Electrochemical Polymerization of Benzene in the Presence of Aluminium Chloride

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Electrochemical oxidation of benzene gives polyphenylene films, which show high spin concentration and an electrical conductivity of *ca.* 10^{-4} S/cm after being doped with SbF_5, and have a structure different from that of linear polyphenylene.

Recently, electrically conducting films were obtained by the electrochemical polymerization of pyrrole[1] and thiophene.[2,3] A similar preparation of polyphenylene films would be of practical importance. The electrochemical oxidation of benzene in liquid sulphur dioxide resulted in the formation of passivating films on a platinum electrode.[4] Free-standing polyphenylene films have been prepared by the electrochemical oxidation of benzene in an HF–benzene, two-phase system[5] and their properties investigated.[6] We now report that the electrochemical oxidation of benzene in the presence of aluminium chloride and water or an amine gives polyphenylene films.

Electrochemical polymerization was carried out under magnetic stirring in a one-compartment cell equipped with platinum electrodes.[3] As the current flowed, the colour of the solution turned black and a black deposit appeared on the

Table 1. Electrochemical polymerization of benzene.[a]

Expt.	Solvent	Additive	Current density/ (mA/cm^2)	Time/h	Yield/ mg
1	$MeNO_2$	H_2O	12	3	20.3
2	$MeNO_2$	Et_3N	12	3	93.1
3	$MeNO_2$	Bu_4NCl	12	3	86.2
4	$MeNO_2$	Bu_3N	12	3	73.2
5	$MeNO_2$	Bu_4NClO_4	12	3	50.2
6	$PhNO_2$	Bu_4NCl	4	6	50.6

[a] Solution composition: C_6H_6 (2 ml), $AlCl_3$ (4 g), solvent (35 ml), additive (200—800 mg).

anode. The results are summarized in Table 1. Nitromethane and nitrobenzene are the preferred solvents. Films were peeled from the anode, heated with 2 M-hydrochloric acid, and washed with methanol. Films are black after drying and their surface is rough and dull.

The i.r. spectra of the films showed the bands at 1000m, 807s, 760m, and 700m cm^{-1} which are commonly observed with poly(*p*-phenylene), together with additional bands at 1090w, 1010w, and 970m cm^{-1}. This suggests that the structure of the present film is different from that of linear poly(*p*-phenylene). The polymer film contains chlorine;† the sum of the H and Cl content is much less than the $C_6(H + Cl)_4$ expected for a linear polyphenylene-type structure, providing further evidence for a basic structural difference.

A current does not flow through the benzene solution containing only aluminium chloride, but addition of a small amount of an amine or water leads to a current flow, possibly owing to the production of electrolytes such as $H^+AlCl_3(OH^-)$ and $R_3N^+AlCl_3^-$. A solution of aluminium chloride in nitromethane is blue in the presence of amines, but becomes brown upon addition of benzene. This colour change provides evidence that benzene and aluminium chloride form a complex, which would presumably have a lower oxidation potential than benzene.

The results of e.s.r. and conductivity measurements are in Table 2. The e.s.r. line shape of the present polymer is almost identical with that of poly(*p*-phenylene) obtained by the cationic polymerization of benzene.[7] The high spin concentration relative to that of poly(*p*-phenylene) obtained by polycondensation of dibromobenzene[8] indicates that many structural defects have been introduced during the electrochemical polymerization.[9]

† For example, found: C, 78.1; H, 3.1; Cl, 16.4; ash, 0.4, corresponding to $C_6H_{2.82}Cl_{0.43}N_{0.13}$.

Table 2. E.s.r. and conductivity results.

Expt.[a]	H_{pp}/G	*g*-Value	Spin concentration[b]	Conductivity/ (S/cm)[c]
2	4.9	2.0035	55	1.1×10^{-5}
3	5.2	2.0034	39	2.4×10^{-4}
6	5.1	2.0036	29	5.9×10^{-4}

[a] No. as in Table 1. [b] Relative to that of poly(*p*-phenylene) obtained by cationic polymerization. [c] After SbF_5 doping.

The conductivity of the polymer film is *ca.* 10^{-4} S/cm after doping with antimony pentafluoride. Iodine-doping of poly(thiophene-2,5-diyl) and polypyrrole films, electrochemically prepared, leads to high conductivity.[3,10] Poly(thiophene-2,5-diyl) films show higher conductivity than the pressed pellet of the same polymer obtained by the polycondensation of 2,5-dibromothiophene. The conductivity of the present polyphenylene films is lower than that of a compaction of powdery linear poly(*p*-phenylene), presumably because of the structural difference.

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