Synthesis of Soluble Conducting Polymers: Polyacetylenes and Polyaromatics

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Soluble polyacetylene and some of its derivatives and soluble polyaromatics have been synthesized by exposure of the monomer, in an arsenic trifluoride solution, to arsenic pentafluoride gas, at temperatures varying between room temperature and −90 °C; an instantaneous polymerization is observed, and the obtained polymers are completely soluble in acetone, methylene dichloride, or tetrahydrofuran.

It is well established that a freestanding film of polyacetylene, prepared using a concentrated homogeneous Ziegler–Natta catalyst, $Ti(OBu)_4$–$AlEt_3$, is a conducting polymer of great interest upon which most of the studies in this field during the last ten years have focused.[1] It can be doped by electron donors or acceptors to give it an electrical conductivity of the order of 10^3 $(\Omega\ cm)^{-1}$.[2] Comparable results have been obtained with conducting polymers such as poly(*p*-phenylene)[3] and other polyaromatics.[4] However, these polymers are not soluble, and therefore are not processible in any way.

Herein we report a unique synthesis of soluble polymers including polyacetylene and some of its derivatives, poly(*p*-phenylene) and its alkyl derivatives, polynaphthalene, and polyanthracene. The polymerizations were carried out in AsF_3 solutions, using AsF_5 gas as the polymerization initiating agent to give homogeneous solutions of the polymers.

Solid or liquid monomers were mixed with the AsF_3 solvent at room or at lower temperatures and the AsF_5 gas was then introduced into the reaction vessel. For gaseous monomers such as acetylene, the AsF_3 solvent was cooled to temperatures below the melting point of the monomer which was then allowed into the reaction vessel and condensed in the solid phase in the AsF_3. The initiating agent AsF_5 was then introduced at the same temperature to initiate the polymerization. In every case, the polymerization occurred instantaneously and is believed to proceed *via* an ionic mechanism to give polymers of molecular weights as high as 10 000 by g.p.c. analysis. At the end of the reaction, excess of AsF_5 was removed by pumping, and the solvent was smoothly distilled from the reaction mixture to give homogeneous polymeric films.

The i.r. spectra of solutions of polyacetylene in methylene dichloride show a strong peak at 700—740 cm^{-1}, which is attributed to the C–H out of plane bending mode in a *cis*-polyacetylene, and two small peaks at 1375 and 900 cm^{-1}, characteristic of a slightly AsF_5-doped polyacetylene. (The *cis–trans* isomerization will be investigated in future experiments.) The corresponding ^1H n.m.r. spectra show several peaks in the range δ 3.5—5.5 characteristic of conjugated carbon–carbon double bonds.

Polyacetylene films cast from maroon solutions in acetone exhibit a conductivity of 10^{-6}—10^{-7} $(\Omega\ \text{cm})^{-1}$ characteristic of a lightly doped *cis*-polyacetylene. The elemental analysis of polyacetylene showed a C/H ratio of 1.036.

A complete analysis is being carried out on solutions of the polyacetylenes and of the polyaromatics, including their electronic properties and this completed study, including the polymerization mechanism, will be reported in a future paper.

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