A Convenient Synthesis of Polyacetylene

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Summary Exposure of acetylene to a small amount of AsF_5 at -75 to -198 °C instantaneously gave *cis*-polyacetylene in the form of thin films.

RECENTLY it has been found that the semiconducting polyacetylene film exhibits a marked increase in electrical conductivity when chemically doped with various donors and acceptors,[1] and so there have been a number of investigations on the electrical conductivity of doped polyacetylene films.[2]

Few studies have been concerned, however, with the polymerization of acetylene, first reported by Natta *et al.*,[3] using the $TiCl_3$–$AlEt_3$ catalyst system. Ikeda *et al.*[4] then succeeded in preparing polyacetylene in the form of films by introducing acetylene gas to an unstirred, concentrated solution of the $Ti(OBu)_4$–$AlEt_3$ catalyst.

We have now found a new, convenient method for preparing polyacetylene in the form of thin films. Acetylene gas was exposed to a small amount of AsF_5 in a glass reaction vessel at -75 to -198 °C, and polyacetylene films formed instantaneously on the glass wall. The i.r. spectra of these polyacetylene films showed a strong peak at 740 cm^{-1}, attributable to the C–H out-of-plane bending mode in the *cis*-polyacetylene, and broad peaks at around 1370 and 900 cm^{-1} characteristic of the AsF_5-doped polyacetylene. A polyacetylene film, for example, obtained at -75 °C with an initial molar ratio of acetylene to AsF_5 of 10 had the composition $[CH_{1\cdot03}(AsF_5)_{0\cdot011}]_x$ and exhibited a conductivity of $4\cdot8 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ at room temperature.

The instantaneous polymerization of acetylene took place even in the dark, but polymerization did not take place by using SO_3 or I_2 in place of AsF_5. Therefore, it may be considered that the polymerization proceeds with the aid of the charge transfer complex formed between acetylene and AsF_5. Polyacetylene films can easily be prepared on the surfaces of various materials by using this method.

A precise study on the polymerization is now in progress and the detailed results will be reported in another paper.

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