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ELECTROCHEMISTRY OF BENZENE AND POLYPHENYLENE IN LIQUID HYDROGEN FLUORIDE

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Liquid HF as a solvent for organic reactions displays some unusual properties, both physical (low boiling and freezing points, low viscosity and surface tension) and chemical (extremely high acidity, powerful dehydration action). It has therefore been frequently used as a catalyst for various organic reactions, including polymerizations. In this presentation the use of liquid HF as a solvent in electrochemical systems is studied. Polymerization of benzene is of particular interest since the resulting polymer, polyphenylene (PP), is known to become electronically conducting upon doping with strong electron acceptors or donors. The polymerization is performed in a two-phase system, the lower being 93% HF, with an upper layer of benzene. When an anodic current is passed using a Pt or glassy carbon electrode immersed in the lower phase, a black layer of PP is deposited on the electrode surface, resulting from electrochemical oxidation/polymerization of benzene dissolved in the HF. The PP appears dendritic, and can be grown to a desired thickness. X-ray diffraction, electron microscope and FTIR analysis indicate that the polymer is composed of mixed types of linkages, and is amorphous in nature. Exposure of the PP to gaseous AsF_5 increases its electrical conductivity from $< 10^{-10}$ ohm^{-1} cm^{-1} to 10^{-4} -10^{-2} ohm^{-1} cm^{-1}. The polymer, which is electrochemically inert in aqueous solution, displays reversible oxidation-reduction waves in 93% HF, at approx. 0.70 V (vs. SCE). This is less anodic by about 1 volt than the corresponding polymer electro-oxidation in organic solvents (e.g., propylene carbonate), and is unique to this solvent, It indicates a considerable stabilization of the polymer radical cation in liquid HF, probably by association with fluoride ions, some of which are reversibly incorporated in the polymer upon oxidation.