Polyactylene: An Organic Metal

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Polyacetylene (PA) has attracted a great deal of interest in recent years due to its unusual ability, as an organic polymer, to conduct electrons [1]. In 1974, Shirakawa reported a synthesis for PA films which were insulators or semiconductors depending on the method of processing [2a]. Three years later the PA was doped with chlorine, bromine, iodine, and arsenic pentafluoride to metallic conductivities [2b]. Because of the range of conductivities obtained, much work has been done in recent years to improve synthetic routes as well as to better understand the characteristics of these films.

Although the Shirakawa film, produced when acetylene gas is passed over a Ziegler-Natta catalyst, has been the starting point for most of the studies done to date, there are problems with the processing of the films. In order to overcome this difficulty, new methods of synthesis have been explored. Feast and coworkers have reported a two-step synthesis (Fig. 1a) involving the production of a derivative polymer (II) that is then defunctionalized to form PA (Durham PA) [3]. Grubbs has also reported a new synthesis for PA involving the ring-opening metathesis polymerization (ROMP) of cyclooctatetraene (Fig. 1b) [4]. Unlike the Shirakawa film, which consists of a fibril network of PA, the Durham and ROMP polyacetylenes have a smooth morphology on the surface of the film [3,4]. However, the cross-sections of these films reveal a fibril network not unlike that found in the Shirakawa PA. The absorption spectra of all the polyacetylenes have similar structure but the band gaps in the Durham and ROMP PA are shifted to slightly higher energy. The infrared spectra of the samples reveal a similar energy shift. These differences may be explained by the amount of disorder in the film [1a].

Fig 1a

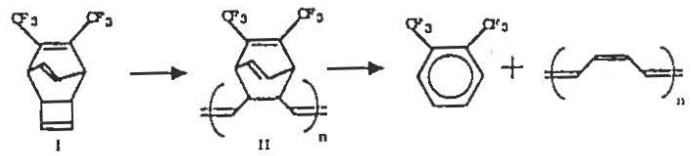
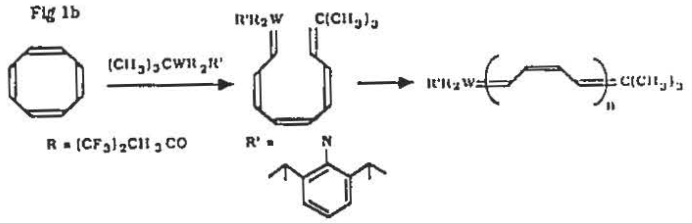


Fig 1b



The PA produced by the above methods are semiconducting. The introduction of a dopant into the PA produces a polymer that has a wide range of conductivities. There are three major processes used to dope PA [5]. First, the PA film may be exposed to a vapor of the dopant at reduced pressures. Second, the PA may be placed in a solution of the dopant salt. Finally, the PA may be used as an electrode in the electrolysis of an appropriate dopant species. The concentration of the species incorporated into PA may be controlled by varying the time of exposure and/or the concentration of the species used. Once incorporated into the PA, the posi-

tion of the dopant species as well as the form of the species itself becomes unclear. Alkali metals form their cations upon doping, and these ions form channels within the PA lattice [6]. Complexes such as metal halides, however, may undergo reactions such as the following:

$$2FeCl_3 + PA \rightarrow FeCl_2 + FeCl_4^- + PA^+$$

Thus, for these complexes it is difficult to characterize the form of the dopant species [7].

Perhaps the most interesting characteristic of doped PA is its conductivity. Several theories have been introduced to explain this phenomenon. Tomkiewicz suggested that the dopants form islands in the PA leading to a percolation model where the conductivity is dependent on the concentration [8]. In low dopant concentrations, particles of the conducting phase are separated by an insulating matrix. As the concentration increases, pathways of conducting materials are formed and the conductivity increases. This model has been discarded since repeated magnetism, EPR, and concentration gradient studies fail to reveal metallic islands [9]. The theory which has recently gained predominance involves the incorporation of solitons into the PA lattice [5c, 10]. Solitons are excitations of a system leading from one minimum of the potential to another minimum of the same energy (Fig. 2) [11]. In trans-PA they correspond to topological kinks that extend over several bonds and gradually lead from a phase A chain segment to a phase B chain segment. The presence of dopants introduces charged solitons (carbocations and carbanions) which are believed to be responsible for conduction.

The above soliton theory predicts many of the characteristics of Shirakawa PA [1a, 12] and preliminary work done with Durham and ROMP PA is also consistent with this model [4c]. Careful characterization of the doped Durham and ROMP PA needs to be done in order to better understand the electronic conduction mechanism which occurs in these compounds. These results are important in the development of practical devices as well as in the creation of derivative polymers which possess desired characteristics.

Fig 2

References

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