Synthesis and Physico-Chemical Characterisation of Polyphenylene Oxides

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ABSTRACT

Homopolymers of the monomers, 2, 6-dimethyl-phenol (DMP) was synthesised by two methods involving oxidative coupling of their phenol monomer. Both the methods were found to be quite different in terms of producing polymers of different physical and mechanical properties. The first method produced polymers of low intrinsic viscosity with fairly good mechanical strength. Where as the second method produced polymers with higher intrinsic viscosity accompanied by enhanced mechanical properties. The synthesised polymers were characterised for structure-property correlations by measuring physical and mechanical properties namely, density measurements, dilute solution intrinsic viscosity measurements, tensile testing and fourier transform infra red spectroscopy (FTIR). The study reveals methodology for tailoring properties of polyphenylene oxides to suit various applications.

Keywords: *Polyphenylene oxide; Oxidative coupling; Characterisation; Properties*

1. INTRODUCTION

Aromatic rings attached directly to a hydroxyl group are called Phenols. The presence of polar hydroxyl groups allow phenols to make strong hydrogen bonding leading to high density, melting and boiling points [1]. However they are weakly acidic compared to alcohols due to the resonance effect of the -OH groups with the ring pi-bonds. Substitution of electron withdrawing groups makes it further weakly acidic while substitution by electron donating groups such as alkyl groups, make it strongly acidic in nature. Sterically hindered phenols have little or no acidic character. Phenols have four active centres (electron rich centres) at the ortho- and para- positions on the aromatic nucleus and also at the hydroxyl group [2]. This particular aspect provide opportunity to produce a variety of synthetic polymers from phenols by reactions at these active groups, via combination of C-C or C-O coupling reactions or oxygenation reactions where the coupling occurs fastest at the position of highest density of free electrons, except where there is steric hindrance.

Polyphenylene ether, a synthetic polymer can be formed from phenols by the reactions at the ortho- and para- and by the reactions with hydroxyl group, a powerful activating group and an ortho- para- directing group. Oxidation of phenols by using a catalyst can result in a variety of products, via proper choice of catalyst, solvent and phenol. For example (1) tetraalkyldiphenoquinones, (2) polyphenylene ethers and (3) o-benzoquinone can be prepared from catalyzed auto oxidation of phenol by using different types of copper salts and amines [3].

Discovery of oxidative polymerization of phenols to poly(phenylene oxide)s, led to the development of an entirely new family of engineering polymers [1]. They are basically polyethers having aromatic groups connected by an oxygen linkage at the backbone. Ether linkage is either at ortho- or para- position or both. When it is at para- position the polymer is called poly(1, 4-phenylene oxide) and when it is at ortho-position it is called (1, 2-phenylene oxide) and 1, 4 and 1, 2 additions may take place at the same monomeric unit. Poly(phenylene oxide)s have been synthesized in various forms since 1916 by Hunter et al. because of their mechanical, chemical and thermal properties [4]. The largest commercial usage of poly(phenylene oxide)s is in Noryl (General Electric Co.) engineering resin, which are alloys of poly(2, 6-dimethyl-1, 4-phenylene ether) [5].

In the past only low molecular weight 2, 6-di-substituted-l,4-phenylene ethers have been prepared by Dewar and James by the thermal decomposition of substituted benzene-1,4-diazooxides but only with limited success [6]. Staffin and Price have extended the work reported by Hunter, and prepared low molecular weight poly-2,6-dimethyl- 1,4-phenylene ether by oxidative displacement of the bromine in 4-bromo-2,6-dimethylphenol [7]. In 1959, A. S. Hay employed oxidative coupling method carried out at room temperature, in which a solution of 2,6-di-substituted phenol is merely passed by oxygen in an organic solvent containing an amine and a copper(I) salt as a catalyst [8]. As shown in Fig.1, when the substituent groups are small, as in 2,6-dimethylphenol, carbon-oxygen coupling occurs and linear polyphenylene ethers with intrinsic viscosities up to 3.4 dl/gm. have been obtained. With bulky groups, as in 2,6-di-tert-butylphenol, carbon-carbon coupling occurs and the diphenoquinone is the sole product. In intermediate cases such as di-isopropylphenol, carbon-carbon and carbon-oxygen coupling compete.
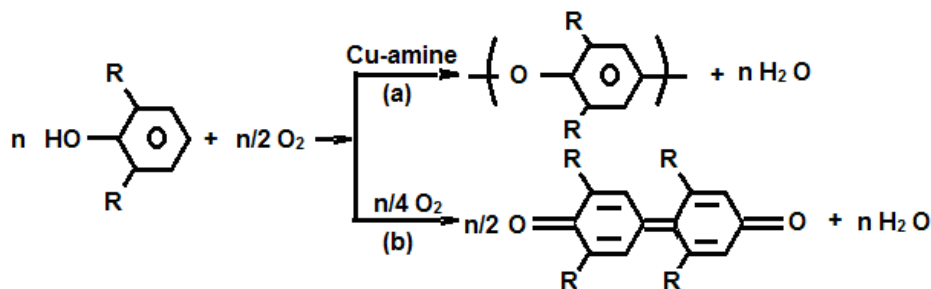
Figure 1. **Oxidation products of phenols (a) polyphenylene ether and (b) diphenoquinone**

Blanchard et al. studied the preparation and characterization of bis(phenolato)- bis(pyridine)-copper(II) complexes [9]. These complexes were decomposed to produce branched polymer under variety of condition. They also proposed a radical mechanism for the decomposition. In 1969, Harrod studied the thermal decomposition of copper (II) complexes containing various amine ligands [10]. They concluded that the phenoxo complexes with chelating ligands are highly resistant to thermal decomposition compared to non–chelating ligands.

Poly(2, 6-dimethyl-1,4-phenylene oxide) (PPO) is a high performance engineering plastic due to its high thermal stability (high glass transition temperature (T_g =210°C), high mechanical strength, and excellent hydrolytic stability. In addition, its distinctive but simple structure allows a variety of modifications in both aryl and benzyl positions: (1) electrophilic substitution on the benzene ring of PPO [11] (2) radical substitution of the hydrogen from the methyl groups of PPO [12] (3) nucleophilic substitution of the bromomethylated PPO (BPPO) [13] (4) capping and coupling of the terminal hydroxyl groups in PPO chains [14] and (5) metalation of PPO with organometallic compounds [15]. These modifications can fine tune PPO with specific properties for specific application. In this article, homopolymers of the 2, 6-Dimethyl-1, 4-Phenol monomer was synthesised using two different methods. These polymers were characterised for intrinsic viscosity, density, mechanical, thermal properties and further chemical structure confirmations were made using FTIR.

2. EXPERIMENTAL
Monomers, 2, 6-Dimethyl-phenol (DMP), Dibutyl-amine (DBA) and anhydrous hydrazine were procured from Merck Chemie, Mumbai; monomer 2, 6-Diphenyl-phenol (DPP) was obtained from Aldrich Chem Co.; Cuprous bromide catalyst from Lancaster and synthesis grade toluene and chloroform from Ranbaxy were procured. Distilled methanol was used for washing the polymer precipitate.

2.1 Synthesis
2.1.1 Synthesis of PPO by Method 1
The synthesis of polyphenylene ethers from their monomers DMP was carried out by oxidative coupling method according to the procedure given in literature [16]. DMP was purified by recystallisation with hexane to at least 99.5%. In a three necked flask, oxygen was introduced into a vigorously stirred solution of CuBr and DBA in toluene for 10 min. Maintaining a molar ratio of CuBr: DBA: DMP equal to 1:22:77, a 25 percent solution of DMP in toluene was added over a period of 20 minutes. The temperature of solution was maintained throughout at 50°C. After 2 hrs of reaction under continuous stirring, the reaction mixture was diluted in toluene to 10 percent. Methanol (5-7 volumes) containing 0.5-1.0 percent acetic acid was added gradually with stirring, to precipitate out the PPO polymer as agglomerates which slowly turn into granular powder. The polymer obtained was filtered and washed with methanol, and dried in a vacuum oven at 60°C. Please refer Table 1.

2.1.2 Synthesis of PPO by Method 2
The synthesis of S(PPO) from its DMP monomer was carried out by oxidative coupling method according to the procedure given in literature [16]. DMP was purified by recystallisation with hexane to at least 99.5%. In a three necked flask, oxygen was introduced into a vigorously stirred solution of CuBr and DBA in toluene for 10 min. A little excess of anhydrous magnesium sulphate (5 w/v %) was added to the solution to remove the water formed as a by-product of condensation reaction. Maintaining a molar ratio of CuBr: DBA: DMP equal to 1:22:77, a 25 percent solution of DMP in toluene was added over a period of 20 minutes. The temperature of solution was maintained throughout at 50°C. After 4 hrs of reaction under continuous stirring, a few drops (2 v/v%) of anhydrous hydrazine (10-15) were added into the reaction mixture to reduce the diphenoquinone by product formed, if any [17]. The inorganic solids were removed by filtration, and the solution was diluted in toluene to 10 percent. Then it was added dropwise to large volumes of methanol (5-7 volumes) containing 0.5-1.0 percent acetic acid, to precipitate the polymer. After stirring the solution for 2 hours, the polymer formed was collected by filtration. The polymer obtained was filtered and washed with methanol, and dried in a vacuum oven at 60°C. Please refer Table 1 for comparison of the two synthesis methods.

Table 1
Synthesis conditions for preparing polyphenylene oxide.

Method	CuBr:DBA:DMP (molar ratio)	MgSO$_4$ (w/v)%	Hydrazine (v/v)%	Solvent	Temp (^{o}C)	Time (hrs)
1	1:22:77	-	-	Hexane	50	2
2	1:22:77	5	2	Hexane	50	4

2.1.3 Purification of Polymers
All the polymers obtained were purified (reprecipitated) by redissolving in chloroform (1 volume) and precipitated in methanol (10 volumes) containing few drops of acetic acid. In the last step a final washing in methanol was carried out on all the polymers. A good yield of more than 95% was obtained. They were dried to a constant weight, in a vacuum oven at 60°C for 6 hours until constant. The measured densities, intrinsic viscosity and physical and mechanical properties of the synthesised polymers are presented in Table 2.

2.2 Polymer Characterization
The intrinsic viscosity of the dilute polymer solutions in toluene was calculated from the flow time measurements, using a Viscometer at 25°C. The required constants were taken from literature [16]. The density was measured by floatation method of the polymer films.

3. RESULTS AND DISCUSSION
The FTIR spectra of all the synthesised homopolymers and copolymers of polyphenylene oxide confirmed the presence of ether groups at 1306 cm^{-1} and 1022 cm^{-1}, and the methyl and backbone phenyl groups at 3036 cm^{-1} and 2954 cm^{-1}.

The measured physical properties of the polymers are presented in Table 2. We clearly observe that the measured intrinsic viscosity for PPO obtained by method 1 (hereafter called as PPO1) has a value lower than that obtained by method 2 (referred as PPO2). Lower the intrinsic viscosity, lesser is the polymer molecular weight. This implies that the PPO1 has a lower molecular weight than PPO2. This could be due to the formation of water molecules as condensation by-products which interferes with the polymerisation process by not allowing the catalyst to accelerate the reaction. On the other hand the removal of water formed as by-product in method 2, by using anhydrous salt helps in build up of molecular weight. Further, the formation of diphenoquinones if any, as explained in the introduction section, is removed by addition of small amounts of hydrazine.

The density of the polymer PPO1 is also smaller than that for PPO2. This is due to the less efficient packing of the polymer chains in polymers with low molecular weight whereas they are better packed in high molecular weight polymers. In the case of PPO2 the chain segments are more or less equally rigid as that of PPO1, as found from glass transition temperature (T$_g$). T$_g$ is characteristic property of a polymer. The mechanical (tensile) properties exhibit a considerable improvement in the tensile strength and % elongation at break with increase in molecular weight, which is due to increase in chain length which builds up load bearing property and improve plastic deformations.

Thus the 2, 6-dimethyl-1, 4-phenylene oxide prepared in two different ways were found to give differing properties. This is due to the differences in reactivity of the monomer in the two cases under the conditions mentioned. Method 2 appears to be reasonably efficient in reducing the by products during the oxidative polymerisation so that the monomers are more efficiently used in polymer formation without wastage.

Table 2
Physical properties of polymers

Polymer	Intrinsic viscosity (dl/g)	T$_g$ (^{o}C)	Density (g/cm^3)	Tensile properties	
				Tensile strength (MPa)	Elongation at break (%)
PPO (Method 1)	0.310	212	1.05	39	16
PPO (Method2)	0.542	215	1.07	98	51

4. CONCLUSIONS

The 2,6-dimethyl-1,4-phenylene oxide prepared in two different ways were found to give differing properties. This is due to the differences in reactivity of the monomer in the two cases under the conditions mentioned. Method 2 appears to be reasonably efficient in reducing the by products during the oxidative polymerisation so that the monomers are more efficiently used in polymer formation without wastage. PPO2 was found to have higher molecular weight than PPO1. Further PPO2 has better mechanical properties than PPO1. Thus method 2 can be suggested as the best method in the preparation of polyphenylene oxide polymers. The research study reveals methodology for tailoring properties of polyphenylene oxides to suit various applications by controlling factors which critically control polymerisation, such as, the time, temperature, catalyst, use of anhydrous salts and of hydrazines.

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