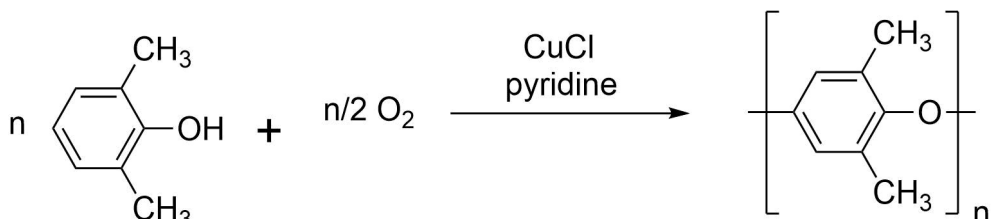


Poly(2,6-dimethyl-1,4-phenylene ether)

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A. By Oxidative Coupling

1. Procedure

To a 500 ml wide-mouthed Erlenmeyer flask in a water bath at 30°C equipped with a Vibromixer stirrer, an oxygen inlet tube, and a thermometer are added 200 ml of nitrobenzene, 70 ml of pyridine, and 1 g of copper(I) chloride. Oxygen (300 ml/min) is bubbled through the vigorously stirred solution and then 15 g (0.12 mol, Note 1) of 2,6-dimethylphenol is added. Over a period of 16 min the temperature rises to 33°C, at which point the reaction mixture begins to get viscous. The reaction is continued for 12 min, then diluted with 100 ml of chloroform and added to 1.1 l of methanol containing 3 ml of conc HCl. The precipitated polymer is filtered and washed with 250 ml of methanol, then with 250 ml of methanol containing 10 ml of conc HCl, and finally with 250 ml of methanol. The polymer is dissolved in 500 ml of chloroform, filtered and reprecipitated into 1.2 l of methanol containing 3 ml of conc HCl. After washing with methanol and drying at 110°C (5 torr) for 3 h, there is obtained 13.5 g (0.11 mol, 91%) of almost colorless polymer, $[\eta] = 0.96 \text{ dl/g}$ (CHCl_3 , at 25°, Note 2).

An alternative method for producing the polymer from 2,6-xyleneol which uses MnO_2 as oxidant has been reported.³

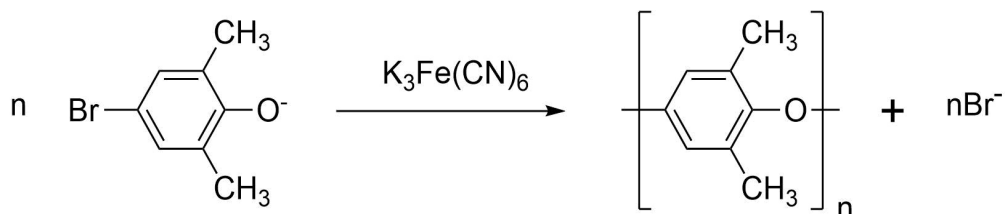
2. Notes

- 2,6-Dimethylphenol was purchased from Aldrich Chemical Co. and twice recrystallized from heptane. Copper(I) chloride was purified by dissolving it in concentrated hydrochloric acid, filtering, and precipitating with water. The copper(I) chloride was washed with alcohol and then with ether, and dried under reduced pressure. Pyridine and nitrobenzene were purified grades.
- This is equivalent to an osmotic molecular weight of 28,000.

B. By Oxidative Displacement of Bromine

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1. Procedure

A 1 l three-necked flask is fitted with an efficient stirrer, a dropping funnel, and a gas inlet tube connected to a stream of prepurified nitrogen (Note 1). A solution of 5 g of potassium hydroxide in 200 ml of water, 4-bromo-2,6-xyleneol (8 g, 0.04 mol, Note 2) and 200 ml of benzene is introduced. The stirrer is started and 1.3 g of potassium ferricyanide in 20 ml of water is added dropwise over a period of 30 min. After an additional 15 min of stirring, the mixture is transferred to a separatory funnel and the lower aqueous phase is removed (Note 3). The yellow benzene solution is transferred to a 300 ml distilling flask and concentrated to 50 ml at ca 20 torr. The concentrate is poured slowly, with stirring, into 250 ml of methanol acidified with 2.5 ml of conc HCl. The precipitate is collected by suction filtration and washed by resuspending it in 150 ml of methanol. It is then collected, redissolved in 50 ml of benzene, and precipitated again as described above.

The reprecipitated polymer is collected and redissolved in 50 ml of benzene contained in a 250 ml round-bottomed flask. The flask is swirled in a Dry Ice-acetone solution until the contents are frozen and then it is quickly connected to a vacuum line protected by a large trap. The pump is started and a pressure of 1 torr is maintained for 5 h. This gives 4.6 g (96%) of spongy white solid; $[\eta]$ in benzene = 0.5-0.6 dl/g (Note 4). The product darkens and softens above 270° (Note 5).

2. Notes

1. If necessary, the nitrogen is freed of traces of oxygen by bubbling it through Fieser's solution.⁴
2. 4-Bromo-2,6-xyleneol is prepared by bromination of 2,6-xyleneol.⁵
3. Separation of the phases, if difficult, may be facilitated by the addition of 10 ml of conc HCl.
4. The intrinsic viscosity corresponds to a molecular weight of 20,000-25,000 as determined by an equation relating osmotic molecular weight to intrinsic viscosity ($[\eta] = 3.8 \times 10^{-4} M^{0.73}$) supplied by Dr. A. S. Hay, General Electric Co., Schenectady, NY. A product of higher molecular weight may be obtained by adding the ferricyanide solution more slowly. When the reaction time was then doubled, the product decomposed without softening at >270°; viscosity 0.9 dl/g.
5. A sample of the polymer gave the following analysis: C, 79.19; H, 7.02; Br, 1.06. The amount of residual phenol group was negligible as determined by titration with tetrabutylammonium hydroxide. Exchange with tritiated water, however, indicated one exchangeable hydrogen per 19,000 molecular weight units.
6. An alternate method for producing the polymer from 4-bromo-2,6-xyleneol in a homogeneous system has been reported.⁶

3. References

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