

ELECTRICAL CONDUCTION IN POLYMER DIELECTRICS*

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The use of polymer dielectrics with moderate resistivities could reduce or eliminate problems associated with spacecraft charging. The processes responsible for conduction and the properties of electroactive polymers are reviewed, and correlations drawn between molecular structure and electrical conductivity. These structure-property relationships have led to the development of several new electroactive polymer compositions and the identification of several systems that have the requisite thermal, mechanical, environmental and electrical properties for use in spacecraft.

INTRODUCTION

One approach to controlling the spacecraft charging phenomena that are the subject of this symposium is the use of moderately conducting dielectrics that would bleed-off accumulated charge before a breakdown or discharge could occur (ref. 1). Despite extensive study, summarized in reference 2, and the recent development of several organic polymers with metallic ($>10^0 \text{ ohm}^{-1}\text{cm}^{-1}$) conductivities our understanding of this process remains unclear. For example there is considerable debate about the mechanism(s) responsible for charge transport in organic polymers and no means to relate molecular structure to conduction mechanism or to the absolute level of conductivity.

As part of a material-based solution we have reviewed (ref. 3) the electrical and mechanical properties of nearly 250 polymers that are believed to have either the electrical, mechanical, thermal, environmental resistance, or other properties necessary for spacecraft use. Our principle conclusions are two-fold. First there exist materials that could be utilized in near-intermediate-, and long-term experimental tests of the proposed materials-based solution. Second, based on the wide range of properties, conduction mechanisms, and chemical structures encountered in the study a general theory of electrical conductivity in polymers has been formulated. The model succeeds both in explaining the wide range of known properties and structures, and in identifying new polymer compositions that possess unusually high electrical conductivities.

The remainder of this paper is divided into four sections. First the observable, characteristic properties associated with various conduction models are reviewed. Second, the electrical properties of several

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semiconducting and conducting polymers are examined. By comparing these properties the relative importance of various models can be assessed and inconsistent phenomena identified. Third, the molecular structure of the conducting polymers and their derivatives are considered to illustrate how structure and morphology influence conductivity. Finally, in the fourth section this information is used to identify candidate materials for use in reducing spacecraft charging phenomena. Included are both contemporary materials and new materials, identified on the basis of mechanism and structure-property relationships in sections two and three, that have been found to possess relatively high electrical conductivities.

CHARACTERISTIC FEATURES OF CONDUCTION MECHANISMS FOR ORGANIC POLYMERS

Electrical conduction in polymers is most frequently interpreted according to band gap conduction models as discussed in reference 4. The position of various energy bands is determined by the interaction of atomic and molecular orbitals that are assumed to form long-range periodic arrays. This picture is analogous to taking the repeat unit structure of a polymer and repeating it at regularly spaced intervals in three dimensions indefinitely as if it were the unit cell of a single crystal. With the possible exception of two polymers that are polymerized as single crystals, the validity of this approach is difficult to understand since organic polymers are highly disordered and the crystalline order that is present extends over relatively short distances. In addition, on an absolute scale the length of a polymer molecule is extremely short and macroscopic transport of necessity must be limited by intermolecular charge transport which is not treated by this model.

Experimentally a metallic band gap material can be characterized as having an inverse ($\log \sigma \propto T^{-1}$) temperature dependence due to increased electron scattering at elevated temperature. Since the number of carriers is relatively insensitive to temperature the overall conductivity is determined carrier mobility, which should be in excess of $1 \text{ cm}^2/\text{V sec}$ for materials to adequately fit a band gap mechanism (ref. 5). Conduction in band gap semiconductors is not mobility limited by scattering but rather by the number of carriers that have been thermally excited into the conduction band. Consequently these systems display a strong thermally activated conductivity (ref. 5).

Because of the inherent high degree of disorder in polymers it is necessary to consider so-called mobility gap mechanisms that successfully describe the electronic properties of amorphous inorganic semiconductors including amorphous silicon and the chalcogenide glasses (ref. 6). In the theoretical description of these materials the band energies are diffuse, sometimes overlapping, and charge transport is mobility limited. Structurally the charge carriers are spatially localized at disordered sites and undergo a variable-range hopping transport. In contrast the mobility gap materials display a weak ($\log \sigma \propto T_0/T^{1/4}$) temperature dependence and mobilities that seldom exceed $1 \text{ cm}^2/\text{V sec}$, above cryogenic temperatures. The optical properties are complex and their interpretation is more complicated than that for a simple band edge absorption.

When the mean free path of a charge carrier becomes very low due to extremely tight binding or deep trapping, a nearest neighbor hopping mechanism

characterized by a positive thermally activated process is encountered as discussed in reference 7. In essence carriers are thermally or photolytically pried out of their molecular orbitals into the continuum where they undergo an electric field modified transport or recombination. The details of this process can be very complicated but this general type of mechanism is responsible for charge transport in most insulating polymers exposed to ionizing radiation or injected charge.

An intermediate temperature dependence of the conductivity ($\log \sigma \propto T_0/T^{1/2}$) is observed for polycrystalline materials composed of conducting regions separated by very thin nonconducting barriers (ref. 8). This could be of particular interest for crystalline polymeric materials since the crystalline regions are extremely small and often distinguished by only a slight shift in molecular orientation.

Finally there exists the possibility of ionic conduction that involves the actual mass transport of ions through the material (ref. 5). These charge carriers may be ionizable pendant groups, inadvertant impurities, or ionized water which is present in small quantities in almost all polymers unless specifically excluded. Because these charge carriers must actually diffuse through and between the polymer molecules ionic conductivity depends strongly on the physical state of the material. Consequently ionic conductivity is inversely dependent on pressure and the temperature dependence can be complicated due to thermal transitions and relaxations in the polymer.

In the following section the properties of some electrically conducting polymers are reviewed in an attempt to understand which conduction mechanisms are involved. Of specific interest is the temperature dependence of the conductivity, in part because only this data is generally available in the literature. While a thorough description requires knowledge about carrier density, mobility, optical properties, etc., these are much less available in the literature and more difficult to measure for polymers.

ELECTRICAL PROPERTIES OF CONDUCTING POLYMERS

In recent years a number of highly conducting polymers have been developed that have stimulated considerable interest concerning the mechanism(s) of conduction and potential applications. The existence of relatively highly conducting materials has facilitated experimental measurements, so there is a large quantity of data in the literature obtained on materials with diverse chemical structures from which general conclusions about polymer conductivity can be drawn.

The most striking example is polythiazyl (SN_x). Needle-like single crystals of polythiazyl can be polymerized directly from single crystals of the cyclic S_2N_2 monomer (ref. 9). Electrical conductivities, which depend strongly on crystal perfection, of from 250 to 1200 (ohm cm^{-1}) have been reported. In single crystalline materials the metallic conductivity shows an inverse temperature dependence characteristic of a band gap mechanism as would be expected from a material with an extremely high degree of long-range order. In even this highly ordered material the importance of intermolecular charge transport is illustrated. It is unlikely that single molecules stretch the entire distance from end to end of a macroscopic single crystal. Even so,

above cryogenic temperatures the intrinsic conductivity parallel to the chain axis is only about ten-times that normal to the chain axis indicating extensive charge transport between chains (ref. 10).

A similar high degree of structural order is found in single crystalline polydiacetylenes. These also are prepared through the radical initiated polymerization of single crystals grown from the corresponding monomer. Amorphous films can also be obtained by casting solutions of the polymer in organic solvents. Although the optical properties discussed in reference 11 are characteristic of the long range delocalized π electron orbitals responsible for band gap conduction the extremely low (10^{-10} to 10^{-12} ohm $^{-1}$ cm $^{-1}$) conductivity and six-fold conduction anisotropy parallel- and normal-to the chain axis indicate that carrier mobility is strongly limited by the rate of intermolecular charge transport (ref. 12). The absorption of as little as one mole percent of iodine raises the electronic conductivity by several orders of magnitude. Mechanistically the role of iodine is unclear but both pristine and doped materials in reference 13 display T^{-1} conductivities. Since iodine is present as I_3^- it is believed that it locally oxidizes the polymer π electron backbone and may serve as an electronic bridge between molecules.

Unlike most of the conducting polymers studied the polydiacetylenes are soluble in organic solvents so their molecular weight can be determined as reported in reference 14. At a fixed dopant level the conductivity increases exponentially with molecular weight and the activation energy decreases linearly to an infinite molecular weight value of 0.4 eV. This illustrates rather clearly that even in the presence of complete electron delocalization along a chain backbone the rate limiting process for carrier transport is intermolecular.

Considerable attention has been focused on polyacetylene because of its potential application to light weight, high power-density batteries. Polyacetylene can be prepared in thin films or as coatings that appear to the eye to be like aluminum foil but microscopically more closely resemble the fibrillar structure of steel wool (ref. 15). The pristine material has a low (10^{-12} ohm $^{-1}$ cm $^{-1}$) conductivity but this value increases rapidly to 10^1 ohm $^{-1}$ cm $^{-1}$ when it is doped to about 10 mole percent with strong oxidizing agents like I_2 or AsF_5 (ref. 16). Although frequently modeled as an ideal one-dimensional delocalized π electron backbone there is a considerable amount of evidence in reference 17 for structural disorder and a $T^{-1/4}$ dependence of the conductivity on temperature characteristic of variable range hopping in amorphous materials. Yet high (~ 60 cm 2 /V sec) mobilities are observed and optical studies (ref. 18) indicate that the transition to a metallic conductivity state is not simply a concentration dependent percolation transition of metallic conducting regions.

Similar observations may be made about the doping and electrical conductivity of polypyrrole. It too is prepared as a thin film or coating, becomes conducting at a dopant level of about 25 mole percent, and displays a $T^{-1/4}$ conductivity dependence (ref. 19). Polyphenylene sulfide and polyparaphenylene also become conducting when doped to high (1:1) repeat unit to dopant ratios and possess a $T^{-1/4}$ temperature dependence of the electrical conductivity (ref. 20).

The vast majority of the remaining electroactive polymers show clear thermally activated conduction mechanisms and many examples could be cited with conductivities ranging from 10^{-12} to 10^{-4} $\text{ohm}^{-1}\text{cm}^{-1}$ (refs. 2-5, 7, 21-22).

Can general conclusions be drawn about the conduction mechanisms operating in organic polymers? The temperature dependence of the conductivity is about the only property that has been determined for enough materials to allow comparisons. More in-depth studies have been made on specific materials, but details are frequently regarded as indications of unique material properties, fragmenting an already confused subject.

The long-range periodic order and inverse temperature dependent conductivity characteristic of metallic band gap conduction are only found in polythiazyl. The temperature dependence of the remaining systems clearly indicates hopping transport between inherently localized states. The hop length and the energy barrier to transport will vary according to morphological structure and chemical composition but the inherent rate limiting process is intermolecular charge transport.

The principle objection to this mechanistic interpretation of polymer conductivity is that it does not provide a good explanation for the high mobilities observed in materials like doped polyacetylene. One way around this objection is to postulate a percolation-type transition at which individual localized states begin to interact facilitating long-range transport within a cluster. The rate limiting step to charge transport is still hopping between localized states but fast long range transport occurs within clusters of localized states. With this general model of the conduction process it is possible to relate chemical composition and molecular structure to conductivity in organic polymers.

THE INFLUENCE OF MOLECULAR STRUCTURE ON CONDUCTIVITY

The process of designing a new polymer, or selecting a known material, for use in a specific application with specific performance requirements relies on some set of relationships between molecular structure and physical properties. Some formal relationships exist for polymers but the intelligent design of materials for specific thermal, mechanical, and electrical properties is largely heuristic.

The predominance of hopping transport mechanisms indicates that the design of a conducting polymer must include a molecular structure that can exist as a stable radical ion. The less stable the radical ion the more energy will be required to form the ion and the greater the likelihood of trapping or an irreversible chemical degradation. The latter is a serious problem with conducting polyacetylene, polypyrrole, and polyphenylene sulfide, which must be protected from atmospheric oxygen and water vapor.

Because the rate limiting step appears to be intermolecular charge transport, not an intramolecular phenomena, it is not necessary for the polymer to possess a delocalized π electron molecular orbital along its entire backbone. The molecular structure of polyphenylene sulfide illustrates this point: its conformation is coil-like and its π electron orbitals are

localized at each individual phenylene sulfide repeat unit.

The optimum size of this localized charge state remains unclear. The molecular weight dependence of the conductivity in the polydiacetylenes, which possess complete π electron delocalization along their rodlike backbone, is only linear, while the addition of a few mole percent of a dopant causes a 10-12 order of magnitude increase in the conductivity at the percolation threshold. Extrapolation of the activation energy for charge transport to infinite molecular weight yields a minimum value of 0.4 eV only one-third the value for an oligomer of 20,000 daltons.

Intermediate between these two extremes of highly extended π orbitals and charge states localized on a single repeat unit lie polyacetylene and polypyrrole. In these systems the localized charge state involves approximately ten and four repeat units, respectively. Whether or not these repeat units are part of the same polymer backbone, or comprise an ordered intermolecular aggregate involving a single dopant, is unknown.

The issue of intermolecular order is an important one since, in the final analysis, it is the intermolecular process that is responsible for macroscopic charge transport. While difficult to quantify, proximity and registry between adjacent localized states is advantageous as is the ability to intercalate oxidizing (or reducing) dopants. Consequently crystallinity, short-range chain stiffness, stereoregularity, and minimal pendant group substitution are believed to be desirable.

These criteria are amply demonstrated in comparisons of the electrical conductivity of polyacetylene or polypyrrole and their derivatives. The addition of pendant groups or copolymerization, which doesn't alter the electronic structure of the backbone appreciably, causes a consistent and often dramatic decrease in conductivity. In other systems containing large fused rings, for example the polyphthalocyanines, pyrolyzed Kapton and polyacrylonitrile, polyvinylcarbazole, and polyacene quinones the influence of intermolecular order between stable charge carriers on conductivity can be seen.

In summary there are a finite set of molecular structural parameters that are responsible for the different degrees of electrical conductivity in organic polymers. They include the electronic structure of the charge bearing state, its size, and the local intermolecular order between states that promotes efficient intermolecular transport. Significantly this model indicates that corrosive dopants (SbF_6 , AsF_5 , etc.) are not necessary and that processable electrically conducting polymers, unlike the intractable materials currently under study, can be prepared.

A MATERIALS-BASED APPROACH TO THE PROBLEM OF SPACECRAFT CHARGING

A successful theory or model should lead to the identification of new materials or phenomena as well as to explain the properties of known materials or previously observed phenomena. The molecular principles discussed above have in fact identified new polymer compositions that are soluble in organic solvents, stable towards atmospheric exposure and are moderately (10^{-4} ohm $^{-1}$ cm $^{-1}$) conductivity. The remainder of this section however describes how these

principles can be used to identify or design materials with semiconducting (10^{-12} ohm $^{-1}$ cm $^{-1}$) electrical properties and the requisite properties for space-based use.

An application like space-based radar requires many square kilometers of a strong polymer film. The material must be stable towards ionizing radiation and temperature extremes for mission lengths of up to five years. These general principles have led to the conclusion that there exist short-, intermediate- and long-term approaches towards identifying the optimum materials.

The short-term approach requires the use of commercially available materials without reformulation or extensive modification. The most promising approach involves the use of a lightly pyrolyzed polyimide film. When commercial aromatic polyimide films are heated under vacuum at temperatures of from 400° to 700°C the polymer molecules condense to form extended, fused-ring structures (ref. 23,24). The conductivity of the films is raised from 10^{-18} ohm $^{-1}$ cm $^{-1}$ to a value, dependent of the pyrolysis temperature, of up to 10^2 ohm $^{-1}$ cm $^{-1}$. While extensive pyrolysis will embrittle the material only slight changes are necessary to arrive at a value of 10^{-12} ohm $^{-1}$ cm $^{-1}$. Since the level of conductivity is variable, the same basic feedstock can be tailored, by control of the processing conditions, to fit specific applications.

The major questions that must be answered in evaluating this approach include how does pyrolysis affect the mechanical properties of the polyimide film and is the partially pyrolyzed product stable in a spacecraft environment. Experimental charging data in reference 25 for Kapton samples on the SCATHA mission indicate an exponential decrease in conductivity of nearly two orders of magnitude over a year's time. The resistivity of Kapton can drop by ten orders of magnitude or more in pyrolysis, so if the change in electrical properties observed on SCATHA are due to the molecular rearrangements observed in pyrolysis the material will have to be stabilized if a narrow tolerance for electrical properties is to be maintained.

Polyacrylonitrile undergoes similar electrical changes on pyrolysis described in reference 26. The molecular changes are complex and not well understood, but providential, since the strength retention of elevated temperatures is improved and some intermolecular crosslinking probably occurs. Potential difficulties inherent in the use of pyrolyzed polyacrylonitrile include elevated temperature properties, embrittlement, and stability. Both of these examples are off-the-shelf materials and experimental investigation of the pyrolyzed materials, their electrical and structural properties, could begin immediately.

There exist a wide range of intermediate-term solutions that involve the modification or further investigation of materials that are known, but not commercially available. The object here is to improve the high temperature performance of materials that otherwise have desirable electrical properties or to provide the necessary conductivity to polymers with inherent thermal and mechanical properties.

For example, materials like polyvinylcarbazole (ref. 27) or polyvinylpyridine (ref. 28) possess the necessary electrical conductivity for this application but mechanically can not withstand elevated temperatures.

The introduction of a few pendant ionic groups would convert these polymers into ionomers that contain ionic crosslinks. The conversion of polyethylene into an ionomer raises its softening temperature by 50° to 100°C (ref. 29) which would be sufficient to make these two materials candidates for space-based use.

One approach to the problem of long-term stability in pyrolyzed polyimide is the use of blends or molecular composites (ref. 30). The polyimide could be blended, either as a physical mixture or as a copolymer, with one of the high strength/thermally stable organic polymers that have been developed in recent years. The structural component would provide the mechanical integrity while the polyimide pyrolysis product would support charge transport.

Finally, some of the derivatives of polyacetylene (ref. 31) and polypyrrole (ref. 19) could be reinvestigated. Many have the requisite electrical properties but have not been thoroughly characterized with regard to strength, thermal stability, and radiation resistance. Almost all could be reformulated as crosslinkable resins that would possess the requisite strength and thermal stability.

A long-term approach to the development of materials for the reduction of spacecraft charging would require the chemist to go "back to the drawing board" and combine the molecular principles already discussed with those for producing high strength, thermally stable, radiation resistant polymers. The principles for molecular design of conducting polymers are just beginning to evolve. They are about at the point where the design of high strength polymers was ten years ago and there is every reason to believe that, with the proper support, they can evolve into successful commercial technologies.

CONCLUSIONS

Comparison of the limited data available in the literature concerning electrically conducting polymers indicates that hopping transport between localized states is the predominant conduction mechanism. Comparison of the various chemical compositions and morphological structures has allowed the development of a general model for conductivity. The three important material characteristics include the electronic structure of the localized state, its size, and the degree of intermolecular order present. This model has led to the development of new conducting polymers as well as providing a rational explanation for existing materials. Specific materials or modifications have been proposed that would produce polymer dielectrics with the level of conductivity believed necessary to reduce spacecraft charging phenomena and have the requisite thermal, mechanical and environmental properties.

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