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Novel Preparation Method for Poly(2,6-dichloro-1,4-phenylene oxide)

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Introduction

Poly(phenylene ether)s have developed into an important commercial engineering thermoplastic. The blend of poly(2,6-dimethyl-1,4-phenylene oxide) with polystyrene has found a variety of commercial applications (automotive, electrical, construction, appliance, etc.).[1] Several preparation methods for poly(phenylene oxide)s are known including oxidative coupling of phenols,[2] decomposition of anhydrous silver phenoxides,[3] pyrolysis of diazoxides or phenol mercuriacetates,[4] and oxidative polymerization of 2,6-xylenol with sodium bismuthate.[5] We now report a novel preparation method for poly(phenylene oxide) using a spiro compound as a starting material via the elimination of formaldehyde (Scheme 1).

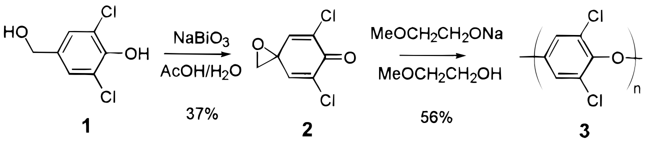
Experimental Section

Synthesis of 5,7-Dichloro-1-oxaspiro[2.5]octa-4,7-dien-6-one (2). The mixture of 3,6-dichloro-4-hydroxybenzyl alcohol (**1**)[6] (3.9 g, 20 mmol), sodium bismuthate (11.2 g, 40 mmol), acetic acid (160 mL), and water (40 mL) was stirred at room temperature for 1 h and filtered. The filtrate was poured into water and extracted with dichloromethane. The extract was washed with sodium hydrogen carbonate solution, dried over magnesium sulfate, and placed under reduced pressure to remove the solvent. The residue was recrystallized from isopropyl ether to give **2** as colorless needles (1.4 g, 37%): mp 122−123 °C; ^{1}H NMR (CDCl$_3$) δ 6.75 (s, 2H), 3.46 (s, 2H); ^{13}C NMR (CDCl$_3$) δ 172.6, 142.5, 135.3, 55.2, 54.6; IR (KBr) 3004, 1637, 1564, 1250, 1033, 910, 773 cm^{-1}. Anal. Calcd for C$_7$H$_4$Cl$_2$O$_2$: C, 44.02; H, 2.11; Cl, 37.12. Found: C, 44.27; H, 1.96; Cl, 36.88.

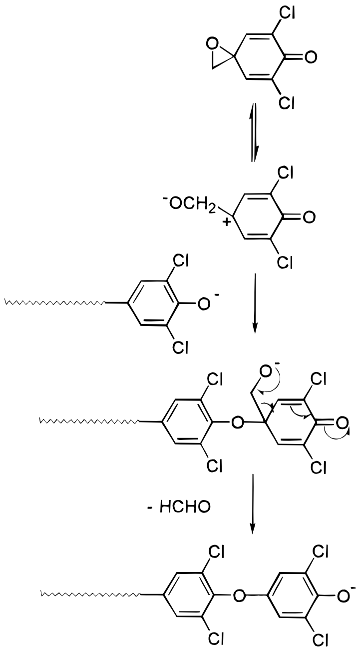
Polymerization of 2. Sodium (1 mg, 0.04 mmol) was dissolved in 10 mL of 2-methoxyethanol. Into the solution was added spiro compound **2** (0.30 g, 1.6 mmol), and the mixture was heated at 90 °C under nitrogen for 5 h. The reaction mixture was poured into a large amount of methanol to give the precipitated product which was purified by redissolution in THF and reprecipitation in methanol to give 0.14 g of white powder.

Reaction of 2 with Sodium Phenoxide. The mixture of spiro compound **2** (0.30 g, 1.6 mmol) and sodium phenoxide (0.56 g, 4.8 mmol) in 10 mL of methanol was stirred at room temperature for 4 h. The reaction mixture was poured into water and extracted with ether. The ether extract was dried with anhydrous magnesium sulfate and placed under reduced pressure to remove the solvent. The residue was recrystallized from hexane to give 2,6-dichloro-4-(2,6-dichloro-4-phenoxyphenoxy)phenol (**5**) as colorless needles in 12% yield: mp 127 °C; ^{1}H NMR (CDCl$_3$) δ 7.42 (t, J = 8.1 Hz, 2H), 7.22 (t, J = 8.1 Hz, 1H), 7.08 (d, J = 8.1 Hz, 2H), 7.01 (s, 2H), 6.80 (s, 2H), 5.57 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 155.5, 155.3, 150.0, 143.6, 141.8, 130.2, 130.1, 124.9, 121.4, 119.9, 118.5, 115.2; IR (KBr) 3462, 1554, 1454, 1430, 1195, 937 cm^{-1}. Anal. Calcd for C$_{18}$H$_{10}$Cl$_4$O$_3$: C, 52.18; H, 2.43; Cl, 33.79. Found: C, 51.97; H, 2.35; Cl, 33.58.

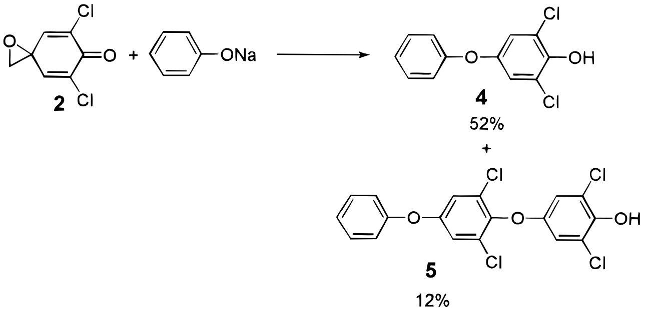
Scheme 1



Scheme 2



Scheme 3



The filtrate was passed through a silica gel column using a mixture of chloroform and hexane as an eluent to obtain 2,6-dichloro-4-phenoxyphenol (**4**) as colorless oil in 52% yield: ^{1}H NMR (CDCl$_3$) δ 7.34 (t, J = 8.1 Hz, 2H), 7.12 (t, J = 8.1 Hz, 1H), 6.97 (d, J = 8.1 Hz, 2H), 6.96 (s, 2H), 5.67 (s, 1H); ^{13}C NMR (CDCl$_3$) δ 156.8, 150.1, 144.1, 129.9, 123.7, 121.3, 119.2, 118.5; IR (KBr) 3458, 1556, 1449, 1196, 943 cm^{-1}. Anal. Calcd for C$_{12}$H$_8$Cl$_2$O$_2$: C, 56.70; H, 3.17; Cl, 27.54. Found: C, 56.47; H, 3.25; Cl, 27.18.

Results and Discussion

The polymerization product was insoluble in acetone or hexane but soluble in chloroform, THF, and DMSO. Its number-average molecular weight was found to be 6600 by gel permeation chromatography (GPC) with polystyrene standards. The structure of the product was analyzed by NMR, IR, and elemental analysis. Its ^{1}H NMR spectrum showed a singlet peak at 6.93 ppm. Its ^{13}C NMR spectrum showed four peaks at 154.4, 141.4, 130.3, and 116.2 ppm as shown in Figure 1. The IR spectrum of the product exhibited no peak at 1637 or 3004 cm^{-1} nor at 1220, 910, or 773 cm^{-1}, assignable to a carbonyl or epoxy moiety, respectively, but a new peak at 1180 cm^{-1} assignable to an ether bond. The elemental analysis of the product was in good agreement

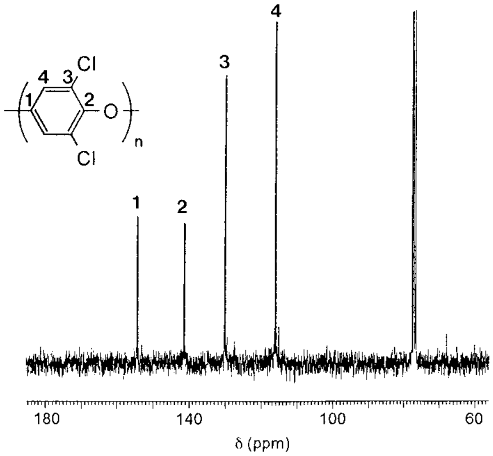


Figure 1. ^{13}C NMR spectrum of the product in $CDCl_3$.

with poly(2,6-dichloro-1,4-phenylene oxide) (**3**) (Anal. Calcd for $(C_6H_2Cl_2O)_n$: C, 44.77; H, 1.25; Cl, 44.04. Found: C, 45.03; H, 1.12; Cl, 44.36.) It was concluded therefore that the obtained product was poly(phenylene ether) **3**, indicating that the elimination of formaldehyde took place during polymerization instead of conventional ring opening of the oxirane. Although the exact polymerization mechanism is unknown at the moment, a possible mechanism includes the dissociation of the C−O bond in the epoxide to form an equilibrium with an alcoxide and a carbocation on the 6-membered ring. Binding between the cation and phenoxide would form an intermediate that could eliminate formaldehyde and generate a new phenoxide to continue the polymerization (Scheme 2). The elimination of formaldehyde was probably driven by the aromatization energy as well as release of strain energy. The reaction of **2** with sodium phenoxide in methanol gave diphenyl ether **4** in 52% yield along with **5** in 12% yield, supporting the abovementioned mechanism (Scheme 3).

Poly(2,6-dichloro-1,4-phenylene oxide) has been prepared by several methods such as a free-radical-initiated decomposition of sodium 2,6-dichloro-4-bromophenolate with benzoyl peroxide,[7] a polymerization of 2,6-dichlorophenol by cupric chloride−sodium methoxide system,[8] a thermal decomposition of bis(2,4,6-trichlorophenoxo)-bis(pyridine)copper(I),[9] and an electrooxidative polymerization of 2,6-dichlorophenol.[10] Our synthetic approach to poly(phenylene ether) is based on a new chemistry of spiro compound, although the molecular weight of the polymer is not sufficiently high. Studies of the detail of the polymerization mechanism and generalization of this reaction to other substituted poly(phenylene oxide)s are under investigation.

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