

Final Report
The Workshop on Conductive Polymers

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Objectives of the Workshop

The field of conducting polymers has made significant growth during the past ten years. As in any field with rapid growth and diverse science and technology development, it is of value to occasionally attempt to stand-back, assess the present goals and directions, and redirect some of these, if necessary. It is also unfortunate that diverse areas of science develop different languages and approaches to the definition and solution of the same problems. Thus it may be difficult at times to intergrate and direct approaches in common for the solution of these problems. The area of conductive polymers has to a large degree within research groups been fortunate in the ability to integrate many efforts. To the extent that such diversity has occurred, the objectives of this workshop were related to the intergration of efforts between research groups from these diverse fields of science, to access the present activities, and to develop new unified approaches in defining future directions. Therefore, this was an attempted "meeting of the minds" of synthetic chemists, physical chemists, polymer physicists and theoretical physicists.

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Organization of Workshop Program and Discussion Groups

After a series of introductory presentations (See Appendix I), participants were divided into the following six discussion groups. About 65 scientists (See Appendix II) participated in the workshop.

Group A: Polyacetylene, Polyphenylene, Polyaniline and Related Systems

Chairman: A. MacDiarmid
University of Pennsylvania

Group B: Molecular, Crystallographic and Defect Structures in Conducting Polymers

Chairman: R. Baughman
Allied Corporation

Group C: Heterocyclic Polymers

Chairman: M. Litt
Case Western Reserve University

Group D: Synthesis of New and Improved Conducting Polymers

Chairman: M.M. Labes
Temple University

Group E: Future Applications Possibilities for Conducting Polymers

Chairman: J. Miller
DuPont

Group F: Challenges for Improved Understanding of Properties

Chairman: A. Epstein
Ohio State University

Recommendations of the Conference (prepared by the Chairman)

Study Group A

Polyacetylene, Polyphenylene, Polyaniline and Related Systems

Chairman

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Study Group Members

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G.L. Baker Bell Communications Research Center

M. Batky Canadian Plastics Institute

J.C.W. Chien University of Massachusetts

J. Ginder Ohio State University

L.H. Tolbert Georgia Institute of Technology

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Introduction

The organic polymers, polyacetylene, $(CH)_x$, poly(p-phenylene), $(C_6H_4)_x$ and polyaniline, $[\{C_6H_4\}-N(H)-(C_6H_4)-N(H)-(C_6H_4)-N=(C_6H_4)=N-]_x$ can all be "doped" to the metallic regime chemically and/or electrochemically. Polyacetylene, frequently referred to as the "prototype conducting polymer", has been very extensively studied during the last eight years since its novel properties were first discovered. Shortly after this discovery it was found that poly(p-phenylene) could likewise be doped to the metallic regime. Polyaniline has been known for approximately 150 years but only during the past two years has an active interest been taken in the different forms in which it can exist and the fact that, unlike all other conducting polymers, it can be doped to the metallic conducting regime by relatively dilute aqueous solutions of non-oxidizing protonic acids. It has also been found that poly(p-phenylenevinylene), $\{(C_6H_4)-CH=CH-\}_x$, which can be regarded as a hybrid between polyacetylene and poly(p-phenylene) can also be doped to the metallic regime. With the exception of polyaniline the term "doping" refers to the partial oxidation or reduction of the pi system of the polymer which is accompanied by a very large increase in electronic conductivity. In the case of the emeraldine base form of polyaniline it appears that doping involves a simple acid-base interaction to form a salt.

In principle, some or all of the hydrogen atoms in all the above polymers can be replaced in whole or in part by a wide variety of organic, organometallic or inorganic groups to give a vast number of new polymers, at least some of which might have their conductivity greatly increased by doping. A few derivatives of this type have already been synthesized. The polymers containing a (C_6H_4) ring in which the substitution is not in the para position can in principle be prepared and some species of this type have been synthesized. The three title compounds represent three basically different types of conducting polymers; those consisting of an aliphatic backbone; those consisting of an aromatic backbone and those consisting

of an aromatic/non-carbon alternating backbone. These types of polymers are excellent models for continued study in order to understand the chemistry and physics of conducting polymers in general.

The overall immediate objective of the research proposed below is to attempt to gain a basic understanding of the interrelationship between the chemistry, structure and morphology of each of the above types of polymers (in their doped and undoped forms), and their electronic and magnetic properties. Such an understanding is essential in attaining the ultimate objective of synthesizing conducting polymers, not necessarily just those or derivatives of those studied in this group, which (i) are processable and environmentally and thermally stable under desired, preselected sets of conditions, (ii) have appropriate mechanical properties and (iii) can be fabricated to exhibit preselected conductivities ranging from the semiconducting regime of approximately 10^{-7} S/cm to that of copper (approximately 10^6 S/cm). In this respect it might be noted that polymers conducting in the potentially technologically important range $\sim 10^{-2}$ to 10^{-7} S/cm have been generally neglected in conducting polymer studies. This study group concentrated on the following general research areas, all of which are closely interrelated.

- (1) Synthetic Control of Chemical Composition, Structure and Morphology of the Doped and Non-Doped Polymers.
- (2) Doping Mechanism and the Effect of Dopant Ion on Chemical, Electronic and Mechanical Properties.
- (3) Degradation Mechanism of the Doped Polymers.
- (4) Processability of, and Composites Containing, Conducting Polymers.

In some instances a given specific research topic could have been equally well incorporated into more than one of these general research areas. No attempt has been made to prioritize these four general areas since it is essential that research continue simultaneously in all areas if the field is to develop with maximum efficiency.

1.1 Synthetic Control of Chemical Composition, Structure and Morphology of the Doped and Non-Doped Polymers

Scope

This research area is concerned with finding the effect of the following factors on the electronic, magnetic, mechanical, thermal and environmental stability characteristics of the doped (conducting) and non-doped forms of the title polymers and their derivatives:

- . chemical purity of the polymer
- . structural homogeneity (e.g. cis-or trans-isomeric forms, etc.)
- . molecular weight
- . conjugation length
- . relative amounts of crystalline and amorphous regions
- . morphology
- . macroscopic alignment of polymer chains
- . type and number of defect sites
- . replacement of H atoms by other groups
- . conduction mechanism (it is highly likely that several different conduction mechanisms will be operative depending on the degree of doping and hence the conductivity of the polymer).

Justification

Many detailed investigations on conducting polymers to date have been carried out on materials which have not been characterized as to chemical and/or structural purity by elemental chemical analysis, etc. This has sometimes resulted in the reporting of different properties for the allegedly same material. The studies outlined will put the field on a sound, reliable, experimental basis.

Status

By far the greatest number of studies have been carried out on polyacetylene, followed by poly(p-phenylene). Only very few studies have been performed on derivatives of these polymers and on poly(phenylenevinylene) and polyaniline. The fact that much is already known about $(CH)_x$ makes it a

particularly important candidate for further investigation since more detailed studies, when combined with those already performed, will hopefully provide sufficient information to answer the fundamental question "why do conducting polymers conduct?" When the amount of knowledge concerning the other conducting title polymers is similar to that for $(CH)_x$ it is highly probable that several technological uses for conducting polymers will thereby be defined clearly.

Research Proposed

(i) Emphasis should first be placed on ascertaining the chemical purity, uniformity of composition and structure, and overall homogeneity of the doped and non-doped forms of the title polymers.

(ii) Determination of the effect of molecular weight, conjugation length, degree of crystallinity, etc. on the bulk conductivity of the title polymers.

(iii) Synthesis of selected derivatives of the title polymers in order to ascertain the effect of certain types of substituents on the polymer chain on the above properties.

1.2. Doping Mechanism and the Effect of Dopant Ion on Chemical, Electronic and Mechanical Properties

Scope

This research area is concerned with (i) determining the doping mechanism which results in the conductivity of the organic polymer being increased by many orders of magnitude and (ii) the effect of the nature of the dopant anion or cation on the following properties of the doped and undoped polymer:

- . bulk conductivity
- . structural homogeneity (e.g. cis-or trans-isomeric forms, etc.)
- . molecular weight
- . conjugation length
- . relative amounts of crystalline and amorphous regions

- . morphology
- . environmental stability
- . ability to mechanically align the polymer
- . processability of the polymer
- . type and number of defect sites

Justification

(i) Essentially all p- and n-doping of conducting polymers to date has been accomplished by chemical and/or electrochemical oxidation or reduction of the polymer pi system. There have been a few scattered and preliminary reports of the doping of $(CH)_x$, polypyrrole and polyaniline to the metallic regime by non-oxidizing protonic acids. These are presumably acid-base reactions, in which no formal oxidation of the polymer occurs. This unusual type of doping is not even qualitatively understood. Very extensive work needs to be done to ascertain the generality of this type of doping and why it leads to an increase in conductivity.

(ii) Until very recently essentially no studies had been performed on the effect of different dopant ions on the properties of the doped polymer. Changing the dopant ion presents a method of modifying the doped polymer which complements and supplements modifications incurred by replacing H atoms on the polymer with substituent groups as described in Section 1.1.

Status

(i) Preliminary studies have very recently shown that the doping of a form of polyaniline to the metallic regime by dilute aqueous HCl involves no oxidation of the polymer. Very little information is available concerning this novel form of doping as found in derivatives or other forms of polyaniline or other pi containing conducting polymers.

(ii) Those few studies using different dopant ions which have been carried out, suggest that environmental stability and processibility might be significantly improved by, for example, the use of polymeric dopant anions with little accompanying loss in bulk conductivity.

Research Proposed

(i) Studies should be carried out on the protonic acid doping (using non-oxidizing protonic acids) of the title compounds and their derivatives, especially the polyaniline class of compounds and other N-containing polymers. The formation of ammonium-type salts, which are known to have good environmental stability in general, as distinct from carbonium-type ions which are usually highly reactive, might be expected to result in increased environmental stability of conducting polymers.

(ii) Synthesis and study of conducting polymers having oligomeric and polymeric dopant ions. Polymers incorporating monomeric ions bearing a charge greater than one (the only type of monomeric ion so far investigated) should be prepared. Such ions may lead to increased inter-chain interactions with marked changes in conductivity and related properties.

1.3 Degradation Mechanism of the Doped Polymer

Scope

This research is concerned with ascertaining the mechanism by which a polymer in its doped or non-doped form degrades thermally, photochemically, oxidatively, hydrolytically or in some specific chemical or electrochemical process, e.g. as when used as an electroactive electrode in rechargeable batteries.

Justification

Essentially all attempts to stabilize conducting polymers to date have been made using a trial and error, "hit or miss", Edisonian approach. In order to synthesize conducting polymers which are stable under some given set of experimental conditions, in a rational manner, it is first necessary

to ascertain how and why the polymer degrades. Only then will it be possible to scientifically build stability into the polymer. It seems not unlikely that larger more polarizable dopant ions will permit distribution of the counter positive or negative charge on the polymer backbone over a larger length of the polymer chain, thus reducing the ease of nucleophilic or electrophilic attack of the polymer backbone with resulting decrease in its chemical reactivity either to its own dopant ion during thermal decomposition or to attack by an external species. Solvation of the ion might also lead to similar stabilizing effects.

Status

At the present time very little effort has been expended on this subject. It is one of the most neglected areas in the conducting polymer field.

Research Proposed

(i) Kinetic decomposition studies should be performed on the title compounds (combined with monomeric dopant ions) when heated in vacuo, when exposed to U/V, oxygen, water etc. in order to determine the rate-controlling factor in their decomposition. Analogous studies should then be performed on the same material combined with polymeric, etc. dopant ions.

(ii) A comparison should be made with corresponding studies conducted on e.g. polypyrrole, polythiophene, etc. in order to ascertain why one class of polymer is more stable than others under a given set of experimental conditions.

1.4. Processibility of, and Composites Containing, Conducting Polymers

Scope

Most conventional organic polymers, in order to be technologically useful, must be compounded or blended, co-polymerized with other polymers, controllably cross-linked or mixed with anti-oxidants or U/V stabilizers, etc. The same processing presumably also applies to conducting polymers.

Justification

The conducting polymer field can only advance technologically by performing processing studies such as those described above for conventional polymers. In order to carry out such studies, however, it is first necessary to have available a relatively large supply of conducting polymer in some specified form defined by a rigid set of specifications.

Status

Only within the last few months has real progress been made in attaining the above objectives. Soluble, processable forms of polythiophene have been synthesized and polypyrrole emulsions with a latex base have been produced from which conducting films of polypyrrole have been cast. Composites of polypyrrole or polythiophene in poly(THF) have been synthesized electrochemically. No such studies have been reported with the title compounds. Only in the case of polypyrrole is there any suggestion that a conducting polymer has been made on a sufficiently large scale with rigid specifications to permit studies of the type described above.

Research Proposed

A technologically processable polymer can in principle be found, and control of mechanical properties can be imparted by:

- (i) The formation of co-polymers of the title compounds with a conventional polymer.
- (ii) The replacement of H atoms in the title polymers with substituent groups which are themselves polymerizable under appropriate conditions.
- (iii) The use of polymeric dopant ions. If the polymeric ion constitutes a large portion of the final polymer, the resulting material is, in effect a homogeneous blend. Each of these three types of research should be actively pursued.
- (iv) Relatively large quantities of selected conducting polymers adhering to a rigid set of specifications should be synthesized for certain of the studies listed at the beginning of this section, 1.4.

1.5 Summary

The chief conclusions resulting from the present study are (i) that in order for the newly and rapidly emerging area of conductive polymers to develop efficiently to the stage where such polymers can be used technologically it is necessary to study selected aspects of the model conducting polymers, polyacetylene, poly(p-phenylene) and polyaniline and certain of their derivatives. These polymers represent three distinctly different types of conducting polymers - those consisting of a totally aliphatic backbone, those consisting of a totally aromatic back-bone and those consisting of an aromatic/non-carbon alternating backbone.

(ii) The proposed method of study of these polymers also applies to other types of conducting polymers.

(iii) Of prime importance in all cases is the determination of the chemical purity, uniformity of composition and structure and overall homogeneity of the doped and undoped polymers before they are subjected to detailed chemical and physical examination.

(iv) Only by gaining a detailed understanding of the nature of the interdependency of (a) the chemical and physical properties and (b) the conductivity of conducting polymers as outlined in this report, can the scientific significance and potential technological application of this challenging new area of non-classical solid state science be realized.

Study Group B

Molecular, Crystallographic, and Defect Structures in Conducting Polymers

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1.0 INTRODUCTION

Structural irregularities in presently available conducting polymers provide major limitations regarding both (1) obtainable properties and (2) understanding of structure-property relationships. These irregularities range on the molecular scale from chemical defects, chain ends, chain kinks, and chain folds to polycrystallinity and dopant nonuniformity. These defects are believed to limit conductivities and conductivity anisotropies, as well as to reduce the prospects for exciting transitions - such as metal-to-superconductor. Similarly, property degradation due to imperfections decreases the likelihood for applications as active components in electronic devices.

Finally, the fundamental physics of transport in conducting polymers is largely obscured by the high imperfect nature of available materials. For these reasons the proposed research deals with (1) development of improved understanding of the molecular, crystallographic, and defect structures of presently-available polymers; (2) using this information to evaluate the effect of structure on properties; and (3) development of synthesis and materials modification methods which improve structural and chemical perfection.

1.1 STRUCTURAL CHARACTERIZATION OF HIGHLY DISORDERED CONDUCTING POLYMERS

Scope

Characterize polymer molecular structure (both before and after doping) regarding chemical nature and regularity, chain geometry,

molecular weight, and conjugation length. Characterize the aggregation of polymer chains and dopant arrays in both crystalline and amorphous regions of the polymer. A focus here should be on derivation of equilibrium structures for the crystalline components, the nature of crystallite aggregation, and the morphological relationship of crystalline and amorphous components.

Justification

While methods might be developed which lead to conducting polymers having single crystal perfection, the materials having the greatest applications potential are expected to be the lower cost compositions which are disordered. Understanding the defect and crystallographic structures of these materials could be the key for design engineering to meet applications needs.

Status

Little detailed information is presently available even for the most thoroughly investigated conducting polymers concerning (1) crystallographic structures, (2) morphology, (3) the nature of polymer chain irregularities, and (4) average conjugation length and the distribution of conjugation lengths.

Research Proposed

(1) Increased application of advanced methods for structure determinations is proposed, including EXAFS measurements to determine local structure, the combination of electron, x-ray, and neutron diffraction on the same samples, and high resolution electron

microscopy. Expanded use of synchrotron radiation for the characterization of small crystals is encouraged. In situ measurements of structural evolution during doping are feasible for certain of these methods and should be pursued.

(2) Increased theoretical effort to model polymer molecular, crystallographic, and defect structures and to compare these model calculations with observables is important - a major problem being the treatment of electrostatic interactions.

(3) Increased effort on using spectroscopic methods (Raman, IR, Solid State C_{13} , UPS) to characterize structural irregularities, chain conjugation length, and the distribution of conjugation lengths is also suggested. Laser desorption/Fourier transform mass spectral analysis of the chemical compositions of doped and undoped polymers should be encouraged. Infrared and neutron scattering spectroscopy coupled with normal mode analysis on polymers such as polyaniline could produce important results. Techniques for characterization of interfacial structures and structural orientation should be developed.

1.2 DEVELOPMENT OF NEARLY DEFECT-FREE CONDUCTING POLYMER COMPLEXES AND EXPERIMENTAL MODEL COMPOUNDS

Scope

Develop an improved understanding of structure-property relationships for nearly defect-free conducting polymers via (1) work on model compounds of low molecular weight; (2) development of improved materials synthesis and molecular processing techniques, so as to obtain high molecular weight materials with improved

perfection; and (3) making the transition from single chain to lattice calculations of electronic properties.

Justification

Property improvements and increased understanding of inherent properties of conducting polymer are expected.

Status

Existing conducting polymers are grossly defective and non-uniform from molecular to micron scales. This structural disorder frustrates properties optimization and the development of fundamental materials understanding.

Research Proposed

(1) Utilize solid-state reactions, epitaxial growth, reactions in ordered host media, simultaneous polymerization and crystallization, and post-synthetic processing to obtain materials having improved perfection. If possible, well characterized, standardized samples should be identified and made available to all workers at a research level.

(2) Expand efforts to derive structure-property relationships for conducting polymers using molecular charge transfer complexes (which are obtainable as single crystals) as model compounds.

Study Group C

Heterocyclic Polymers

Chairman

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1.0 Introduction

Most of the people in this section were involved with synthesis and the topics reflect this bias. As the overall study concerns conducting and semiconducting polymers, characterization techniques are well developed and research topics for that area are considered in other sections. The broad area of heterocyclic polymers was broken down into three sections based on the synthetic approach and treatment of the polymer to make it interesting electrically. The three subdivisions were:

1. Electropolymerized heterocycles which are conducting as formed.
2. Preformed polymers with heterocyclic units which are insulating unless doped. [The equivalent non-heterocycle would be poly(p-phenylene).]
3. Heterocyclic polymers with extended conjugation when made, i.e. intrinsic semiconductors or conductors.

1.1 Electropolymerized Heterocycles

Scope

There are many materials made this way. The two best known are poly(pyrrole) and poly(thiophene). The effect of substituents has also been studied. Also, polycyclic analogues have been reported recently. Most electropolymerized polymers are made from five membered ring heterocycles, and are generally produced in a cross-linked form of uncertain structure. While most of such polymers are poor conductors, some of the polypyrroles and polythiophenes are excellent conductors.

Justification

Such polymers are easily made by electropolymerization and are conductive as such. They tend to be stable towards oxygen when oxidized and some can be completely unaffected by water. This is a tremendous advantage over many of the other types of conducting polymers.

Status

Some of these materials are being commercialized to produce conducting films, antistatic materials, and organic electrodes. The various starting heterocycles allow oxidation potentials to be varied systematically over a broad range for many different uses. However, while applications are developing and the range of polymerizable compounds is enlarging, their basic structures and the detailed nature of the polymerizations are still unclear.

Research Proposed

1. Study of the basic chemistry of their polymerization, which includes the effect of the counter-ion, polymerization method, etc.
- 2a. Study of the polymer structure, perhaps by generating soluble polymers which can be characterized much more easily than the cross-linked ones. Here too, the counter-ion could be an important factor in structure formation.
- 2b. Newer techniques of characterization: Solid state NMR, EXAFS, small angle X-ray, neutron scattering, etc. can be applied to the study of the polymer structures.
3. New polymerizable monomers which could allow one to vary E_0 , σ , etc.
4. Nature of transport in these systems - electrical and ionic.
5. Polymer electrodes have been made. Work on polymer semiconductor interactions and polymer-polymer junctions has been started and should continue.

1.2 Preformed Heterocyclic Polymers, Dopable for Conductivity

Scope

Polymers of this type have been made for twenty-five years as part of the drive for thermally stable polymers. Undoped, many of this class are extremely oxidatively and thermally stable. It includes poly-quinoxalines, oxadiazoles, triazoles, thiadiazoles, benzoxazoles, benzothiazoles, benzimidazoles, phthalocyanines, porphorins, etc. While most are insulating as made, some have been doped and can show high conductivity in the doped state. Only one of the polymers is made in large quantity, a poly(benzimidazole), while a few are produced experimentally. Work to date has been on off-the-shelf polymers synthesized for other programs, with uncertain history.

Justification

These polymers can be made easily and are very stable. Many are soluble and can be preformed into fibers or films before doping. Others can be made in fiber or film form from soluble pre-polymers.

They can be easily handled and formed and doped when in the final configuration. While the doped polymers tend to be air and water sensitive, they can be highly conductive and can serve as polymer electrodes. The wide variety of structures can generate a wide variety of properties.

Status

Work on these materials has been reported only in the last few years. Very few of the systems have been studied and none in depth.

Research Proposed

1. A survey of the various polymers with various doping agents should be carried out.
2. In the interesting cases, structure-property relationships should be determined.
3. Does structure alter with doping?
4. For interesting polymers, the syntheses should be optimized, and analogues made to clarify structure-property relationships.

1.3 Aromatic Ladder Polymers: Potential Intrinsic Semiconductors or Conductors

Scope

This class of materials is mainly ladder polymers, both of the fully aromatic type - the heterocyclic equivalent of polyacenes where an aromatic carbon is replaced by aromatic nitrogen - and those which have aromatic groups replaced by sulfur and/or oxygen. Such polymers have been made recently by direct synthesis. They have one or two parallel sets of alternating double and single bonds, either as they are made, or after oxidation for those polymers with O and S in the backbone.

Justification

Such polymers may be intrinsically conducting. Calculations on polyacenes show that there is no localization of π electrons in this system. We hope that this will also be true of the heteroaromatic systems. In the worst case, they should be intrinsic semiconductors and become conductors when doped. Recent work on one such system shows that this is true. Many of these polymers are extremely thermally and oxidatively stable. Some are soluble in exotic solvents and may be processable. In many cases, the polymers have a regular structure and may be crystallizable. Most can be liquid crystal when processed properly.

Status

Very few from a potentially wide range of polymers have been made, and even fewer studied in any depth. Characterization of even the basic structures is almost non-existent. Doping and electrical characterization is just starting for some of the polymers. Undoped systems have been made which are semiconductors with $\sigma_{25} = 10^{-5}$ S/cm. In doped systems, a conductivity of 1 S/cm has been reached.

Research Proposed

1. Many novel structures remain unsynthesized. Some of the potential structures could be intrinsic conductors.
2. Besides linear polymers, some of these systems could generate helical polymers which may become electromagnetic.
3. Many of the syntheses should lead to well defined structures. Structural characterization should be easier than for polyacetylenes, and should be important for understanding properties.
4. As the systems develop, characterization of the electrical properties will become very important, first empirically and later theoretically for the important systems.

1.4 Summary

Heterocyclic conducting polymers have wider structural variety than carbocyclic polymers. They can be readily synthesized. Both preformation and direct electrosynthesis have been used and many types of conducting and semiconducting materials have been made. In general, these polymers are air and water stable and many are very thermally stable. This is a great advantage compared to many other conducting polymers. Some double stranded, ladder, heteroaromatic polymers have been made and many more could be made. They could have qualitatively different properties from the standard single stranded polymers. One could have conduction along the chain as well as carrier exchange between chains with such polymers.

INTRODUCTION

The field of conducting polymers owes its growth to the strong interdisciplinary interactions between chemist and physicist and the development of an appropriate theoretical framework to guide system design. As a consequence, a target system for synthesis should be chosen keeping in mind the following criteria.

- (1) A system should be chosen in which there is a theoretically valid reason for anticipating conductive properties, e.g. band structure calculation, strong orbital overlap, etc.
- (2) The choice should reflect an awareness of potential applications for polymeric conductors.
- (3) Systems which would assist in evaluating a theoretical prediction should be targets irrespective of their anticipated physical and chemical properties.
- (4) Stability (chemical, thermal) and processibility (solution, melt) are important design considerations.
- (5) Direct preparation of polymers in macroscopically ordered forms via appropriate techniques, e.g. electropolymerization, topochemical polymerization, should be attempted.
- (6) The potential of the system for structural modulation via facile synthetic routes should be evaluated.
- (7) The conversion of conventional polymers which are already stable and processible into conductive systems, and/or copolymerization, blending or doping of new systems with such conventional polymers is an important area for investigation.
- (8) Conductivity is achieved in many systems by doping -- the development of novel dopants or doping procedures is of considerable interest.

Keeping in mind these criteria, we now give a specific discussion of five important materials areas where synthetic efforts need to be focussed.

ORGANIC BASED SYSTEMS

Scope

Development of organic based conductive polymer systems should include aromatic, heteroaromatic and olefinic systems, and co-polymers thereof. Studies should especially focus on the development of polymerization techniques which provide high molecular weight polymers employing free radical, anionic, cationic, or metathetic processes. Emphasis should be placed on techniques which will provide polymers with known chemical structures based on the chemistry employed to prepare them. Such techniques should provide materials of high chemical purity, devoid of catalyst residues and defect structures.

Additionally, efforts should be directed toward the synthesis and development of novel dopants aimed at improving the thermal stability, environmental stability and mechanical properties of conductive systems. Novel dopant systems will include those which can be activated thermally or photo-chemically.

Emphasis should also be directed toward the synthesis of intrinsically conductive systems and systems which employ dopant-species as an integral part of the polymeric structure.

Justification

- (1) Preparation of clean polymeric materials of known chemical composition provides a basis for careful chemical and physical studies for the development of a better theoretical understanding of conducting polymers.
- (2) The formation of high molecular weight polymers will provide materials with improved electrical and physical properties eventually necessary for applications.

Status

High molecular weight polymers have now been realized for polyacetylene, polyphenylene and polyphenylene vinylene systems employing Ziegler-Natta catalysis reactions, olefin metathesis reactions and free radical processes. Likewise, high molecular weight polyheterocyclic polymers have been prepared by electrochemical polymerization. Much remains to be done on the further development of chemical and electrocatalytic polymerization techniques for the preparation of structurally diverse, highly conjugated organic systems.

Research Proposal

- (1) Expand the scope of electrochemical polymerization techniques to include electrocatalytic processes.
- (2) Synthesize and develop new organic structures containing functionalities capable of polymerization by free radical, cationic, anionic, and metathetic techniques which are generally applicable to the construction of a wide range of conjugated systems.

(3) Study mechanisms of polymerization useful for preparing highly conjugated systems with the aim of development of new polymerization processes (photochemical, radiation induced, etc.)

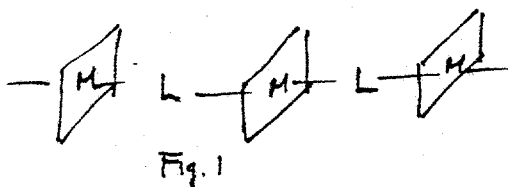
(4) Preparation of novel organic systems with intrinsic conductivity (small band gap).

(5) Synthesize novel dopants (e.g. light or thermally activated, integral part of polymer structure).

POLYMERIC MACROCYCLIC METAL COMPLEXES AS QUASI ONE DIMENSIONAL CONDUCTORS

Scope

Macrocyclic metal complexes can be used as organic conductors (or semiconductors) if they are polymerized in a cofacial arrangement, linked together by bridging ligands. The basic structure is shown in Fig. 1.



If M is a transition metal which achieves an octahedral arrangement, e.g. Fe, Ru, Co, Rh, etc., L is a linear organic ligand like pyrazine, 1,4-diisocyanobenzene or CN^- and the macrocycle is (□); e.g. phthalocyanine, stable polymers (or oligomers) can be synthesized which may exhibit conductivities up to 1 S/cm without additional external doping (M. Hanack et al, since 1980 in various journals).

Polymers of this type have been described first by Kenney and Marks, who used phthalocyanine as the macrocycle, Si, Ge, Sn, Al and Ga as the central metal atom and O and F as bridging ligands. Doping of the corresponding polymers with oxidants, e.g. iodine, led to conductive materials (conductivities up to 1 S/cm).

Justification

The polymeric structure shown in Fig. 1 is highly variable. By changing systematically the three variables, namely the macrocycle M (e.g. from phthalocyanine to tetrabenzoporphyrine, etc.), the central metal atom (e.g. from Fe to Ru) and the bridging ligand L (e.g. from pyrazine to tetrazine), polymers are obtained which, according to MO-calculations, show a band structure (intrinsic conductors). The band-gap can be controlled by the variation of the structure.

Research Proposal

Polymers of the type shown in Fig. 1 should be studied systematically concerning the synthesis and their general properties. By putting substituents in the peripheral positions of the macrocycle, the polymers can be made soluble in most of the organic solvents. The solid state properties, e.g. crystallinity must be studied (if possible). Nothing or only very little is known about the relation between chain length and conductivity.

Beside phthalocyanine as the macrocycle in Fig. 1, tetrabenzoporphyrine, naphthalocyanine and other planar thermally stable systems must be investigated. The band structure can be altered by electron donating and electron accepting groups in the macrocycle. The synthesis of these substituted macrocycles should be worked out. New bridging ligands (which are also responsible for a band structure) should be studied, e.g. SCN^- , N_3^- , etc.

Advantages of These Systems

- (1) Conductivity without external doping is expected (and has been proven in various examples).
- (2) The synthesis of polymers is easy and not expensive.
- (3) The polymers are thermally stable.
- (4) Composites with other polymers are possible.

MODIFICATION OF CONVENTIONAL POLYMERS

Scope

In the past 10 - 20 years numerous efforts have been focussed on preparation and characterization of novel conductive polymers. However, commercially available polymers or readily synthesizable polymers may be modified to conductive materials.

Surface Treatments

Carefully controlled oxidation, reduction, or elimination of certain groups (cf HCl , HF and H_2O) may produce semi- and conductive materials.

- (1) Elimination of hydrogen halides from polyvinyl halide and copolymers of vinyl halide and olefinic monomers.
- (2) Elimination of halogen from polyhalogenated olefinic polymers.
- (3) Radiation effects on polyolefinic polymers.
- (4) Metal ion implantation on polymers.

Research Proposal

The above areas need to be reinvestigated on better controlled materials without destruction of their physical form or physical properties. In addition a new area to be investigated is the synthesis of composite systems.

- (1) Formation of polypyrrole, polythiophene, etc. on conventional polymers to combine desirable physical properties.
- (2) Stabilization of conductive polymers by treating (coating, blending, bonding) with polymers.

TOPOTACTIC/TOPOCHEMICAL CONTROL IN PREPARATION OF CONDUCTING MATERIALS

Scope

The rational synthesis of conducting materials requires attention to control of structure during the preparation of these materials.

Justification

Although topotactic methods for the preparation of inorganic composites and refractory materials (e.g. epitaxial growth) has been an area of intensive research, similar strategies have not been thoroughly explored for conducting materials composed of two-dimensional conducting polymers and quasi-1-D linear chain compounds. The ability to predictably control the structure of the material of interest will allow the synthesis of conducting systems with desired electronic and structural properties.

The fundamental problem can be divided into two areas: (1) control of macroscopic morphological structures; (2) synthesis of new materials based on topochemical reactions. The major area of interest includes the use of "substrate control" in the synthesis of new materials, and the chemical and electrochemical polymerization/crystallization of materials at well-characterized, epitaxially oriented surfaces. Also included is control of morphology by the environment of the growth medium.

Research Proposal

(1) Studies to understand the relationship between ordered structures of conducting materials and the structure of their precursor. This has been exploited in some systems (e.g. covalently linked phthalocyanines and fused heterocyclic polymers) and requires further attention in 1,2-D materials. These studies can include monomers whose lattices are nearly degenerate with their polymer lattices. Information regarding crystal structure of reactive monomers under conditions relevant to polymerization is insufficient to allow prediction of the direction of solid state polymerization.

(2) Initiation of chemical polymerization at well-defined, epitaxially oriented surfaces. Polymerization may be initiated thermally, photochemically or via chemical reactions with functional groups on the surface. Systematic investigation of the effect of well-defined surfaces on the morphological identity of chemically and electrochemically grown phases needs to be performed. Such surfaces include, but are not exclusive, surfaces modified by covalent attachment of appropriate reagents and Langmuir-Blodgett films.

(3) Spectroscopic investigation of monolayer and sub-monolayer films of dimensional materials on well-defined surfaces. Such techniques include infrared, Raman, SERS and EXAFS.

(4) Investigation of the growth of dimensional materials in anisotropic media. Examples include crystallization in liquid crystalline media, clathrates or in the presence of orienting electromagnetic fields.

(5) Investigation of directional control of crystal growth as a route to macroscopic organized structures.

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 of properties available to the inorganic chemist with the use of the transition metals.

In the context of conductive polymers, the use of transition metals offers the following advantages over the conventional carbon based systems. The larger radial extension of the d - orbitals is likely to result in more favorable bonding interactions resulting in wider band structures and more highly conducting systems. Strong metal-metal bonding in many transition metal complexes as well as the highly conducting tetracyanoplatinates are clear manifestations of this property. In addition, the mixed valence behavior so important to conductive polymers is easily satisfied with transition metals and their multivalence behavior. Systematic changes 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 remained innocent (i.e. not participating in the conduction process). Further work is needed in this area to extend this field to include the heavier transition metals.

(SN) 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 in purely inorganic polymers.

The chevrel phases are just one important example of the third category. The chevrel phase, formed from stacked molybdenum-sulfur clusters exhibits low dimensional conductivity at room temperature and superconductivity at low temperature under pressure.

Research Proposal

Intensified research building on what is already known from dimeric and small cluster chemistry is likely to be a fruitful endeavor and greatly enhance this area of conducting polymers.

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 $[\text{Pt}(\text{CN})_4]^{n-}$ 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.

$(\text{SN})_x$ 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 $(\text{SN})_x$ provides impetus for further effort with purely inorganic polymers.

The Chevrel phases are just one important example of the third category. The Chevrel phases are composed of $[\text{MoX}_8]^{n-}$ anionic clusters where X = S, Se, Te, and stack to form low dimensional conductors at room temperature and superconductors at lower temperatures (with critical temperatures as high as 13 K).

Research Proposal

Closer inspection of the characteristics of conventional inorganic polymers is warranted and is likely to reveal many new candidates for further studies. Synthesis of new materials is also an important goal and is likely to be a fruitful endeavor. Electron delocalization in low molecular weight analogs of these polymers (i.e., mixed valence complexes such as the famous Taube-Creutz ion) suggest that these materials will be interesting conductors if extended to polymers. Such past work provides a rational starting point for the synthesis of new inorganic conductive polymers.

Study Group E

Potential Applications of Conducting Polymers

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1.0 Introduction

Applications of conducting polymers will be driven by the unique combination of electronic, mechanical, as well as fabrication properties that are anticipated for this class of materials. The delocalized electronic structure frequently enables high electrical conductivity and those properties in conjunction with traditional properties of polymers (e.g., good mechanical properties, ease of fabrication, low cost, and low weight) are anticipated to enable this class of materials to be commercially more important in the future. Commercial use of conducting polymers has been inaugurated by the Xerox Corporation which is marketing a copier containing static dissipation brushes comprised of an conductive polymer. In addition to conductivity, these compounds exhibit highly anisotropic optical properties and uses based on these properties may arise in the future. Our study group, which was unfortunately composed of nonexperts in application areas, attempted to identify potential uses of conducting polymers and further identify potential research areas which, if successfully undertaken, might ultimately enable development and commercialization of these applications. The group took a broad brush long term view and thus avoided development types of projects.

1.1 POTENTIAL APPLICATIONS OF CONDUCTING POLYMERS

SCOPE

Research samples of polymers exhibiting high dc electrical conducting have been developed and samples suitable for

commercial evaluation are just becoming available. The scope of this workshop report is to identify those applications where this class of materials as currently understood or as envisaged to be available in the future might find utility. Preference was paid to where new markets would open up as opposed to those markets where introduction of conducting polymers would have to displace current technology. Relatively poorly conducting materials suitable for electrostatic charge dissipation are emerging. Important as these applications are this Study Group has chose to avoid development types of projects requiring these types of materials and focus on a longer term prospects for conducting polymers.

JUSTIFICATION

Polymers are one of many important materials with applications ranging from low to high technology. These applications have been developed over many years of intense research and development activities both from a scientific research and business marketing points of view. Due to the wide range of properties exhibited by polymers, this work has shown large number of ways polymers can be used. New applications often result form combining properties of blended (composites etc) materials or by manipulation of pure materials. In some instances polymers have replaced exiting materials, while in other instances whole new applications and industries have been developed.

Conducting polymers now introduce new phenomena to the polymer property repertoire i.e., control of electronic and ionic transport. By combining ion and electron transport to a polymer's general ease fabrication at moderate conditions (in contrast to the such conditions for metals and ceramics) a new class of materials with potential applications in electromagnetic interference shielding (EMI), resistive heating, sensors (chemical, pressure, temperature), batteries, solid state electronic or electrooptic devices, thermoelectric devices, ferromagnetic materials as well as testing concepts associated with the Holy Grail of molecular electronics are hoped to emerge.

STATUS

A wide range of conducting polymers are presently know. These include intrinsic (e.g., (SN)_x or pyropolymers) conducting polymers or those which must be doped (e.g., (CH)_x, polypyrrol). Evaluation for potential applications are limited by the availability and stability of these substances as well as their ability to be suitably fabricated. Very recently, and most notably at this meeting, a few cases where conducting films, fibers, composites, latex and moldable resins based on conducting polymers have been reported. Control of morphology and processing, however, are

not as well developed. The processing of conducting materials for evolutionary reasons is the least well understood area.

The physics of conducting polymers, although intensely studied, remains in some areas controversial. This is especially true for morphologically related phenomena. For example, the importance inter vs. intra particle size and contacts or molecular weight as well as morphological variations on conductivity are not well understood. Microscopic phenomena such as the role of solitons, polarons, and bipolarons are also not universally accepted.

Environmental stabilities of these materials are essential properties which limit their application. Recent studies have begun to understand the factors which control their thermal, oxidative, hydrolytic as well as chemical stabilities. Likewise reliable reproducible preparation of samples large enough to enable commercial evaluation for possible products has only been achieved for a few materials. For these reasons there are currently only a limited number of commercial applications of these materials. Nonetheless, an example where a conducting polymer is used is in a commercial xerographic copier. The substantial work aimed at developing an organic battery, has yet to lead to a commercial success.

PROPOSED RESEARCH

The Study Group did not want propose developmental research aimed at a specific product and preferred to identify areas of general research that, if successful, could ultimately be used to exploit applications. These are:

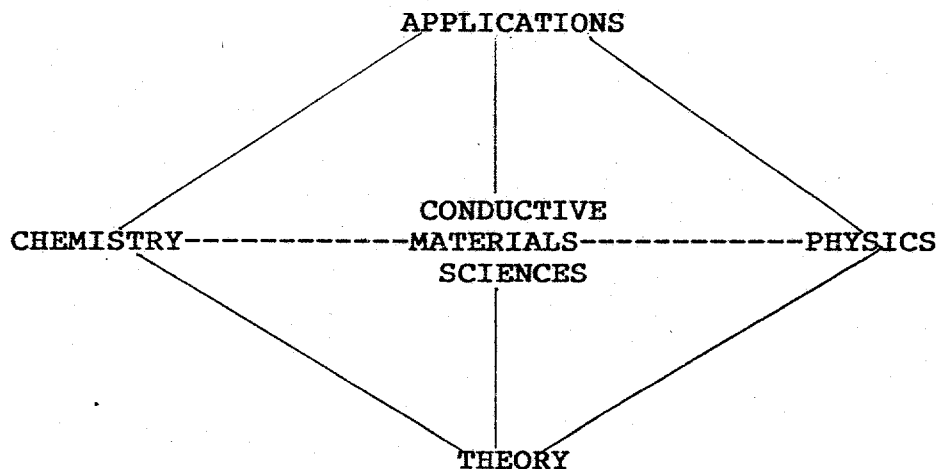
- 1) Understanding the chemistry and physics of composites including active/passive homogeneous and/or heterogeneous blends.
- 2) Fundamental understanding and characterization of single polymeric units vs. aggregates. This includes understanding of the conductivity of highly ordered vs. disorder systems as well as the study of interface phenomenon of conducting materials with classical inorganic conductors, semiconductors, and insulators.
- 3) Developing capabilities to control morphology and understand its effect on ionic and electron transport.
- 4) Improve characterization capabilities for conductive polymers.
- 5) New synthetic endeavors include the development of highly ordered polymeric systems with controlled morphology, intrinsic conductors (especially pyropolymers) and controlled properties via electrochemical techniques. The synthesis needs also extends to blends and composites.
- 6) Processing and synthetic scale up technologies will also be important to assure availability of interesting materials for commercial evaluation.

1.2 Summary

In addition to the fundamental studies aimed at understanding chemistry and physics of conducting polymers, materials are just becoming available for evaluation in terms of commercial application. It appears that adding high electrical conductivity to the host of advantageous properties polymers have become associated with would lead one to expect many commercial applications in the future. This may come to pass, however, at the present time merging of the electrical properties of conducting polymers with the expected mechanical/fabrication properties of polymers has required a compromise in expectations. Some samples are becoming available for study and the Study Group has reviewed a variety of areas where applications of these materials might find a home in the future. The Study Group strongly suspects that conducting composites/blends might lead to a variety of important opportunities for conducting polymer.

1.0 Introduction

The investigation of conducting polymers and in the broader sense the investigation of conducting molecular and organic materials has been intensely pursued for a decade now. The scope of this **CONDUCTIVE MATERIALS SCIENCE** is defined by the breadth of materials and concepts studied. This broad interdisciplinary field requires the close interaction of four diverse disciplines: chemistry or synthesis of new materials, physics or experimental study of these unconventional materials, development of theoretical concepts germane to these molecular and polymeric systems, and applied research into these novel solids that may lead to applications. Each of these four disciplines interact with the other three and together they form the conductive materials science. This may be illustrated by the diagram below.



The basis of the field has been developed through intense study of several model systems including charge transfer salts such as tetrathiofulvalene-tetracyanoquinodimethane and polyenes such as polyacetylene and its various isomers and doped forms. New synthetic procedures were developed during the study of the chemistry of these systems, and tools were developed for measuring the electrical, magnetic, spectroscopic and other properties of these highly anisotropic systems. New theoretical concepts such as strong electron-phonon interaction, Peierls transition, solitons, bipolarons, etc. were developed to understand these materials and research initiated into application of these novel systems as electrostatic eliminators and battery materials.

It is our assessment that these studies into chemistry, physics, application and theory are together forming a new conductive materials science. Several developments are already visible which point to a rapidly evolving materials base and an understanding of conductive materials. Presentations at this Workshop point to many opportunities in new formulations of polyenes such as polyphenylene and polythiophene, and the development of environmentally stable and processable materials based on polycrystalline inhomogeneous and/or composite systems. The development and understanding of the nonlinear optical response of these solids opens up new opportunities for nonlinear signal processing based on the strong electron-phonon coupling of polyene chains. As the science of conductive materials is extremely broad, it is necessary to bring to bare a very wide variety of tools including, but not limited to measurement of the electronic structure of monomers, oligomers and polymers; measurements of the three-dimensional ordering of polymers and molecules and solids; measurement of the role of the counterions in effecting the reactivity of conducting polymers and its effects on the structural order of conducting polymers; and direct measure of the charge transport, magnetic, optical, and rheological properties of these materials and their composites. Theory has made a great deal of progress in the field, but many opportunities for new science remain. These include application of quantum chemistry to small and medium sized molecules and oligomers and to development of more sophisticated phenomenological models of the electronic structure and defects of polyenes, and to understanding the macroscopic properties of real samples of conductive materials and their polycrystalline or composite

formulations. All four of the disciplines indicated in the tetrahedron participate, although not equally, in each of these areas. The study group focused on four broad categories including novel materials and design methods analytical methods, physical properties, and theory. The objective was to take the broad view of problems in the field and a long term look into the future. No attempt was made to prioritize the areas or the research topics given the amount of time available. In general, a healthy conductive material science requires progress in each of these four areas and contributions from chemistry, physics, application and theory. The following summaries address scope, justification, status and research needed for each of the four topics.

1.1 Novel Materials and Design Methods

Scope

Conductive materials science is driven by the development and synthesis of novel polymeric or molecular materials which are electron and sometimes ion conducting systems and/or have magnetic or optical properties that are unusual. The development of systems with desirable environmental, mechanical, or processing parameters is also an objective.

Justification

The development of conductive materials science is in many ways materials limited. The design and synthesis of new materials and novel synthesis of established materials is a way of building on the present understanding of conductive materials. In testing of the many current concepts, development of the design criteria for the synthesis of materials with the desired electrical, magnetic, optical, and mechanical properties is an ultimate goal.

Status

A considerable information base has already been built based on the study of polymers such as polyacetylene and charge transfer salts such as TTF-TCNQ. The recent development of new conducting polymers such as polypyrrole blends with latex and similiarly the development of new superconducting charge transfer salts demonstrate the beginning of the ability to design new materials with tailored properties. However this is only the beginning.

Research Proposed

The synthesis of new materials and interplay of synthetic, measurements, applications, and theoretical researchers has been a unique and invaluable aspect of the conductive materials science area. However our understanding of the chemistry occurring in many polymerization and "doping" processes is at a very primitive level. More careful chemical studies should be carried out on existing systems with close coupling to physical measurements. Modification of the synthesis and post processing of conducting polymers should be explored as well as the control of "ordering" both at the microscopic and morphological level. New synthetic techniques such as electrochemical deposition, and formulation of new kinds of composite systems as well as vacuum techniques should be explored. Attempts should be made to develop long range order in polymers. Synthetic routes to new types of materials should be vigorously studied. We must understand better how to construct new types of conductive polymer materials. In parallel with the development of new materials is a search for new properties in polymers including better control of conductivity, its absolute value and temperature dependence, stable magnetic molecular and polymeric systems, soluble and liquid conducting polymers, fast response nonlinear optical materials based on conjugated polymers, and inorganic polymer systems. In parallel with this development of new materials is a development of applied quantum chemistry that includes a better understanding of the molecular electronic structure and its relationship to macromolecular electronic structure. It is essential that there is an adequate level of manpower support as well as the requisite equipment (glove boxes, vacuum lines, GC, HPLC, crystal growing equipment etc.) for the progress of this program.

1.2 Analytical Methods

Scope

The application and increased sophistication of analytical methods in the characterization of the structure and chemical composition of conducting materials.

Justification

New and unusual materials cannot be understood until the knowledge of what material is being studied is developed.

Status

A significant number of traditional and new analytical techniques have been developed by different portions of the materials science community. These techniques include x-ray diffraction, synchrotron diffraction, low angle x-ray scattering, diffuse x-ray scattering, neutron diffraction and scattering, electron, and ion spectroscopies, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and other sophisticated chemical and analytical tools. The array of analytical techniques have not been applied consistently to this broad range of materials.

Research Proposed

The available analytical techniques as well as new techniques specific to the problems of conductive materials need to be brought to bear in this area. The advent of the use of cyclic voltammetry in the conducting polymer field is an example of greatly increased understanding which results from the overlapping of this conductive materials science and measurement science. Examples of the more traditional techniques that need to be more consistently applied include fourier transform infrared spectroscopies, mass spectrometry using modern sampling techniques, synchrotron radiation and x-ray diffraction as well as sophisticated magnetic resonance measurements. Because of the broad materials questions that arise, the ability to handle the large amount of data generated is an important limiting factor. Hence, software and hardware for computer manipulation of the data is an important consideration. Sufficient funding is necessary to enable the collaborative mode of interaction that is a part of application of these techniques to these new novel materials.

1.3 Physical Properties

Scope

How do we go from a chemical or physical understanding of model compounds to an understanding of the real materials to be used in applications?

Justification

The transfer of novel materials to engineering groups and the realization of applications requires an understanding of the relationship of the macroscopic properties to the chemical and physical properties of the model systems usually studied.

Status

At present, the chemical and physical knowledge of model compounds and polymers is much greater than the current understanding of real processable and environmentally stable compositions of conductive materials.

Research Proposed

Continued detailed study of model synthetic materials and the physics of these model systems is important for gaining the underlying knowledge for understanding the complicated macroscopic systems. In parallel with this continued study, development of new materials preparation techniques is encouraged. These techniques would include preparation of new forms of composite materials containing conducting and nonconducting polymer systems as well as the formation of polycrystalline or other macroscopic materials formulations.

The broad spectrum of analytical techniques needs to be applied to these model systems as suggested in paragraph 1.2. That includes study of the chemical, crystal and electronic structure as well as the reactivity of the component materials. Detailed physical studies of these model materials need to be performed. This includes measurement of the electronic excitation spectrum of these materials via spectroscopy from the far infrared through the vacuum ultraviolet and a detailed determination of the electronic structure or density of states in the vicinity of the fermi level of these materials. Insight into the mechanism of charge conduction in various conductive materials can only be gained through careful coordinated measurements of a broad spectrum of transport parameters including temperature dependent dc conductivity, electrical field dependence of conductivity, the frequency dependency of conductivity from dc through microwave frequencies, the magnetoresistance and Hall effect as well as other related experiments such as thermoelectric power and thermal conductivity. The dynamics of defect states is also an important aspect. Relevant studies includes photoinduced optical effects and photomagnetic effects. In the absence of this broad spectrum of studies an incomplete and inaccurate picture of the electronic structure and properties of these systems is obtained.

A full study of the electronic properties of the macroscopic formulation of these materials, directly synthesized in the end form, processed as neat polymer or processed in composite form is also warranted. That includes a broad spectrum of transport studies and spectroscopic studies. In addition, the mechanical and rheological properties become more important.

Determination of the processability of these polymers and polymer composites, as well as the environmental stability and half life, are necessary for commercial applications. Adequate funding is necessary in order to accomplish these broad goals which includes adequate manpower as well as access to the necessary equipment. Because the techniques and skills involved are resident among different groups of scientists, it is suggested that collaborative interdisciplinary research be encouraged. In support of this, the funding mechanisms must be set up to accommodate joint proposals, interdepartmental activities, and interinstitutional activities. An important component is the funding for travel and residence in other laboratories.

1.4 Theory

Scope

The development of a theoretical understanding that enables the induction from molecular and structural properties to the macroscopic properties of solids. The development of design criteria for preparing materials of desirable electrical, magnetic, optical and mechanical properties is an ultimate goal.

Justification

The development of microscopic and phenomenological theories provides a framework for understanding known properties of materials and the determination of the underlying microscopic materials parameters. An understanding on this microscopic level should allow a the prediction and/or design of new materials and their properties. The theoretical prediction of new phenomena is an important driving force for experimental study. The observation of new phenomena and anomalous behavior in turn is an important impetus for new theoretical development.

Status

The theoretical understanding in the field is currently at a rudimentary level. Conductive material science encompasses a broad array of problems ranging from study of molecular monomers to oligomers, to isolated chains, to chain defects (solitons, polarons, bipolarons, etc.), to crystals, to addition of disorder, to the modeling of composite systems. Development of models of the electronic structure of this broad array of systems and the prediction of their physical properties is still in an early stage.

Proposed Research

Research needs to be conducted in parallel in the broad areas of study of the isolated units through the electronic structure of the polymers and interfaces that are involved in real macroscopic formulations. In addition, there is an absence of real understanding of the measured physical properties of the real material including conductivity, magnetism, etc. The development and availability of supercomputers should allow the application of quantum chemistry to larger molecular or oligomeric and chain model units. This should enable a better understanding of the relationship between the molecular and macromolecular architecture, electronic structure, electron-phonon interaction, and charge transport mechanisms. The role of coulomb correlation has been insufficiently explored. Questions arise as to whether it is large or small, and whether it can be controlled to create a ferromagnetic ground state. The effects of interchain interaction and interchain screening need to be investigated. An understanding of photogenerated defects in polymers other than polyacetylene has yet to be developed. The actual conducting polymers synthesized are far from microscopic ordered single crystals. The role of disorder needs to be determined. For example, which properties that are observed are unique to conducting polymers and which are common to all of the disordered systems, for example amorphous silicon. Would doped ordered conducting polymers behave the same or quite differently?

A particularly important question that remains controversial is: why do conducting polymers conduct? Indeed almost all doped polymers have a room temperature conductivity of ten siemens/centimeter. These polymers generally also have a similar concentration of curie spins. Is this central to the properties?

Polymers provide a unique opportunity for the fabrication of new types of composite materials, including the growth of interpenetrating polymer networks as well as growing conducting polymers within microporous systems. These new structures and their properties will challenge the theoretical community to expand the current understanding of composites, for example effective medium theory and Maxwell Garnett theory need be modified to account for these nonspherical structures.

1.5 Summary

After nearly a decade of work, a new conductive materials science has begun to emerge. This science is interdisciplinary requiring close interaction from chemistry, physics, applications research, and theory. The frontiers of the field are expanding rapidly. Novel materials and design methods are emerging, new and sophisticated analytical methods are being applied, a broad spectrum of physical properties are being studied, both of the simpler model compounds and the more complicated microscopic materials formulations, and a broad range of theoretical concepts is being developed. A significant investment in this materials science is being carried out in other places including Japan and Europe. It is essential that there be an adequate level of support for manpower, as well as for the necessary equipment in the United States. In light of the breadth and depth of conductive material science, collaborative interdisciplinary and interinstitutional programs need to be encouraged. Cognizance needs to be taken of the increased cost for communication under these circumstances including extensive travel expenses.

THE WORKSHOP ON CONDUCTIVE POLYMERS

Date: October 7,8, and 9, 1985

**Place: Brookhaven National Laboratory
Upton, Long Island, New York**

Sponsors:

- **Department of Energy,
Division of Materials Sciences**
- **Polymer Research Institute,
Polytechnic Institute of New York**
- **Brookhaven National Laboratory**

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Organizing Committee

R.H. Baughman	Allied Corporation
A. Goland	Brookhaven National Labs
A.G. MacDarmid	University of Pennsylvania
Y. Okamoto	Polytechnic Institute of New York
E.M. Pearce	Polytechnic Institute of New York
F.J. Salzano	Brookhaven National Labs
D.J. Sandman	GTE Laboratory
G. Wewerke	Los Alamos National Laboratory

Objective

The area of conducting polymers has been characterized by a large degree of interdisciplinary integration within research groups. Cooperation among chemists, physicists and theorists has greatly strengthened research programs. The objective of this workshop is to bring about a similar enrichment via greater integrations among different research groups. Consequently, the workshop will promote intergroup interactions focussing on common problems related to materials, syntheses, properties, and applications, as well as future directions.

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Sunday, October 6

Time: 7:00 - 9:00 PM

Registration, Refreshments at Brookhaven Center

Monday, October 7

8:30 - 9:00	Registration Coffee and Danish, Brookhaven Center
<u>CHAIRMAN</u>	Y. Okamoto Polytechnic Institute of New York
9:00 - 10:00	S. Baron Brookhaven National Laboratory
	I. L. Thomas Department of Energy, Division of Materials Sciences
	E. M. Pearce Polytechnic Institute of New York
<u>CHAIRMAN</u>	S. Tripathy GTE Laboratories
10:00 - 10:30	R. Baughman Allied Corporation
	Overview: "Structure-Property Relationships in Conductive Polymers"
10:30 - 11:00	Coffee Break
11:00 - 11:30	A. Heeger University of California, Santa Barbara
	"Physics of Polyheterocyclic Systems - Recent Developments"
11:30 - 12:00	A. MacDiarmid University of Pennsylvania
	"Polyaniline: A New Concept in Conductive Polymers"
12:00 - 1:30	LUNCHEON

CHAIRMAN

1:30 - 2:00

R. Liepins
Los Alamos National Laboratory

R. R. Chance
Allied Corporation

Overview: "Physics of Conductive Polymers"

2:00 - 2:30

A. J. Epstein
Ohio State University

"Conduction in Conductive Polymers"

2:30 - 3:00

J. Collman
Stanford University

"A Search for Experimental Models to Test Little's
Theory of Excitonic Superconductivity"

3:00 - 3:30

Coffee Break

3:30 - 4:00

T. Marks
Northwestern University

"Conductive Polymers Constructed from Metal-
locycles"

4:00 - 4:30

M. Aldissi
Los Alamos National Laboratory

"Comparative Study of Polyacetylene, Its Copolymers
and Composites"

CHAIRMAN

4:30 - 6:00

F. J. Salzano
Brookhaven National Laboratory

POSTER SESSION

- o K. Y. Jen
Allied Corporation

"Facile Route to Stable Conducting Polymers"

- o O. Inganas, T. A. Skotheim and S. W. Feldberg
Brookhaven National Laboratory

"Photoelectrochemistry with Polymer Solid
Electrolytes"

- o Z. Iqbal
Allied Corporation

"The Synthesis, Properties and Structure of
Poly(peri-Napthalene)"

- O. Kim
Naval Research Corporation
"Electrical Conductivity of Heteroaromatic Ladder Polymers"
- W. K. Kobel
R.C.A. Ltd. (Switzerland)
"Polythiophene Conductive Polymers"
- T. M. Keller
Naval Research Laboratory
"High Performance Conductive Polymers"
- J. T. McDevitt and J. P. Collman
Stanford University
"Spectroscopic Studies of Shish-kebab Polymers"
- L. H. Tolbert
Georgia Institute of Technology
"A Carbanion Approach to Polyacetylene"
- E. Tsuchida
Waseda University (Japan)
"Highly Conductive Metallophthalocyanine Crystals"
- G. Tourillon
Brookhaven National Laboratory
"Orientations and Structure of Pyrrole and Thiophene Absorbed on Pt (1,1,1,)"
- G. E. Wnek
Massachusetts Institute of Technology
"Reactions of n-type Polyacetylene with Alkyl Halides"
"The Mechanism of Conduction in Polyaniline"
"Ion Implantation of a Polyquinoline"
- D. Weber
Naval Research Laboratory
"Synthesis and Properties of Extended Ring Phthalocyanines"

6:00 - 7:00

Cocktails

7:00 - 9:00

DINNER

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Tuesday, October 8

<u>CHAIRMAN:</u>	A. Goland Brookhaven National Laboratory
8:30 - 8:55	T. Skotheim Brookhaven National Laboratory "Polypyrrole - Phthalocyanine"
8:55 - 9:20	D. J. Sandman GTE Laboratories "Polydiacetylenes and Analogues to Inorganic Semiconductors and Graphite"
9:20 - 9:45	L. W. Shacklette Allied Corporation "Battery Applications of Conductive Polymers"
9:45 - 10:10	J. Chien University of Massachusetts "Mechanism of Electronic Conduction in Organic Polymers"
10:10 - 10:30	COFFEE BREAK
<u>CHAIRMAN</u>	Z. Iqbal Allied Corporation
10:30 - 10:55	G. Baker Bell Communication Research "New Co- and Homopolymers of Polyacetylenes"
10:55 - 11:20	M. M. Labes Temple University "Poly(cyanogen)"
11:20 - 11:45	M. Litt Case Western Reserve University "Soluble Linear Heterocyclic Ladder Polymers"
11:45 - 12:10	G. Dandreaux and G. E. Wnek Massachusetts Institute of Technology "Polysuccinonitrile"
12:10 - 1:30	LUNCHEON

CHAIRMAN

- D. J. Sandman
GTE Laboratories
- 1:30 - 1:55 R. L. Elsenbaumer
Allied Corporation
"Processable and Environmentally Stable
Conductive Polymers"
- 1:55 - 2:20 M. Druy
GTE Laboratories
"An Experimental Approach Towards Achieving
Environmental Stability and Processibility in
Conducting Polyheterocycles"
- 2:20 - 2:45 S. Jasne
Polaroid Corporation
"Processable Polypyrrole"
- 2:45 - 3:10 R. Liepins
Los Alamos National Laboratory
"High Temperature Conductive Polymers"
- 3:10 - 3:35 J. Williams
Argonne National Laboratory
"Sulfur Based Organic Superconductors"
- 3:35 - 3:55 COFFEE BREAK
- CHAIRMAN
- J. Chien
University of Massachusetts
- 3:55 - 4:21 J. Frommer
Allied Corporation
"Polyphenylene Sulfide - Conductive Polymer
Solutions"
- 4:20 - 4:45 S. I. Yaniger
Nicolet
"Infrared Studies of Conductive Polymers"
- 4:45 - 5:10 C. E. Brown
Medical College of Wisconsin
"Laser Desorption/Fourier Transform Mass
Spectral Analysis of Various Conducting
Polymers"

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5:10 - 5:35 Y. Okamoto
Polytechnic Institute of New York
"Poly(carbon diselenide)"

5:35 - 5:50 E. M. Pearce
Polytechnic Institute of New York
"Strategy for Study Group Meetings"

6:00 - 8:00 BUFFET DINNER

Wednesday, October 9

8:30 - 10:00 Meeting of Study Groups

10:00 - 10:30 Coffee Break

10:30 - 12:00 PREPARATION OF STUDY REPORTS

12:00 - 1:00 LUNCHEON

1:00 - 3:00 FINAL SESSION
PRESENTATION OF STUDY REPORTS

Program of Direction of Problem Areas
and Potential for the Future - Chemistry, Physics
and Technology

- Group A: Polyacetylene, Polyphenylene, Polyaniline
and Related Systems
- Chairman: A. MacDiarmid
University of Pennsylvania
- Group B: Molecular, Crystallographic and Detect Structures
in Conducting Polymers
- Chairman: R. Baughman
Allied Corporation
- Group C: Heterocyclic Polymers
- Chairman: M. Litt
Case Western Reserve University
- Group D: Synthesis of New and Improved Conducting
Polymers
- Chairman: M. M. Labes
Temple University
- Group E: Future Applications Possibilites for Conducting
Polymers
- Chairman: J. Miller
DuPont
- Group F: Challenges for Improved Understanding of
Properties
- Chairman: A. Epstein
Ohio State University

Appendix II

The Workshop on Conducting Polymers

Participant's List
(October 1, 1985)

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Over one dozen graduate students and research associates from the following institutes were also attended the workshop.

The Ohio State University

The State University of New York at Stony Brooke

Polytechnic Institute of New York

City University of New York