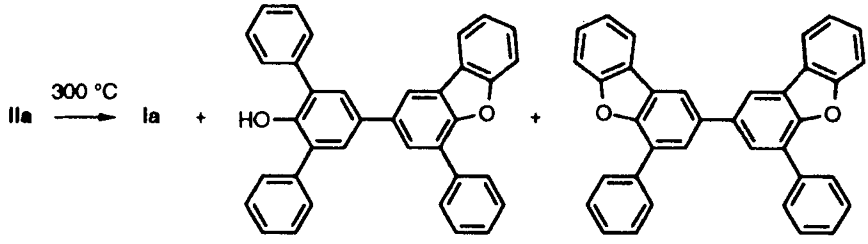
TABLE 1. Properties of Polymers

Polymer	η_{inh}[a]	MW × 10^3[b]	T_g, °C[c]	TGA (air/N_2)[d]
IVa	0.21	40.0	259	515/518
Va	0.23	56.8	251	525/526
VIa	0.11	10.0	226	477/481

[a] Inherent viscosity in $CHCl_3$ (0.5 g/dL) at 25°C.
[b] GPC by using polystyrene as a standard.
[c] DSC at 20°C/min.
[d] TG/DTA 5% weight loss at 10°C/min.

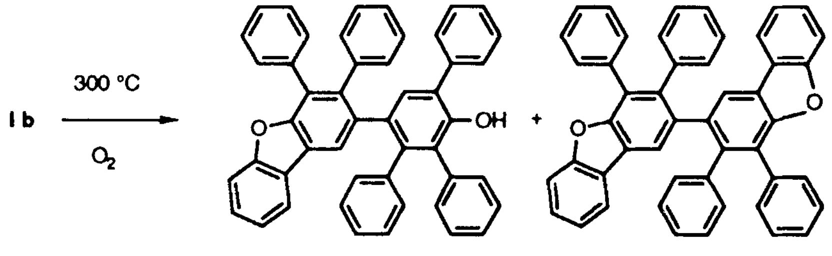
polymers are shown in Table 2. The reduced forms, which are colorless, show one band at 290–300 nm, which is assigned to a π–π^* transition, while the oxidized forms, which are the color of potassium permanganate in solution, show two bands at 290 and 500–530 nm, which are π–π^* and n–π^* transitions. The n–π^* transitions of **IVb** and **Vb** are shifted about 30 nm compared to **IIIb**, due to the electronic effect of the methoxy group.

The glass transition temperatures of **IVa**, **Va**, and **VIa** are in the 226–259°C range, and the polymers have excellent thermoxidative stability in the 477–526°C range (5% weight loss) in air and in nitrogen.



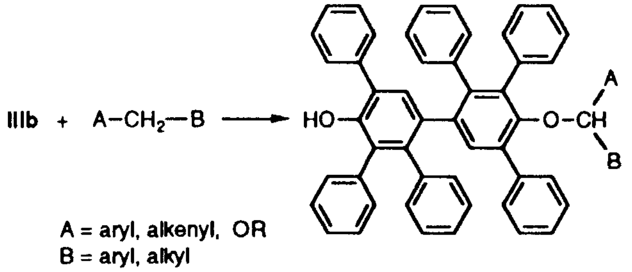
XIV **XV**

(1)



XVI **XVII**

(2)



A = aryl, alkenyl, OR
B = aryl, alkyl

XVIII

(3)

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TABLE 2. UV-Visible Absorptions and Absorption Coefficients[a]

Polymer	λ_{max}, nm	$\epsilon_{mol} \times 10^{-4}$
IIIa	302	1.44
IIIb	294, 508	1.36, 4.93
IVa	290	3.23
IVb	290, 530	3.06, 0.64
Va	290	3.81
Vb	292, 530	4.02, 0.63
XIa	290	2.61
XI	292, 528	3.15, 2.78

[a] Measured in chlorobenzene at room temperature.

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Polyphenols are generally not considered to be thermoxidatively stable materials. Therefore, it is surprising that the stability of these materials as measured by TGA in air is comparable to the stability in nitrogen. We have previously shown that when **Ia** is heated to 300°C, three products are formed (Eq. 1). The dibenzofuran-containing molecules **XIV** and **XV** must result from the attack of a phenoxy radical on the pendant phenyl groups. A similar reaction occurs when the biphenoxy radical **IIIb** is heated, and we have also determined that at 300°C in the presence of air the biphenol **Ib** is slowly oxidized to give the monodibenzofuran **XVI**- and the bisdibenzofuran **XVII**-containing molecule as the principal products. The thermoxidative stability of polymers **IVa**, **Va**, and **VIa** is therefore explained because the principal reactions taking place at the elevated temperatures are the intramolecular ring closure reactions to give the stable dibenzofuran moieties in the polymer. We have also demonstrated that the biphenoxy radical **IIIb** reacts cleanly with a variety of benzylic and allylic compounds as well as simple ethers to give the corresponding ethers or acetals **XVIII** (Eq. 3), thus giving a facile method for the functionalization of methylene groups which can be extended to the use of the polymeric phenoxy radicals **IVb**, **Vb**, and **VIb**. The reactions are very easily followed since the intense permanganate color of the biphenoxy radical disappears to give colorless or pale yellow reaction mixtures. This work will be discussed in detail in a subsequent paper.

CONCLUSIONS

High molecular weight poly(aryl ether)s containing 2,2′,3,3′,5,5′-hexaphenyl-[1,1′-biphenyl]-4,4′-diols as monomer units have been synthesized. The diol moieties in the polymer undergo reversible oxidation–reduction reactions and therefore represent a new class of redox polymers. Model reactions have shown that the oxidized form of diols of this type exist as phenoxy radicals which are powerful oxidizing agents. Future work will concentrate on the uses of these redox polymers.

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