

Preparation of Adherent Films of Poly-*p*-Xylylenes on Aluminum by Electrolysis

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Synopsis

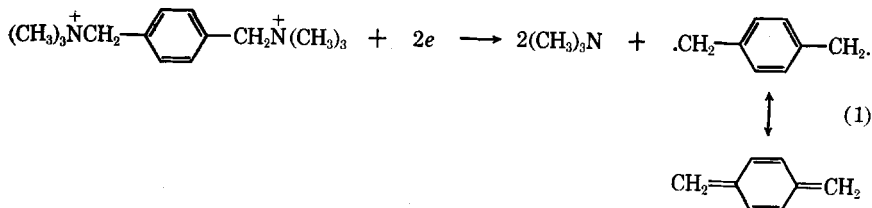
The electrolysis of solutions of *p*-methylbenzyltrimethylammonium nitrate or, better, *p*-xylylenebis(trimethylammonium nitrate) or *p*-xylylenebis(triphenylphosphonium chloride or bromide) in a polar organic solvent with an aluminum cathode and a platinum anode results in the formation of adherent coatings of poly-*p*-xylylene on the cathode. The mechanism of this reaction involves the electrochemical generation of *p*-xylylene and its subsequent polymerization on the aluminum cathode. Competing reactions are formation of *p*-xylene and reduction of the solvent.

Poly-*p*-xylylene (PPX), originally prepared by the pyrolytic dehydrogenation of *p*-xylene,¹ is now being prepared commercially in a two-stage process in which *p*-xylene is first converted to di-*p*-xylylene ([2.2]paracyclophane), which on pyrolysis at 600°C. cleaves to two molecules of *p*-xylylene. On condensation the *p*-xylylene spontaneously polymerizes to give a quantitative yield of high molecular weight, linear poly-*p*-xylylene.² The polymer (PPX) has also been obtained by a 1,6-Hofmann elimination reaction of *p*-methylbenzyltrimethylammonium hydroxide,³⁻⁵ by coupling of xylylene dihalides with divalent chromium,⁶ and by the electrolytic reduction of α, α' -dihalo-*p*-xylenes at controlled cathode potentials.⁷

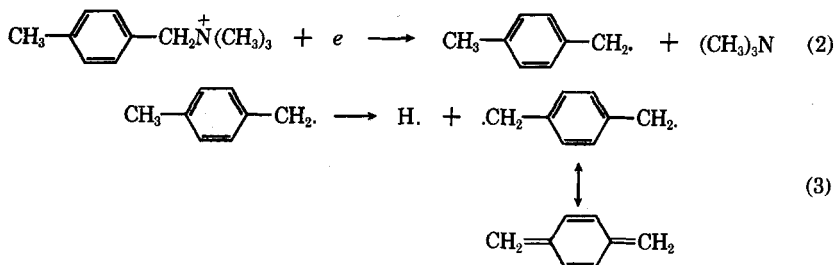
We now report an additional electrochemical method for obtaining PPX, this time as an adherent coating on aluminum. When a solution of a *p*-methylbenzyltrimethylammonium salt, a *p*-xylylenebis(trimethylammonium salt) or a *p*-xylylenebis(triphenylphosphonium salt) in a polar solvent is electrolyzed with a platinum anode and an aluminum cathode, the cathode becomes coated with a strongly adherent film of poly-*p*-xylylene when the current density is sufficiently high. In a constant current electrolysis the voltage increases with time; at constant voltage the current decreases with time.

The ammonium salts were electrolyzed as the nitrates and the phosphonium salts as the chlorides or bromides. Suitable solvents for the reaction are those of the dipolar, aprotic type, e.g., dimethylformamide, dimethyl sulfoxide, propylene carbonate, tetramethylene sulfone, and 1,2-propylene glycol sulfite, and in general, dimethyl sulfoxide is the preferred solvent.

It has been shown previously that the electrochemical reduction of a benzyltrialkylammonium ion⁸⁻¹⁰ or a benzyltriphenylphosphonium ion¹¹⁻¹³ involves a one-electron transfer at the cathode to form a benzyl radical and either a trialkylamine or triphenylphosphine. In the present reactions with the *p*-xylylenebis(trimethylammonium) cation it is reasonably certain that a two-electron transfer at the cathode is involved as shown in eq. (1).



The bisphosphonium salt involves the same reaction except that the leaving group is now triphenylphosphine. With the *p*-methylbenzyltrimethylammonium cation only a single-electron transfer from the cathode is probable, but the sequence of the two reactions shown below can result in the same *p*-xylylene intermediate.



When the electrolysis conditions are such as to create a sufficiently high concentration of the *p*-xylylene intermediate at the cathode, polymerization ensues, and an adherent coating of PPX forms. The structure of the polymer was established by comparing its infrared spectrum (Figs. 1 and 2), obtained on a Perkin-Elmer Model 237B grating infrared spectrophotometer equipped with a frustrated multiple internal reflectance (FMIR) attachment, with the spectrum (Fig. 3) of authentic poly-*p*-xylylene, prepared by the Hofmann elimination reaction on *p*-methylbenzyltrimethylammonium bromide.³⁻⁵ No significant distinctions are discernible in the spectra.

Competing reactions are hydrogen abstraction from the solvent, which results in chain termination or in *p*-xylylene formation if the abstraction is by *p*-xylylene, and reduction of the solvent. From one electrolysis of *p*-xylylenebis(trimethylammonium nitrate) in formamide, in which two equivalents of charge per mole of salt were passed, 40% of the starting salt was recovered, and a 1% yield of *p*-xylylene was found in the solvent. In addition, three unidentified, higher-boiling components were present in

very low yields ($\sim 0.1\%$). Electrolyses in dimethyl sulfoxide, the preferred solvent, are accompanied by progressive yellowing of the solution, and eventually contaminants preventing polymer formation result. Such a spent solution was poured into water, and the aqueous solution was extracted

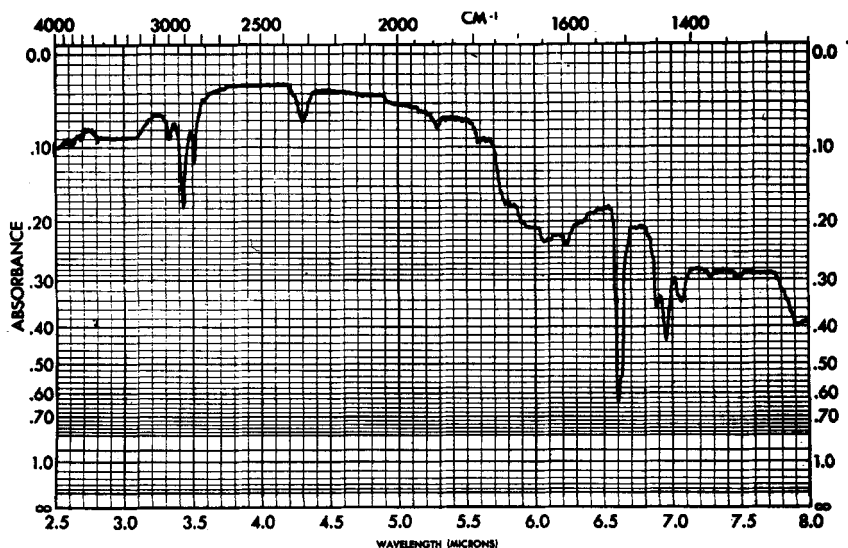


Fig. 1. FMIR spectrum of PPX coating on aluminum. The polymer was prepared by electrolysis of *p*-xylylenebis(triphenylphosphonium bromide) in propylene carbonate.

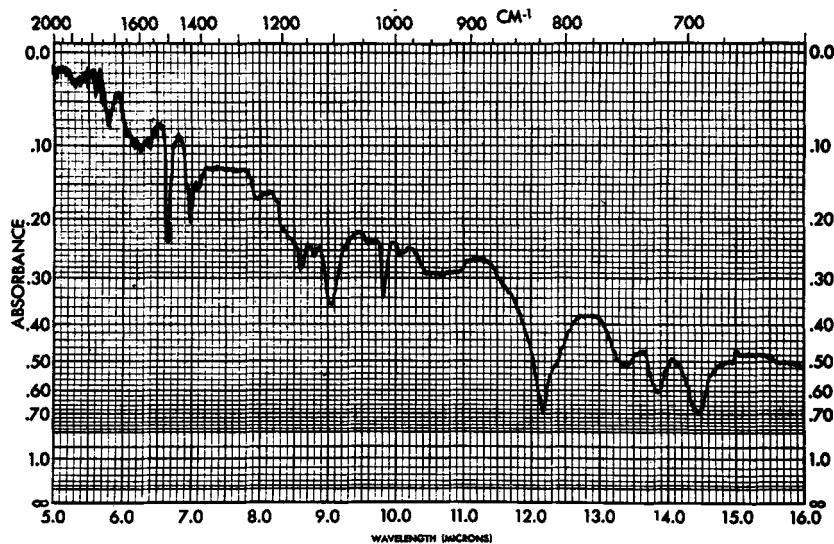


Fig. 2. FMIR spectrum of PPX coating on aluminum. The polymer was prepared by electrolysis of *p*-xylylenebis(triphenylphosphonium bromide) in propylene carbonate.

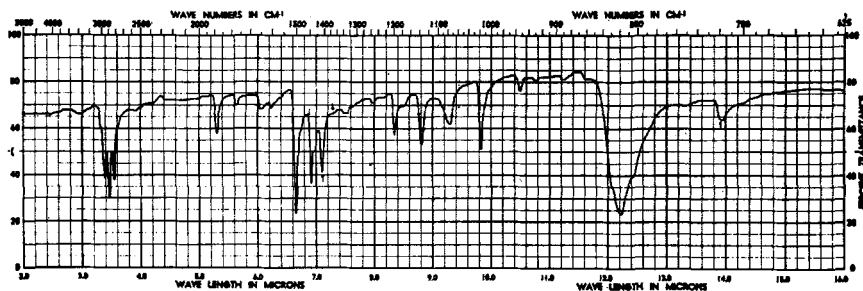


Fig. 3. KBr disk spectrum of PPX. The polymer was prepared by a Hofmann elimination reaction in *p*-methylbenzyltrimethylammonium bromide.

with carbon tetrachloride. Analysis of the extract by vapor-phase chromatography showed the presence of dimethyl sulfide in a 4% yield, based on the charge passed assuming that two Faradays are required per mole of the sulfide formed. It is probable and suggested by the observed odor that methanethiol is also formed and eliminated by the nitrogen bubbling through the solution.

A final limitation on the polymerization reaction is the fact that the build-up of the polymer coating on the cathode eventually interferes with transport of the cation to the electrode. A typical coating, prepared by electrolysis of *p*-xylylenebis(trimethylphosphonium bromide) in dimethyl sulfoxide was estimated to have a thickness of 6000 Å. from the gain in weight of the cathode and the assumption of uniform coverage.

Ring-substituted poly-*p*-xylylenes may also be obtained by this method, and adherent coatings of poly-2,3,5,6-tetrachloro-*p*-xylylene were obtained, although this reaction was not studied in detail.

EXPERIMENTAL

***p*-Xylylenebis(trimethylammonium Bromide).** Trimethylamine (11.8 g., 0.2 mole), as a 25% solution in methanol, was added dropwise with magnetic stirring to a solution of α,α' -dibromo-*p*-xylene (26.4 g., 0.1 mole) in methanol (200 ml.). The reaction mixture was refluxed 3 hr. after the addition and then cooled. The product was precipitated by adding ether and crystallized from methanol containing 1% water; yield, 29.5 g. (77.2%). The compound does not melt. Slow decomposition begins at 310°C., but the salt is not completely decomposed even at 335°C.

ANAL. Calcd. for $C_{14}H_{26}Br_2N_2$: Br, 41.82%. Found: Br, 42.26%.

***p*-Xylylenebis(trimethylammonium Nitrate).** (I). The above salt (3.82 g., 0.01 mole) was dissolved in water and converted to the hydroxide by treatment with a slight excess of silver oxide. The solution was filtered and just neutralized with nitric acid. The water was removed with the water pump, and the crude product was crystallized from methanol; yield, 3.1 g. (89.6%); m.p., 292°C. (dec.).

ANAL. Calcd. for $C_{14}H_{26}N_4O_6$; C, 48.54%; H, 7.57%; N, 16.18%. Found: C, 48.59%; H, 7.37%; N, 15.85%.

***p*-Methylbenzyltrimethylammonium Nitrate (V).** *p*-Methylbenzyltrimethylammonium bromide³⁻⁵ was converted to the nitrate by the procedure described above. The yield was quantitative; m.p. 180–182°C. after crystallization from methanol-ether.

ANAL. Calcd. for $C_{11}H_{18}N_2O_3$; C, 58.39%; H, 8.02%; N, 12.38%. Found: C, 58.44%; H, 8.21%; N, 11.88%.

2,3,5,6-Tetrachloro-*p*-xylylenebis(trimethylammonium Bromide). Trimethylamine (5.9 g., 0.1 mole), as a 25% solution in methanol, was added dropwise with magnetic stirring to a refluxing solution of 1,4-bis(bromomethyl)-2,3,5,6-tetrachlorobenzene¹⁴ (12.05 g., 0.03 mole) in carbon tetrachloride (200 ml.). The refluxing was continued 1.5 hr. after the addition. The solution was cooled and ether was added to precipitate the product. The yield was quantitative; m.p. 276°C. (dec.) after crystallization from methanol-water.

ANAL. Calcd. for $C_{14}H_{22}Cl_4Br_2N_2$; Br, 30.75%. Found: Br, 31.31, 30.24%.

2,3,5,6-Tetrachloro-*p*-Xylylenebis(trimethylammonium Nitrate) (IV). The above bromide was converted to the nitrate by the previously described procedure. After crystallization from water the product melted with decomposition at 276°C.

ANAL. Calcd. for $C_{14}H_{22}Cl_4N_4O_6$; C, 34.73%; H, 4.58%; Cl, 29.29%; N, 11.57%. Found: C, 35.18%; H, 4.73%; Cl, 29.35%; N, 10.86%.

***p*-Xylylenebis(triphenylphosphonium Bromide) (II) and *p*-Xylylenebis(triphenylphosphonium Chloride) (III).** Both salts were obtained from Columbia Organic Chemicals Co., Inc., Columbia, South Carolina and used without further purification.

Solvents

Formamide (97.7%) from Aldrich Chemical Co., Inc. was used without further purification. Dimethyl sulfoxide (DMSO) from Stepan Chemical Co. was distilled from calcium hydride; b.p. 74.5°C./12 mm. Propylene carbonate (PC) and tetramethylene sulfone (S), both from Aldrich Chemical Co., Inc. were redistilled; b.p. 111°C./12 mm. and 144°C./14 mm., respectively. 1,2-Propylene glycol sulfite (PGS) was obtained from Chemische Werke Hüls AG., Marl, Germany and redistilled before use; b.p. 69°C./12 mm. Dimethylformamide (DMF) was redistilled before use; b.p. 39°C./10 mm.

Electrolysis Procedure

The cell used was a flat-bottomed cylinder, 7.7 cm. high and 5.0 cm. in diameter and fitted with a Teflon cover to which the electrodes were attached. The anode was of 0.005 in. platinum, 7 cm. × 2.5 cm., and

immersed to a depth of 5 cm. The cathode was of 0.02 in. 99.999% Super Raffinal aluminum from AIAG Metals, Inc., Zurich, Switzerland. It was 6 cm. \times 2.5 cm. and immersed to a depth of 4 cm. The separation between the two electrodes was 2.5 cm.

In a typical electrolysis 75 ml. of the salt solution was used, and the potential was applied by means of a variable voltage d.c. power supply. The current was measured with a milliammeter in series with the circuit. Some representative initial electrolysis conditions are compiled in Table I. The

TABLE I

Salt	Solvent	Concentration, g./100 ml.	i_0 , ma.	v_0 , v.	Coating appearance
I	DMSO	5.0	260	17	Good
	PGS	<1.0	54	40	Soft, uneven
	PC	<3.3	150	40	Slightly soft
	S	<4.0	25	40	Good
II	DMSO	4.0	300	30	Good
	PC	2.7	160	40	Good
	S	4.2	80	40	Good
III	DMSO	4.0	80	15	Soft, brown
	PC	<4.0	180	40	Soft
IV	DMSO	<1.2	200	25	Uneven Yellowish

reactions were carried out at room temperature while bubbling dry nitrogen through the solution and stirring with a Teflon-coated magnetic bar. At the currents used there was no observable increase in the temperature of the solution. After the desired reaction time the electrolysis was stopped, and the PPX-coated cathode was leached in several portions of distilled water for several hours to remove residual solvent and salt from the coating and finally dried at 110°C.

These electrolyses may be run at either constant current or constant voltage. In actual practice it was generally most convenient to vary both the current and the voltage simultaneously, letting the current decrease while the voltage was gradually increased. The best results were obtained with II in DMSO. As in the other systems, the initial current is critical. When i_0 is greater than 100 ma., a hard, smooth, translucent, white coating forms evenly over the cathode in 15 sec. When $i_0 = 25$ ma., an uneven coating is formed after 7 min. When $i_0 = 10$ ma., no coating is readily visible after 25 min. During this time the current has decreased to 2.4 ma., and a soft, transparent coating can be detected by scratching the electrode surface. The best appearing coatings were obtained using initial currents in excess of 200 ma.

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Résumé

L'électrolyse de solutions de nitrate de paraméthylbenzyl-triméthylammonium ou mieux de paraxylylènebistriméthylammonium nitrate ou *p*-xylylènebistriphénylphosphonium chlorure ou bromure dans un solvant organique polaire avec une cathode en aluminium et une anode en platine, amène à la formation de polyparaxylylène sous forme de revêtement adhérent à la cathode. Le mécanisme de cette réaction comporte la formation hydrochimique de paraxylylène et sa polymérisation subséquente à la cathode d'aluminium. Il y a deux réactions compétitives à savoir la formation de paraxylylène et la réduction du solvant.

Zusammenfassung

Die Elektrolyse von Lösungen von *p*-Methylbenzyl-trimethyl-ammoniumnitrat oder besser *p*-Xylylen-bis(trimethylammonium-nitrat) oder *p*-Xylylen-bis(triphenylphosphoniumchlorid oder -bromid), in einem polaren organischen Lösungsmittel mit einer Aluminiumkathode und einer Platinanode führt zur Bildung anhaftender Überzüge aus Poly-*p*-xylylen an der Kathode. Der Mechanismus dieser Reaktion besteht in einer elektrochemischen Bildung von *p*-Xylylen und seiner darauffolgenden Polymerisation an der Aluminiumkathode. Kompetitive Reaktionen sind *p*-Xylylbildung und Reduktion des Lösungsmittels.

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