

Research Article

A New Method for Synthesis of Poly(2,6-dimethyl-1,4-phenylene oxide) and Poly(2,6-diphenyl-1,4-phenyl oxide)

Naser M. Al Andis

Chemistry Department, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

Correspondence should be addressed to Naser M. Al Andis; nandis@ksu.edu.sa

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The polymerization of two monomers 2,6-dimethylphenol and 2,6-diphenylphenol was carried out by an oxidative route in the presence of Cu(I) as a catalyst and amine complex as a solvent assisted by microwave heating. The synthesized polymers were characterized by NMR spectroscopy, differential scanning calorimetry (DSC), and gel permeation chromatography (GPC). It was observed that this process of polymerization gives high yield (98 wt%) of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(2,6-diphenyl-1,4-phenylene oxide) (PPPO) with a molar mass of 1180 (\overline{M}_n), 1400 (\overline{M}_w) and 28000 (\overline{M}_n), 46500 (\overline{M}_w) gm/mol, respectively. A negligible amount of diphenoquinone was also observed and its dispersity was rather moderate, 1.17 and 1.68, respectively.

1. Introduction

Microwave-assisted reaction was introduced in 1986 [1]. Comparing with conventional heating, it requires lesser time with higher yield. It was attributed to dielectric heating [2] and to specify the microwave effect by others [3]. However, the main advantage of microwave reaction is to maintain a uniform temperature throughout the reaction period, as a result of internal heating by irradiation [4].

An atom transfer radical polymerization (ATRP) was introduced in 1995, which allows an efficient polymerization with well-defined molar masses and narrow dispersity of polymers produced. Microwave-assisted ATRP has been successfully used for polymerization of vinylic or acrylic monomers such as styrene [5–7], methyl methacrylate [6–8], vinyl acetate, acrylonitrile, and *n*-octyl acrylate [9]. In ATRP, an organic halide (RX) is used to initiate a transition-metal compound in its lower oxidation state along with an electron-donating compound for catalyzing polymerization [10].

An oxidative polymerization of 2,6-dimethylphenol was discovered in 1956 [11, 12], leading to the formation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Polymerization occurred at room temperature using an amine complex of copper (I) salt as a catalyst in the presence of oxygen (Scheme 1). A high molar mass linear PPO was formed

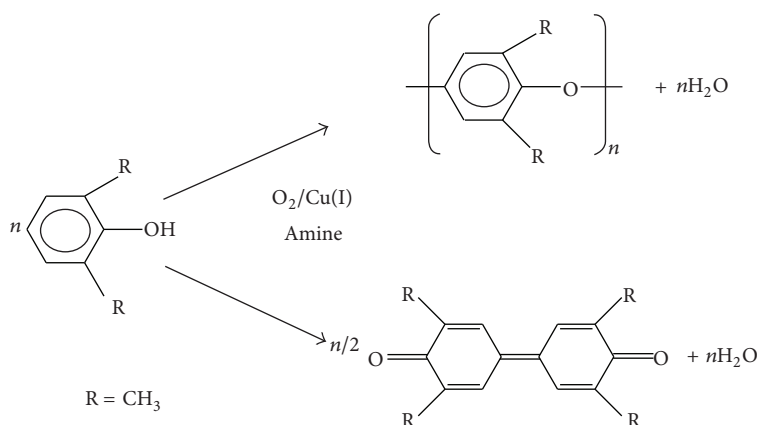
along with a small amount of diphenoquinone [13]. In this investigation it was observed that the length of the polymer chain depended on the amine type used, its molar ratio, and polarity of the solvent. According to Hasy works [14] in a similar reaction, it was noted that the diphenoquinone became its major product at a high temperature.

In this work PPO and PPPO were synthesized for the first time by oxidative polymerization using the Cu(I) in amine complex as catalyst, heating by microwave.

2. Experimental

2.1. Materials. The N,N,N,N-tetramethylethylenediamine (TMEDA), 2,6-dimethylphenol (DMP), and 2,6-diphenylphenol were purchased from Aldrich Chemical, Germany. Benzyl chloride (BC) and dimethylformamide (DMF) were obtained from BDH, England, acetonitrile (ACN) from M & B England, and copper(I) chloride (CuCl) from Riedel-Dettaen AG, Germany. All chemicals were used as received. The reactions were performed in a CEM Discover microwave instrument, Matthews, NC, USA.

2.2. Polymerization. In a typical run, 0.2 gm (2 mmol) of CuCl was added to 5 mL of ACN into a single-necked



SCHEME 1: Polymerization reaction of 2,6-phenylphenol by oxidation using the CuCl in amine.

100 mL round bottom flask at room temperature. Then, 0.5 gm (4.3 mmol) of TMEDA and 0.03 gm (0.27 mmol) of BC were added simultaneously. The mixture was sonicated for 2 minutes at room temperature and transferred to a Pyrex tube of 100 mL. The monomer was added to the reaction mixture after one minute. The tube was fitted with reflux and transferred to the microwave. The reaction was performed at 100 Watt for 3 min then at 300 Watt for 6 min. The polymer was cooled, treated 10 times with 10 mL of HCl/methanol (10 wt %), and then isolated in excess methanol. The polymers synthesized were purified by repeated dissolution in THF and precipitation in *n*-heptane, then isolated by filtration, and dried to a constant weight at 40°C in a vacuum oven for 5 days. Contrarily to PPO which has a white yellow color, the PPPO was light red.

2.3. Characterization. ¹³C and ¹H NMR spectra of the PPO and PPPO in deuterated chloroform were recorded with a JEOL ECLIPSE 400 spectrometer, using tetramethylsilane (TMS) as an internal standard. The glass transition temperature (T_g) of PPO and PPPO was measured with a DSC (Shimadzu DSC 60), previously calibrated with indium. The samples were heated from 30 to 240°C at a heating rate of 20°C min⁻¹. The dispersity of PPO and PPPO was determined at 30°C with a Viscotek Complete Tetra Detector Platform and GPCMax front-end chromatography setup equipped with 2 × 1-MBMMW column by using standard polystyrene and tetrahydrofuran (THF) as a solvent.

3. Results and Discussion

A viscous solution appeared immediately after adding the monomer to the reaction mixture and viscosity was increased during the reaction. Under the same condition, a maximum of 98 wt % conversion was obtained for PPO and PPPO after 3 min of the reaction time with a negligible amount of diphenoquinone. From the results of the molar mass of these two polymers, it was observed that the PPPO was relatively more active than PPO. The structures of the two polymers were confirmed by ¹H and ¹³C NMR techniques.

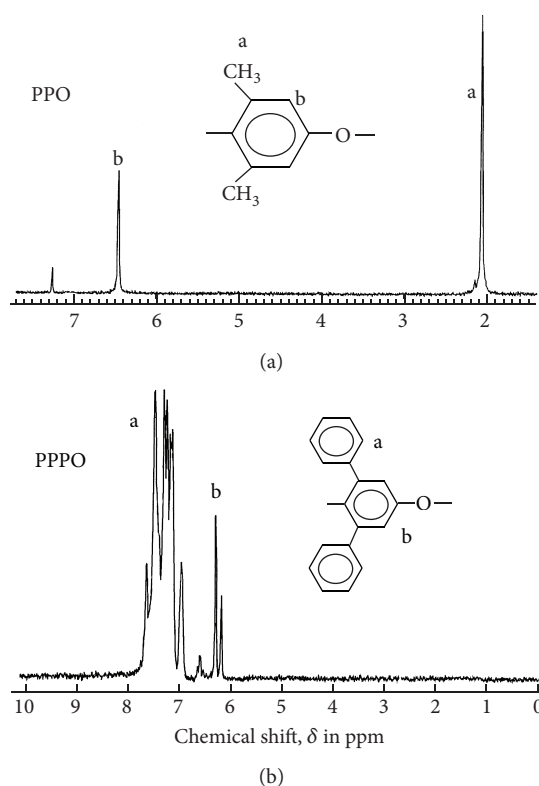
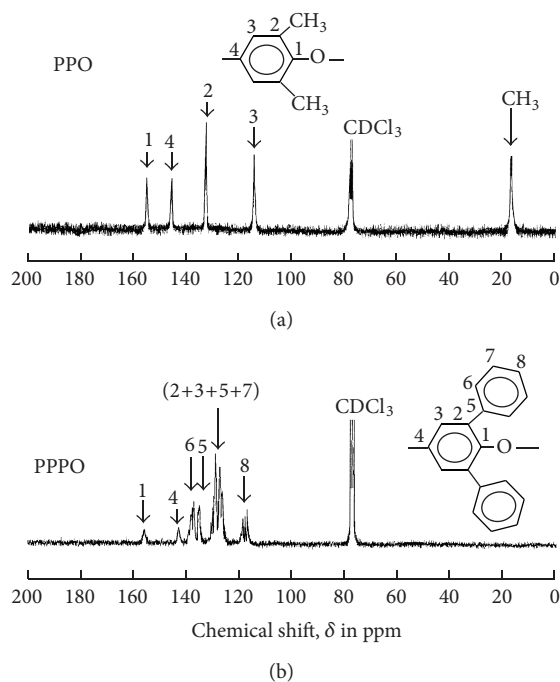


FIGURE 1: ¹H NMR spectra of PPO and PPPO.

The ¹H NMR spectra of PPO and PPPO are illustrated in Figure 1. It shows two sets of peaks. In the spectra of PPO, a triplet centered at 2.11 ppm was observed which can be assigned to the methyl protons, and one multiplet centered at 6.46 ppm was also seen, which can be attributed to the aromatic protons. The spectra of PPPO in Figure 1 show the presence of one large multiplet between 7.04 and 7.70 ppm assigned to 10 protons of the two substituted phenyl and another between 6.87 and 7.04 ppm attributed to the 2 protons of the phenylene of the backbone. The absence of any peak between 4 and 5 ppm clearly indicates the disappearance

FIGURE 2: ^{13}C NMR spectra of PPO and PPPO.

of hydroxyl groups, which supports the formation of the polymer.

The ^{13}C NMR spectra of PPO and PPPO are gathered in Figure 2. The spectra of PPO show a peak at 16.88 ppm that can be assigned to the methyl carbons. Furthermore there are four sets of carbon peaks attributed to the phenyl at 154.62, 145.50, 134.2, and 114.59 ppm assigned to the carbons C_1 , C_4 , the symmetric lateral C_2+C_6 and C_3+C_5 , respectively. Concerning the PPPO, the presence of one large multiplet between 128 and 130 ppm was assigned to the 12 carbons (C_2 , C_3 , C_5 , and C_7). The peaks at 156.2, 143, 136.2, and 137.8 ppm were attributed to C_1 , C_4 , C_6 , and C_5 , respectively. The multiplet between 116.5 and 118.2 ppm was assigned to the two carbons C_8 . The average molar mass, \overline{M}_n and \overline{M}_w of the isolated PPO are 1180 and 1400 gm/mol, respectively, and those of PPPO are 28000 and 46500 gm/mol, respectively, as shown in the Chromatograms of Figure 3. Their dispersity is rather moderate 1.17 and 1.68 respectively. As can be noticed, PPPO is unexpectedly obtained with the highest molar mass; PPO has two methyl groups and would rather polymerize to a lower molar mass with a tendency towards a monodisperse polymer. The DSC thermograms of PPO and PPPO plotted together in Figure 4 show a T_g at 210°C and 90°C, respectively.

4. Conclusion

From these results, it can be concluded that the polymerization of 2,6-dimethyl-phenol and 2,6-diphenylphenol assisted by microwave led to the formation of poly(2,6-dimethyl-1,4-phenylene oxide) and poly(2,6-diphenyl-1,4-phenylene oxide), respectively. Heating by the microwave technique

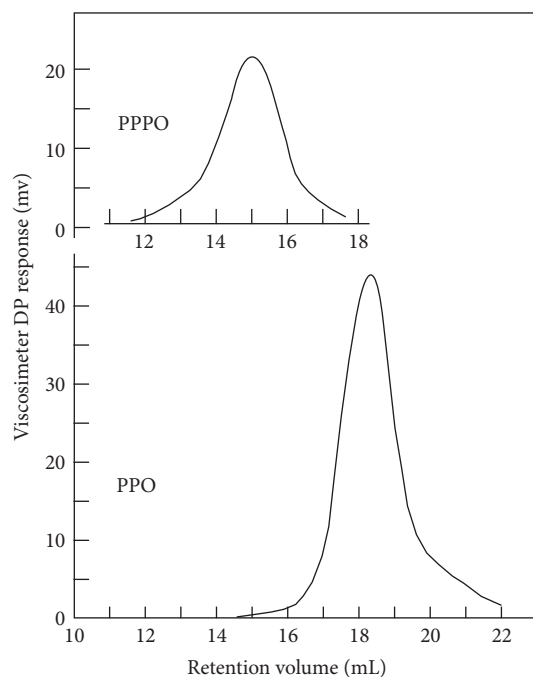


FIGURE 3: GPC chromatogram of PPO and PPPO.

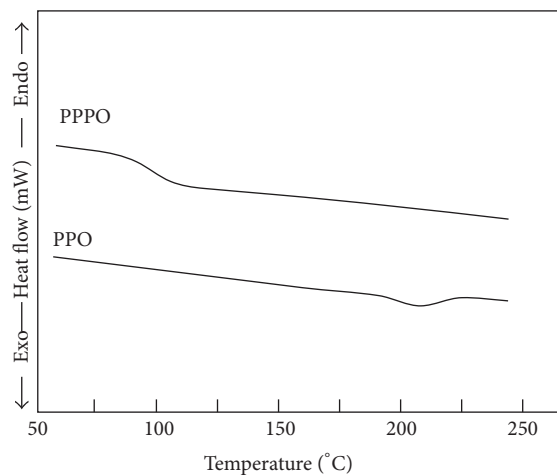


FIGURE 4: DSC thermograms of PPO and PPPO.

resulted in a high conversion to polymers after only 3 min and allowed obtaining moderate molar masses. From these data it was also noted that the poly(2,6-diphenyl-1,4-phenylene oxide) was relatively more active than poly(2,6-dimethyl-1,4-phenylene oxide) due to the $R = \phi$ substitute group, which increases the radical stability by resonance effect.

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