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Crosslinkable poly(phenylene oxide) containing pendent 1,2-diphenylcyclopropane groups

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Crosslinkable poly(phenylene oxide)s containing pendent 1,2-diphenylcyclopropane groups have been synthesized by oxidative polymerization from four new phenols containing the 1,2-diphenylcyclopropane group. The monomers were prepared by base-catalysed decomposition of the corresponding hydroxy-substituted 3,5-diphenyl-2-pyrazolines, which were the products of the reaction between hydroxy-substituted chalcones and hydrazine monohydrate. Characterization of and crosslinking studies on these polymers were carried out utilizing differential scanning calorimetry, thermogravimetric analysis, gel permeation chromatography and nuclear magnetic resonance. The polymers can be thermally cross-linked when heated to 350°C and the glass transition temperatures (T_g) of the polymers increase after crosslinking. The resulting crosslinked networks are insoluble in all solvents examined. Thermogravimetric analysis shows that no significant weight loss accompanies the crosslinking reaction.

(Keywords: poly(phenylene oxide); 1,2-diphenylcyclopropane; crosslinking)

INTRODUCTION

In 1959, a novel synthesis of a high-molecular-weight linear poly(phenylene oxide) (PPO® resin) by the oxidative polymerization of 2,6-dimethylphenol was reported[1,2]. PPO has excellent mechanical properties along with exceptional electrical properties, such as low dielectric constant and a low dielectric dissipation factor, as well as relatively good heat resistance[3]. PPO has excellent resistance to acids, alkalis and hot water, and would be an excellent candidate as a material for printed circuit-boards except that it has poor resistance to solvents, particularly aromatic hydrocarbons and chlorinated hydrocarbons, in which it is soluble.

Crosslinkable poly(phenylene oxide) copolymers containing allyl groups have been synthesized by copolymerization of 4-bromo-2,6-dimethylphenol with 2-allyl-4-bromo-6-methylphenol[4]. The polymers containing the allyl groups can be thermally cured to give insoluble materials. In addition the alkylene groups of the resulting polymers can be epoxidized, which results in polymers that can be cured in the presence of amines or anhydrides as catalysts.

More recently allyl- and propargyl-substituted poly(phenylene oxide)s have been synthesized by metallation of PPO with butyllithium followed by reaction with allyl chloride or propargyl chloride. The resulting resins were combined with triallyl isocyanurate and cured by the reaction with peroxides[5].

Curable resins have also been synthesized by the introduction of amino substituents on PPO, synthesized by nitration of PPO followed by reduction. These materials can be combined with epoxy resins[6]. PPO has been combined with various epoxy resins and the mixtures have been cured[7], and blends with diallyl phthalates have been cured in the presence of a free-radical catalyst[8].

Our efforts have been directed towards the synthesis of crosslinkable poly(phenylene oxide)s by synthesizing new monomers containing reactive groups that are stable under oxidative coupling conditions and can subsequently give crosslinked polymers when heated above their glass transition temperature without producing volatile compounds. In this manner the composition of the polymers can be easily controlled to achieve any desired amount of crosslinking.

Recently we have developed a new type of crosslinkable polymer containing the *trans*-1,2-diphenylcyclopropane moiety[9]. The polymers, which have been synthesized from the monomer *trans*-1,2-bis(4-hydroxyphenyl)cyclopropane by solution polycondensation, can be thermally crosslinked when heated above their glass transition temperatures without producing volatile by-products. The resulting crosslinked networks are insoluble in all solvents tested. We also developed a facile method for the synthesis of mono- and dihydroxy-substituted 1,2-diphenylcyclopropanes by the base-catalysed decomposition of the corresponding hydroxy-substituted 3,5-diphenyl-2-pyrazolines, which were synthesized by the reaction between hydroxychalcones and hydrazine monohydrate[10].

In this paper we will discuss the synthesis and thermal crosslinking of novel poly(phenylene oxide)s containing the 1,2-diphenylcyclopropane moiety.

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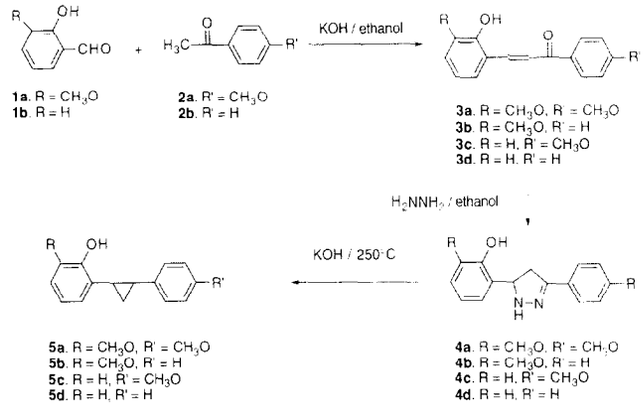
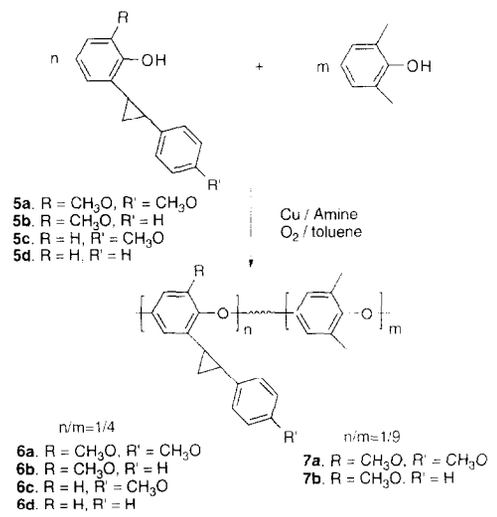


Scheme 1



Scheme 2

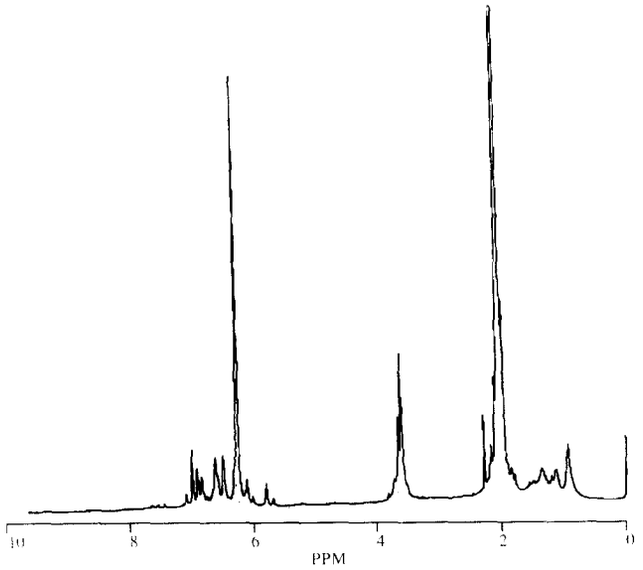


Figure 1 ^{1}H n.m.r. spectrum of copolymer **6a**

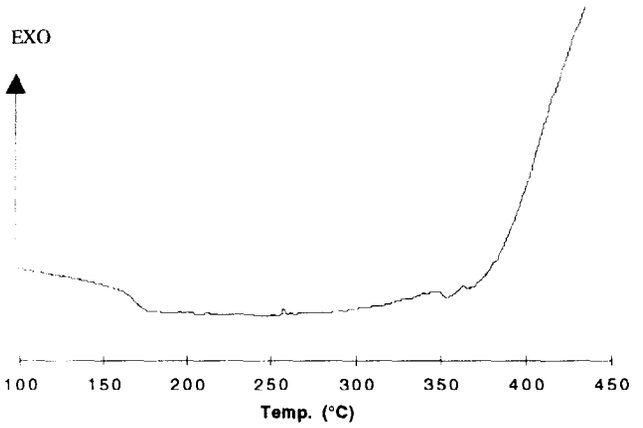


Figure 2 D.s.c. scan of copolymer **6b**

RESULTS AND DISCUSSION

Four new phenols **5a–d** containing the 1,2-diphenylcyclopropane group were synthesized according to the method we recently developed[6] (*Scheme 1*). 2-Hydroxychalcones **3a–c** were prepared by the reaction of 2-hydroxybenzaldehydes **1a–b** with acetophenones **2a–b**[11,12]. The hydroxy-substituted 3,5-diphenyl-2-pyrazolines **4a–d** were prepared by refluxing the ethanol solution of the hydroxychalcones **3a–d** in the presence of a two-fold excess of hydrazine monohydrate. The conversion in this step, as determined by h.p.l.c., is quantitative. Only the *trans* isomer was obtained as indicated by proton n.m.r. A small amount of sodium hydroxide was mixed with the hydroxy-substituted 3,5-diphenyl-2-pyrazolines, and the mixture was then heated to 250°C under nitrogen. The decomposition of the hydroxy-substituted 3,5-diphenyl-2-pyrazolines was completed in less than 30 min to give the hydroxy-substituted 1,2-diphenylcyclopropanes **5a–d** in quantitative yield. The mixture obtained was shown to consist of 5–10% of the *cis* and 90–95% of the *trans* isomers. After recrystallization, pure *trans* isomer could be readily obtained.

The oxidative polymerization of a large number of 2,6-disubstituted phenols has been studied in detail[3]. It was found that polymer formation readily occurs only if the substituent groups are relatively small and not too electronegative. Phenols with substituents of intermediate size, such as 2-methyl-6-methoxyphenol, readily undergo oxidative polymerization to give high-molecular-weight polymers.

The cyclopropane-functionalized monomers were incorporated into PPO by copolymerization with 2,6-dimethylphenol, according to a recently described procedure[13], as shown in *Scheme 2*. *N*,*N*′-Di-t-butylethylenediamine, *N*,*N*′-dimethyl-n-butylamine and di-n-butylamine were employed as ligands for the copper catalyst. A vibromixer was used to maintain efficient mixing of the oxygen in the liquid phase to avoid mass-transfer effects. The stirrer rod attached to the vibromixer motor was placed just below the surface of the solution, which caused the liquid to spray above the solution in a foundation that gave efficient liquid–oxygen mixing. Either 10 or 20 mol% of the functionalized monomers were used in the preparation of the copolymers. The phenylcyclopropanyl-substituted monomers **5a** and **5b** can be directly incorporated into PPO to give copolymers **6a–b** (20 mol% of **5a–b**) and **7a–b** (10 mol% of **5a** or **5b**) by simultaneous oxidation of a mixture of 2,6-dimethylphenol and phenylcyclopropanyl-substituted monomers, **5a** and **5b**. The incorporation

Table 1 Properties of poly(phenylene oxide) copolymers

Polymer	*n/m* theoretical	*n/m* obtained	Yield (%)	M_w/M_n [a]	η_{inh} [b] ($dl\,g^{-1}$)	T_g [c] (°C)	T.g.a. (−5%) [d] (°C)	T_{onset} [c] (°C)
6a	1/4	0.23	70	27600/17947	0.30	176	409	335
6b	1/4	0.22	65	28676/14751	0.31	167	412	320
7a	1/9	0.09	75	29781/10648	0.32	180	419	340
7b	1/9	0.10	80	26032/10152	0.28	182	418	340

[a] G.p.c., based on polystyrene standards
[b] $0.5\,g\,dl^{-1}$ in $CHCl_3$ at 25°C
[c] D.s.c., heating at $20°C\,min^{-1}$
[d] T.g.a., heating at $20°C\,min^{-1}$
[e] D.s.c., heating at $20°C\,min^{-1}$

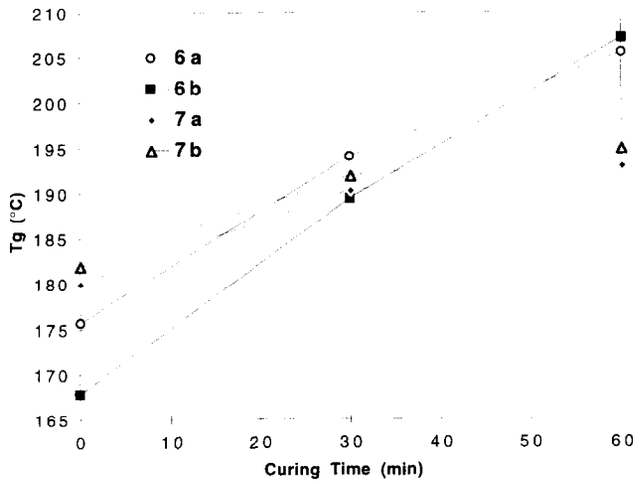


Figure 3 Effect of curing time on the T_g values of copolymers. Curing is at 350°C in nitrogen

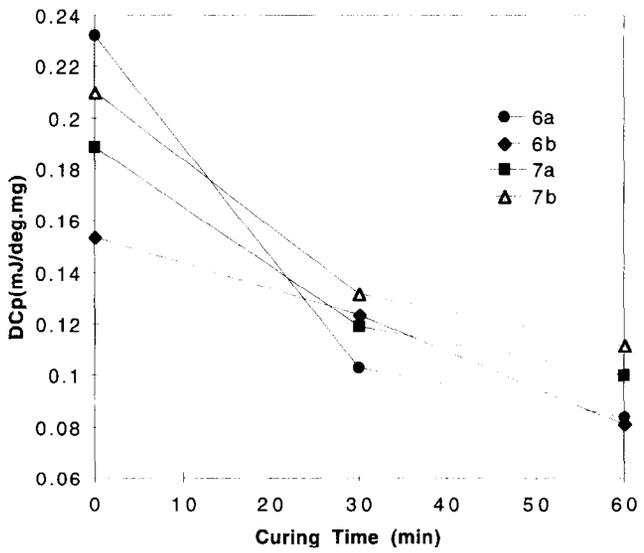


Figure 4 Effect of curing time on the DC_p of copolymers. Curing is at 350°C in nitrogen

of these substituted monomer units into PPO was confirmed by proton n.m.r. (*Figure 1*). The extra peaks at 6.0–7.4 ppm, 3.6–4.0 ppm and 1.0–2.0 ppm correspond to the signals of aromatic, methoxy and cyclopropane protons on the dimethoxyphenylcyclopropane moiety in the copolymer **6a**. The resulting copolymers **6a–b** and **7a–b** were then subjected to thermal curing. We were not successful in copolymerization of **5c** or **5d**, which have open *ortho* positions, with 2,6-dimethylphenol.

Table 1 lists the molecular weight, inherent viscosity, composition by n.m.r., weight loss by thermogravimetric analysis (t.g.a.), glass transition temperatures and the onset temperature for crosslinking (T_{onset}) from the d.s.c. scans of the copolymers **6a–b** and **7a–b**. The onset temperature for the crosslinking reaction was found to be in the range of 335–340°C. A typical d.s.c. scan of copolymer **6a** is shown in *Figure 2*. In the d.s.c. scan a T_g at 176°C and a sharp exotherm starting at 335°C were observed.

Thermal analysis is frequently used to characterize crosslinked polymers. It is well known that the T_g rises while the difference in specific heat capacity (DC_p) at T_g decreases with increasing number of crosslinks. The effect of curing time on the difference in specific heat capacity (DC_p) at T_g (*Figure 3*) and on the T_g (*Figure 4*) of copolymers **6a**, **6b**, **7a** and **7d** containing 20 and 10 mol% of cyclopropane moieties has been studied. After copolymers **6a**, **6b**, **7a** and **7d** were cured at 350°C under nitrogen in a t.g.a. furnace for different time periods, the cured polymers were examined via d.s.c. to determine the T_g increase and DC_p decrease. It was found that DC_p decreased rapidly and T_g increased as curing time increased as a result of the crosslinking of the polymers. After 30 min curing the changes in DC_p and T_g slowed down significantly. As expected, for the same curing time, the higher the content of cyclopropane groups in the polymers, the larger is the change in T_g and DC_p. No T_g is detected by d.s.c. after 2 h curing at 350°C in nitrogen when the content of cyclopropane groups in PPO copolymers is higher than 20%.

As expected for crosslinked polymers, the cured cyclopropane-containing PPO polymers were significantly more solvent-resistant than the uncured polymers. The polymers that were cured at 350°C were placed in chloroform at room temperature to test solubility and swelling. Visual observation of the cured cyclopropane-containing polymers, which before curing are readily soluble in chloroform at room temperature, indicated that they were no longer soluble in chloroform and they did not swell to any significant extent. When PPO was heated at 350°C for 30 min under nitrogen, only a trace amount of the resulting polymer was insoluble in chloroform at room temperature and the T_g decreased by less than 2°C.

From the CP/MAS ^{13}C n.m.r. studies[9] of poly(ether

sulfone)s, polyformals and polyesters containing the 1,2-diphenylcyclopropane moiety, the opening of the cyclopropane rings in the polymers at 350°C and formation of aliphatic linkages are believed to occur in the crosslinking reaction. This is most probably also involved in the crosslinking chemistry of the poly(phenylene oxide)s containing the 1,2-diphenylcyclopropane pendent groups, which occurs at a lower temperature. A variety of substituted cyclopropanes have been shown to undergo thermal structural and geometrical isomerization[14]. Kinetic determinations of the thermal, reversible *cis–trans* isomerization of 1,2-diphenylcyclopropane in the liquid state over the temperature range 160–220°C have been studied. It is believed that a diradical is the intermediate for the *cis–trans* isomerization. Three-membered rings can also be cleaved, thermally, to unsaturated products. In the simplest case cyclopropane gives propene when heated to 400–500°C[15]. This mechanism is also generally regarded as involving a diradical intermediate. We found that *cis–trans* isomerization of 1,2-bis(anisyl)cyclopropane proceeds at 350°C in nitrogen. Only 10% of *trans*-1,2-bis(anisyl)cyclopropane was converted into the *cis* isomer after heating at 350°C in nitrogen for 20 min. Only 17% of the starting material *trans*-1,2-bis(anisyl)-cyclopropane remained, and many new peaks appeared in the h.p.l.c. trace. G.p.c. indicates that most of the products of thermolysis of *trans*-1,2-bis(anisyl)cyclopropane are higher-molecular-weight oligomers. N.m.r. spectra and mass spectra of the mixtures obtained indicate that the products resulted from the ring opening of the cyclopropane moiety, probably proceeding through the singlet diradical as intermediate.

EXPERIMENTAL

Characterization of polymers

Glass transition temperatures of the polymers were obtained using a Seiko 220 DSC instrument at a heating rate of 20°C min^{-1} in N_2 (50 ml min^{-1}). When recording T_g values, samples were never heated above 300°C, to avoid crosslinking, and the values recorded are from the second scan. The T_g was taken from the midpoint of the change in slope of the baseline. The weight-loss data were obtained from a Seiko 220 TG/DTA instrument at a heating rate of 20°C min^{-1} in nitrogen and air. Polymer samples were cured at 350°C under nitrogen in the t.g.a. instrument. A d.s.c. was then employed to determine the T_g increase. Inherent viscosity data were obtained with a calibrated Ubbelohde viscometer. The measurements were performed in $CHCl_3$ at 25°C with a 1B(205) instrument. Molecular weights were obtained by gel permeation chromatography (g.p.c.) relative to polystyrene standards in chloroform solution using a Waters 510 HPLC instrument equipped with μ-Styragel columns (500, 10^3, 10^4 and 100 Å) arranged in series and a u.v. detector. ^{1}H n.m.r. spectra were recorded at 500 MHz using a Varian XL-500 spectrometer in $CDCl_3$ with $(CH_3)_4Si$ as the internal standard.

Materials

2-Hydroxychalcone **3** was purchased from Aldrich Chemical Co.

2-Hydroxy-3,4′-dimethoxychalcone **3a**. 2-Hydroxy-3-methoxybenzaldehyde **1a** (3.00 g, 0.02 mol) and 4-methoxyacetophenone **2a** (3.0 g, 0.02 mol) were dissolved in 50 ml of boiling alcohol. To this solution at 55°C was added 13 ml of 60% potassium hydroxide solution and the resulting solution was allowed to stand at room temperature for one week. The mixture set to a solid mass. It was worked up by acidification in the cold and recrystallization of the product from alcohol: yield 80–85%; m.p. 100–102°C. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 3.90 (s, 6H), 6.40 (s, 1H), 6.90–8.10 (m, 9H). M.s. (*m/e*, relative intensity %): 268 (M^+, 100).

The following compounds were prepared using the same method.

2-Hydroxy-3-methoxychalcone **3b**. Yield 80–85%; m.p. 135–138°C. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 3.93 (s, 3H), 6.29 (s, 1H), 6.87–8.08 (m, 10H). M.s. (*m/e*, relative intensity %): 254 (M^+, 100).

2-Hydroxy-4′-methoxychalcone **3c**. Yield 80–85%; m.p. 132–133°C. ^{1}H n.m.r. (500 MHz, DMSO) δ 3.81 (s, 3H), 6.62–8.10 (m, 11H). M.s. (*m/e*, relative intensity %): 254 (M^+, 100).

trans-*3-(4-Methoxyphenyl)-5-(2-hydroxy-3-methoxyphenyl)-2-pyrazoline* **4a**. To a solution of 30.7 g (128 mmol) of 4,4′-dihydroxychalcone in 300 ml of ethanol, 30 ml (618 mmol) of hydrazine monohydrate was added. The resulting solution was refluxed for 1.5 h. Ice–water was then added. The precipitate was collected, dried and crystallized from ethanol: yield > 90%; m.p. 115–117°C. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 2.99–3.50 (octet, 2H), 3.84 (s, 3H), 3.89 (s, 3H), 5.00–5.13 (sextet, 1H), 6.03 (s, 1H), 6.82 (s, 3H), 6.89–7.64 (quartet, 4H). M.s. (*m/e*, relative intensity %): 298 (M^+, 100). Calculated for $C_{17}H_{18}N_2O_3$ (298): C, 68.44; H, 6.08; N, 9.39. Found: C, 68.32; H, 5.96.

The following compounds were prepared using the same method.

trans-3-Phenyl-5-(2-hydroxy-3-methoxyphenyl)-2-pyrazoline **4b**. M.p. 118–119°C. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 3.10–3.53 (octet, 2H), 3.89 (s, 3H), 5.07–5.18 (triplet, 1H), 6.11 (s, 1H), 6.81–7.70 (m, 8H). M.s. (*m/e*, relative intensity %): 268 (M^+, 100). Calculated for $C_{16}H_{16}N_2O_2$ (268): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.43; H, 5.97; N, 10.22.

trans-3-(4-Methoxyphenyl)-5-(2-hydroxyphenyl)-2-pyrazoline **4c**. M.p. 160–162°C. ^{1}H n.m.r. (500 MHz, DMSO) δ 2.66–3.40 (octet, 2H), 3.75 (s, 3H), 4.93–4.97 (triplet, 1H), 6.73–8.03 (m, 9H). M.s. (*m/e*, relative intensity %): 268 (M^+, 100). Calculated for $C_{16}H_{16}N_2O_2$ (268): C, 71.62; H, 6.01; N, 10.44. Found: C, 71.11; H, 6.05; N, 10.23.

trans-3-phenyl-5-(2-hydroxyphenyl)-2-pyrazoline **4d**. M.p. 196–197°C. ^{1}H n.m.r. (500 MHz, DMSO) δ 2.72–3.45 (octet, 2H), 5.02–5.06 (triplet, 1H), 6.74–7.63 (m, 9H), 9.64–9.65 (s, 1H). M.s. (*m/e*, relative intensity %): 238 (M^+, 100). Calculated for $C_{15}H_{14}N_2O$ (238): C, 75.61; H, 5.92; N, 11.76. Found: C, 75.41; H, 6.02; N, 11.82.

trans-*1-(4-Methoxyphenyl)-2-(2′-hydroxy-3′-methoxyphenyl)cyclopropane* **5a**. In a test tube 4.8 g (16 mmol) of *trans*-3,5-bis-(4-hydroxyphenyl)-2-pyrazoline **4a** was mized with 1.1 g of powdered potassium hydroxide. The mixture was heated to 250°C under nitrogen and the decomposition proceeded for 30 min. The cooled reaction

product was dissolved in water, neutralized with hydrochloric acid and extracted with ether. The ether layer was washed with water to remove the salt. Removal of the ether left the product, which was crystallized from acetic acid: yield > 90%; m.p. 63–65°C. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 1.34–1.43 (sextet, 2H), 2.14–2.40 (m, 2H), 3.81 (s, 3H), 3.90 (s, 3H), 6.59–7.15 (m, 7H). M.s. (*m/e*, relative intensity %): 270 (M^+, 77) 134 (100), 121 (47). Calculated for $C_{17}H_{18}O_3$ (270): C, 75.56; H, 6.71. Found: C, 75.60; H, 6.82.

The following compounds were prepared using the same method.

trans-1-Phenyl-2-(2′-hydroxy-3′-methoxyphenyl)cyclopropane **5b**. M.p. 40–42°C. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 1.39–1.48 (t, 2H), 2.18–2.48 (m, 2H), 3.90 (s, 3H), 5.75 (s, 1H), 6.60–7.34 (m, 8H). M.s. (*m/e*, relative intensity %): 240 (M^+, 100). Calculated for $C_{16}H_{16}O_2$ (240): C, 79.97; H, 6.71. Found. C, 79.49; H 6.76.

trans-1-(4-Methoxyphenyl)-2-(2′-hydroxyphenyl)cyclopropane **5c**. M.p. 55–56°C. ^{1}H n.m.r. (200 MHz, DMSO) δ 1.26–1.43 (t, 2H), 2.10–2.20 (m, 2H), 3.82 (s, 3H), 6.88–7.18 (m, 8H). M.s. (*m/e*, relative intensity %): 240 (M^+, 100). Calculated for $C_{16}H_{16}O_2$ (240): C, 79.97; H, 6.71. Found. C, 79.83; H, 6.73.

trans-1-Phenyl-2-(2′-hydroxyphenyl)cyclopropane **5d**. ^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 1.28–1.41 (m, 2H), 2.04–2.42 (m, 2H), 4.89 (s, 1H), 6.74–7.27 (m, 9H). M.s. (*m/e*, relative intensity %): 210 (M^+, 100). Calculated for $C_{15}H_{14}O$ (210): C, 85.68; H, 6.71. Found C, 85.21; H, 6.61.

General procedure for polymerization reactions

The following toluene stock solutions were prepared for the polymerization reactions.

Stock solution I: Cu, 0.054 mmol ml^{-1}; Br, 0.29 mmol ml^{-1}. Bromine (5.9 ml, 114.5 mmol) was added to a chilled solution of cuprous oxide (1552 g, 10.85 mmol) and 2,6-dimethylphenol (26.4 g, 216.09 mmol) in methanol (200 ml) over 0.5 h. The solution obtained was diluted with toluene to 400 ml.

Stock solution II: DBEDA (*N*,*N*′-di-t-butylethylenediamine), 0.164 mmol ml^{-1}.

Stock solution III: *N*,*N*-dimethylbutylamine (DMBA), 1.64 mmol mol^{-1} + *N*,*N*-di-n-butylamine (DBA), 0.77 mmol ml^{-1}.

A 50 ml three-necked flask equipped with a condenser, a thermometer, an oxygen inlet and a vibromixer stirrer was placed in a water bath at room temperature and charged with toluene (12.5 ml), stock solution I (0.76 ml, containing Cu^+ 0.041, Br^- 0.22 mmol), stock solution II (0.5 ml, contained DBEDA 0.082 mmol) and stock solution III (0.5 ml, containing DMBA 0.82 mmol and DBA 0.39 mmol). Oxygen was bubbled through the solution for 10 min and the colour of the solution turns to red instantly. Then a solution of 2,6-dimethylphenol (4.636 g) and 2-methoxy-6-(2-phenylcyclopropanyl)-phenol (0.540 g) in toluene (12.5 ml) was added in one portion and a deep red colour developed immediately. Upon the addition of the phenol, a 4°C exotherm of the reaction mixture was observed. The viscosity of the reaction mixture was checked every 10 min from the time of addition of the phenol by passing the sample (1 ml) from the mixture through a pipette and fed back to the reaction mixture immediately. At 50 min the viscosity increases significantly. After 60 min the viscosity of the reaction mixture become so high that stirring ceased. The reaction mixture was then added into methanol to precipitate the copolymer, which was dried at 80°C under vacuum.

CONCLUSION

Crosslinkable poly(phenylene oxide)s containing pendent 1,2-diphenylcyclopropane groups have been synthesized by oxidative polymerization from new phenols **5a–d** containing the 1,2-diphenylcyclopropane group. The monomers were prepared by base-catalysed decomposition of the corresponding hydroxyl-substituted 3,5-diphenyl-2-pyrazolines, which were the products of the reaction between hydroxychalcones and hydrazine monohydrate. Characterization of and crosslinking studies on these polymers were carried out utilizing d.s.c., t.g.a., g.p.c. and n.m.r. The polymers can be thermally crosslinked when heated to 350°C and the glass transition temperatures (T_g) of the polymers increase after crosslinking. The resulting crosslinked networks are insoluble in all solvents tried. Thermogravimetric analysis shows that no significant weight loss accompanies the crosslinking reaction.

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