A New Free-standing Dopable Electrically Conducting Polyene Film

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Summary The synthesis and initial characterization of a new free-standing dopable electrically conducting polyene film, poly(hepta-1,6-diyne), are reported.

There has been much recent interest in electrically conductive polymers, spurred by the discovery of a technique for *in situ* formation[1] of free standing dopable[2-4] films of polyacetylene. We now report the synthesis of the second example of such a free-standing dopable polyene film formed *in situ.*

Under heterogeneous Ziegler–Natta catalysis conditions hepta-1,6-diyne ($HC{\equiv}C[CH_2]_3C{\equiv}CH$) has been polymerized to a soluble product.[5] We now report that under homogeneous Ziegler–Natta catalysis conditions insoluble free-standing golden-green films with a metallic lustre are formed. The films are up to several hundred μm thick. The conductivity of the films when prepared is *ca.* 10^{-12}, compared to *ca.* $10^{-9}\ \Omega^{-1}\ cm^{-1}$ for *cis*-polyacetylene.[4] The i.r. spectrum of thin films is similar to that of polyacetylene in that it possesses a band at 1610 cm^{-1} attributable to a highly conjugated polyene,[6a] in addition to bands attributable to trisubstituted double bonds (*ca.* 910 cm^{-1}) and allylic methylene groups (*ca.* 1430 cm^{-1}).[6b] The spectrum is consistent with a cyclopolymer structure. The diamagnetic susceptibility of the films is very close to that calculated from Pascal's constants for a diamagnetic conjugated polymer with Curie spin impurity.

However, in contrast with polyacetylene[1,4] the poly(hepta-1,6-diyne) films are not fibrillar but continuous, as shown by scanning electron microscopy. The density is $> 1\ g\ cm^{-3}$. *X*-Ray diffraction studies indicate that the films are totally amorphous, in contrast with polyacetylene which possesses some degree of crystallinity.[1]

Poly(hepta-1,6-diyne) films can be doped with acceptors such as iodine and arsenic pentafluoride.† The maximum achievable doping levels are very similar to those reported for polyacetylene[3,4] in terms of moles of dopant per double bond. We have observed conductivity increases of up to eleven orders of magnitude, as compared to *cis*-polyacetylene which undergoes a 10^{12} increase and *trans*-polyacetylene which increases by 10^8. The magnetic susceptibility of poly(hepta-1,6-diyne) upon doping shows a slight increase in Curie spin concentration; this behaviour is in contrast with that of polyacetylene.[7]

Differential scanning calorimetry (DSC) under nitrogen shows no glass transition from 230 to 600 K. Two exotherms (*ca.* 390 and 530 K) are observed. The first has been tentatively assigned to a *cis–trans* isomerization of the double bonds which is seen at 420 K in polyacetylene.[8]

Poly(hepta-1,6-diyne) is more sensitive to oxygen than polyacetylene. However, like polyacetylene[9] it is initially doped and then degraded. Like polyacetylene the process is partially reversible.

In summary, we have reported the second example of a free-standing dopable polyene film prepared *in situ*; this suggests that there exists a general class of such dopable polyene structures.

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† Doping was carried out by exposing the film, which was attached to platinum wires with Electrodag conductive paste, to the dopant vapours at 25 °C *in vacuo* (I_2, AsF_5) or on a stream of purified argon (I_2).

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