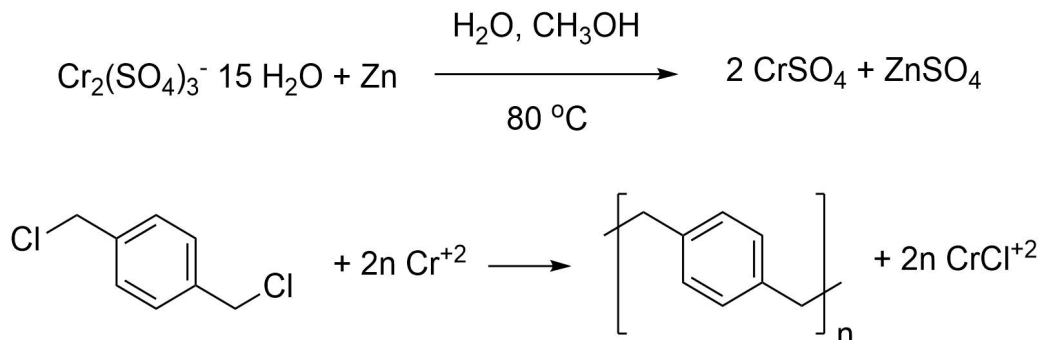


Poly-*p*-xylylene

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1. Procedure

Caution! Some individuals have developed dermatitis when preparing poly-*p*-xylylene by this general method (Note 1).

A. Apparatus

An aqueous methanolic solution of chromous sulfate is prepared in the 1 l upper reaction flask of Fig. 1 which is modified with a 6 mm stopcock for bottom draw-off and is heated with the inverted upper half of a heating mantle. The solution flows by gravity through filter A (Note 2) into the 2 l lower reaction flask, where it reacts at reflux with α, α' -dichloro-*p*-xylylene added in *p*-dioxane from the 250 ml pressure-equalizing addition funnel. The lower flask should be equipped with an efficient bulb condenser. Asco Teflon glands (Note 3) provide convenient stirrer bearings. Glass or stainless steel stirrer shafts and blades may be used. The 1 l filter flask B serves as a ballast to prevent air intake. An oil bubbler C to indicate nitrogen flow and a mercury pressure release valve D are included.

B. Nitrogen Purge

Because chromous ion solutions are rapidly oxidized by air, the entire system must be flushed with nitrogen before starting and must be kept under nitrogen throughout the reaction. Pinch clamp E is closed and nitrogen passed through the reaction flasks and oil bubbler C for about 20 min. Care is taken to flush the addition funnel. The pinch clamp E is then removed and the nitrogen stream adjusted so that a moderate flow passes through the oil bubbler C to blanket the entire system.

C. Chromous Sulfate

Into the upper flask are introduced chromium sulfate pentadecahydrate (116 g, 0.175 mol, Note 4), 20 mesh granular zinc (10.0 g, 0.153 g atom, Note 5), 425 ml of deionized water, and 250 ml of methanol (Note 6). The contents of the flask are stirred and heated to reflux (80°C) as rapidly as possible. Refluxing and stirring are continued until only a few particles of zinc are visible; this usually requires 1-1.5 h (Note 7). The blue-green solution contains 270-295 mmol of chromous sulfate (Note 8). It is filtered into the lower flask and rapidly reheated to reflux. The filtration requires 10-20 min (Note 9).

D. Polymer Preparation

A solution of α, α' -dichloro-*p*-xylene (17.5 g, 0.100 mol, Note 10) in 150 ml of dioxane (Note 11) is added from the pressure-equalizing funnel to the refluxing, filtered chromous sulfate solution as rapidly as possible, with good stirring. The addition requires 20-30 sec. After 30 min of refluxing and stirring, the reaction is complete. About 90-100 mmol excess chromous sulfate remains unreacted (Note 8). The flask is cooled at once with a bucket of cold water.

E. Polymer Isolation (Caution! Hood; see Note 1.)

Without delay the polymer is collected on a tared, fritted glass funnel (Note 12). The filter cake is promptly washed with ten successive 100 ml portions of deionized water. The cake is dispersed well with a spatula after each addition of water and is then sucked dry with a water aspirator. Immediately it is washed with ten 50 ml portions of acetone (Note 13) and dried in vacuum at 50°C; yd 8.8-9.1 g (85-88%) of white, friable solid (Note 14); ash content 0.05-1.6% (Note 15).

2. Characterization

Inherent viscosity is conveniently determined in a Cannon-Fenske viscometer (Note 16) heated in a benzophenone vapor bath (305°C). Arochlor 1242 (Note 17) is used as solvent, and an inhibitor (Note 18) must be added (1%). The polymer sample, solvent, and inhibitor are placed in the viscometer, and nitrogen is slowly bubbled through the mixture for about 20 min. A nitrogen atmosphere is maintained in the viscometer throughout the determination. The viscometer is placed in the vapor bath, and a stopwatch is started to show cumulative time in the bath. Polymer dissolves completely in 3-7 min. Successive viscosity determinations are started as soon as solution is complete and are repeated as rapidly as possible over a period of about 20-30 min, noting the cumulative bath time at the start of each determination. A plot is made of the decreasing inherent viscosities against cumulative bath time. A smooth, downward trend should be observed. Extrapolation to zero bath time gives inherent viscosities ranging from 0.83 to 1.24 dl/g (0.40 g/100 ml).

The infrared absorption spectrum of the polymer is in accord with a published spectrum for poly-*p*-xylylene.³ An x-ray diagram of one sample showed d-spacings of 5.3, 4.4 and 3.9 Å, indicating the presence of both the α - and β -forms of poly-*p*-xylylene.^{4,5} When placed on a temperature gradient bar (modified Dennis bar)⁶ at temperatures above 400°C, the polymer melts with decomposition.

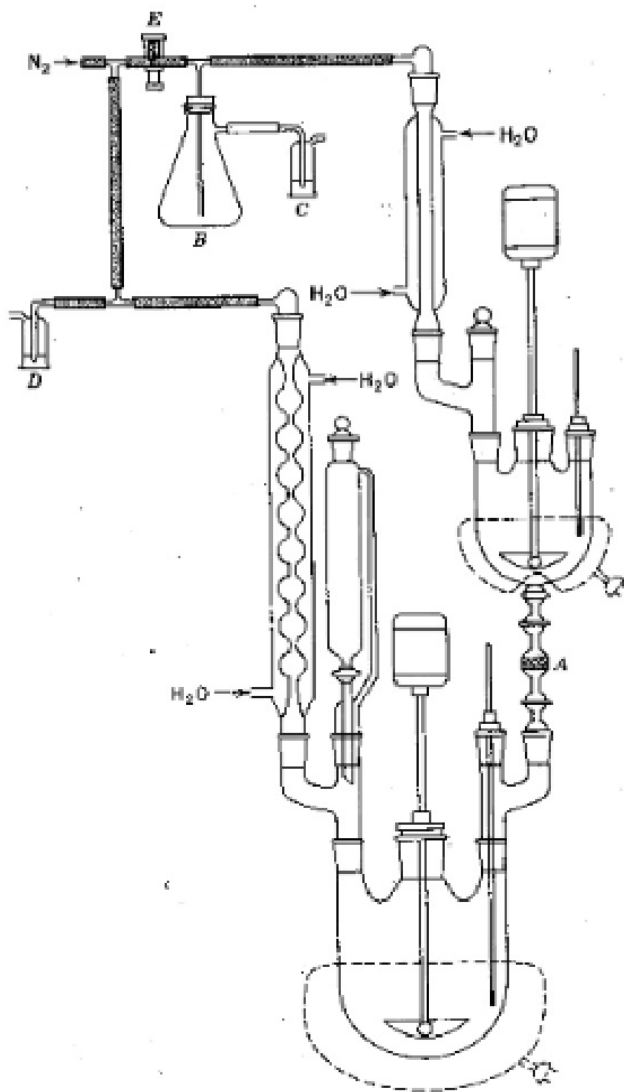


Fig. 1.

3. Notes

1. Workers of the Research Division of the U.S. Industrial Chemicals Co. developed a skin irritation resembling sunburn during the initial study of this reaction. Careless handling of α,α' -dichloro-*p*-xylylene may have been responsible, but the evidence is not conclusive. The submitters repeatedly used the procedure described here without such difficulty. The apparatus shown in Fig. 1 was attached to a rack in a well-ventilated laboratory. All operations with α,α' -dichloro-*p*-xylylene, however, such as recrystallization, solution makeup and polymer isolation, were confined to a hood.
2. The detachable filter is fabricated from a reduced-end sealing tube, Corning No. 39580, containing a 40 mm dia. coarse-porosity glass frit, and is fitted with 18/9 ball and socket joints.
3. Asco glands are available from Matheson Scientific, Inc.
4. Reagent chromium sulfate crystals, $\text{Cr}_2(\text{SO}_4)_3 \bullet 15 \text{H}_2\text{O}$, from Matheson, Coleman and Bell, are used.
5. Zinc metal, A.C.S., 20-mesh, from Matheson, Coleman and Bell is preferred. Mossy zinc, A.C.S., from the same source serves equally well. Zinc dust is not recommended because it reacts more slowly.
6. A.C.S. grade methanol from Fisher Scientific Co. is employed.
7. The checker found that a 3 h reflux period is needed. Even then, 0.23 and 0.71 g of unreacted zinc were recovered in duplicate experiments. The length of tubing leading to the bottom stopcock of the upper flask should be minimized to reduce trapping zinc.
8. As indicated by Castro,⁷ chromous sulfate can be determined by removing 1 ml samples with a syringe and injecting them into 25 ml portions of 0.25 M aqueous ferric chloride solution under nitrogen. A drop of Ferroin indicator (*o*-phenanthroline-ferrous sulfate complex, 0.025 M, Fisher Scientific Co.) is added and the solution is titrated to the green end-point with standard ceric ammonium sulfate solution. The titrations are unnecessary if essentially all the zinc has been consumed and the system is well-blanketed with nitrogen.
9. The checker observed slower filtration (40-60 min.).
10. α,α' -Dichloro-*p*-xylylene, mp 98.5-99.5°C, from Diamond Alkali Co. is used as received.
11. A purified grade of *p*-dioxane from Fisher Scientific Co. is used as received. Further purification did not lead to improved results. The *p*-dioxane solution of α,α' -dichloro-*p*-xylylene is sparged for about 15 min with nitrogen before addition (*Caution! Hood*).
12. A 350 ml, coarse-porosity, sintered glass funnel is recommended.
13. After about eight acetone washes, the wash should not show cloudiness on dilution with water. If it does, acetone washing should be continued until no cloudiness is observed on dilution.
14. The checker obtained 9.1 and 9.3 g (88% and 89%).
15. The submitters found 0.05-0.24% ash (3 polymers); the checker found 1.6% (1 polymer). The need for prompt and thorough washing of the polymer at the end of the synthesis is emphasized.
16. Poly-*p*-xylylene is soluble only at elevated temperatures ($\sim 300^\circ$) in solvents such as the Arochlors and benzyl benzoate. Schaeffgen⁸ has shown that it degrades rapidly in solution at these temperatures. With adequate precautions, however, reasonably reproducible inherent viscosities can be measured.

The submitters used a special viscometer similar to that described by Schaeffgen.⁸ The solvent was distilled and stored under nitrogen, and the samples were carefully degassed. The checker, however, obtained comparable inherent viscosities with a Cannon-Fenske viscometer and undistilled Arochlor 1242 containing 1% antioxidant 2246 (Note 18). His method seems more convenient.

The accompanying tabulation shows comparative viscosity determinations made in both laboratories.

Schaeffgen⁸ used the term "inherent viscosity at zero time" to denote the viscosity when complete solution was achieved. The submitters and the checker adopted the alternative practice of reporting inherent viscosity extrapolated to zero bath time. The extrapolated values are a little (<10%) higher than the first measured values, having been obtained after 5-10 min of bath time.

A mixture containing 0.50 g of polymer per 100 ml of Arochlor 1242 at room temperature contains 0.40 g/100 ml at 305°C because solvent density falls from 1.37 g/cc at 25°C to 1.10 g/cc at 300°C.⁹

| Polymer No. | Inherent Viscosity ^a | |
|---|--|--|
| | Results using Submitters Viscometer ^{8,b} | Results of Checker, Cannon-Fenske Viscometer used ^c |
| Submitters' Samples | | |
| No. 1 | 0.94 | 0.83 |
| No. 2 | 1.23 | 1.19 |
| No. 3 | 1.31, 1.38 | 1.13 |
| Checker's Samples | | |
| No. 1 | --- | 1.12 |
| No. 2 | --- | 1.24 |
| ^a Extrapolated to zero bath time, 0.40 g/100 ml at 305°C. ^b No inhibitor used. ^c Antioxidant 2246 used (1%). | | |

17. Arochlor 1242, Monsanto Chemical Co., is a chlorinated biphenyl mixture. The checker found that distilled and technical grade solvent sparged with nitrogen give the same viscosity if inhibitor is used.
18. Antioxidant 2246, 2,2'-methylene-bis-(4-methyl-6-*t*-butylphenol) was obtained from American Cyanamid Co.

4. Methods of Preparation

The method described here was previously reported.¹⁰ It provides a convenient laboratory synthesis of soluble, high molecular weight poly-*p*-xylylene from commercial starting materials.

Soluble poly-*p*-xylylene of comparable molecular weight can also be prepared by the Hofmann degradation of *p*-methylbenzylammonium salts^{6,11,12} but the starting materials are less readily available.

Poly-*p*-xylylene is also obtained by the fast-flow, vacuum pyrolysis of *p*-xylene first reported by Szwarc¹³ and later studied by other workers.^{14,15,16,17} Elaborate equipment and extreme temperatures (800-1000°) are required. The very reactive intermediate, *p*-xylylene or *p*-quinodimethane, is formed in the pyrolysis and polymerizes as it condenses on cool surfaces. The pyrolysis polymer appears to be more or less crosslinked.^{4,14,15,16,8} Quenching the pyrolysis stream in cold (-78°C) solvents affords fairly stable solutions of monomeric *p*-xylylene.¹⁷ When the *p*-xylylene solutions are allowed to polymerize to completion at low temperatures, a relatively tractable, soluble polymer is produced.⁴

Recently the pyrolysis method was modified to yield initially the cyclic dimer, di-*p*-xylylene.^{18,19} Thermolysis of the latter in vacuum at 600° to regenerate *p*-xylylene permits thin films of the polymer to be deposited on various substrates. Elaborate equipment and careful control are again required, but the method provides commercially useful forms of the polymer (Parylene polymers of Union Carbide Corp.).

The literature contains many references to the conversion of xylylene dihalides to xylylene polymers with coupling agents like sodium,^{20,21,22} lithium,²³ transition metal powders,²⁴ and phenyllithium.²³ The chemistry of *p*-xylylene, its analogs, and its polymers has been reviewed.²⁵

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