INORGANIC CONDUCTIVE POLYMERS

Scope

From a synthetic point of view, probably the most ignored area in the field of conductive polymers has been that of inorganic chemistry. The lack of effort in this area is quite surprising in view of the myriad properties exhibited by inorganic systems not present in the more familiar carbon based systems.

The use of heavy transition metals and main group elements offer several advantages over purely organic systems through their larger radial extension of orbitals and their multivalence behavior. The larger radial extension of the valence orbitals in the heavier elements is likely to result in more favorable bonding interactions, resulting in wider band structures and more highly conductive systems. This phenomenon is illustrated well in the TTF and TMTSF charge transfer salts in which the conduction process is thought to involve mainly the S and Se atoms, respectively, and not the carbon based orbitals. An additional example of this behavior is found with the highly conductive Krogman salts. The Krogman salts are formed from a one-dimensional stacking of $[Pt(CN)_4]^{n-}$ complexes. Overlap between the platinum d_{z^2} orbitals is responsible for the structural and metallic properties of these compounds.

In addition to the increased overlap, inorganic systems, especially the transition metals, offer multiple oxidation states. The mixed valence character so important to conductive polymers is thus easily satisfied with the use of transition metal complexes. Systematic variation in the energetics and band filling can be made in a predictable way with the proper choice of transition metal.

Status

Most of the important contributions to the field thus far have included work in the following three areas:

(1) Stacked macrocyclic compounds.

(2) Purely inorganic polymers.

(3) Ordered clusters.

Although much work has been completed in the first category, the central metal in most of these complexes has not participated in the conduction process. Further work in this area is needed to extend this field to include the heavier transition metals where the transition metal is expected to dominate the conduction process.

$(SN)_x$ and the polysilanes are examples of the second category. Many attempts to extend this work have ended in frustration; however, the initial success with these materials including the superconductivity of $(SN)_x$ provides impetus for further effort with purely inorganic polymers.