

Electrically and Magnetically Active Polymers: Not Just Insulating Plastics

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Abstract: The advent of organic materials for electroluminescent devices has allowed a wide variety of applications in displays, communications, sensors, and the like. The demonstration of organic magnetic materials has offered the challenge of finding polymer (organic) materials in which there is sufficient electronic exchange as well as stability in both thermally and chemically. The intrinsically conductive and semiconductive polymers have allowed designers the liberties of flexibility and conductivity to meet needs from batteries to solar cells. This paper gives an overview of this search past, present, and future and the synthesis of promising new complex polymer building blocks which can yield conductive, semiconductive, luminescent, ferro-, ferri-, and super-paramagnetic materials for devices of the future in power, storage, displays, and communications devices. The use of these materials to produce electrically active polymeric materials has changed our way of thinking about how to fabricate devices with properties heretofore unrealizable. There are three laboratory exercises described in this paper. They have been given both as in-class demonstrations and as student laboratories.

Key Words: Electrical Polymers, Magnetic Polymers, Luminescent Polymers, Molecular Electronic Materials.

Introduction

Molecular Magnetic Materials

When the early civilizations made the discovery that iron was indeed attracted to lodestone, the era of magnetism and its devices and effects was launched. After that time, the earliest device recorded was the compass, an invention of the Chinese. Since then, ferromagnetic (Fe, Ni, Co, etc.), ferrimagnetic (e.g. F_3O_4), and paramagnetic materials have been used in technology applications such as magnets, magnetic tapes and disks, magnetic resonance imaging contrast enhancers, and magneto-optic memories, to name a few. Organic/molecular based materials, with *p* or *d* orbitals aiding the magnetic properties, have been a source of scientific curiosity for a number of years^{1,2}, but only recently have such materials become a reality^{3,4,5}. This new class of magnetic materials is, for the most part, non-metallic, being made from simple to complex organic molecules. Their structure can be uni- or bi-dimensional and need not have the three-dimensional format necessary for conventional ferromagnetic, ferrimagnetic, paramagnetic, and antiferromagnetic materials. These materials can be simply fabricated from a variety of solvents at or near room temperature. These should not be confused with bimetallic complexes such as those formed by pyrolysis or partial oxidation.⁶ Other work postulated the use of a new class of

pi-biradicals called the non-Kekule polynuclear aromatics, shown in Figure 1 below.³ The high spin nature of these systems should drive

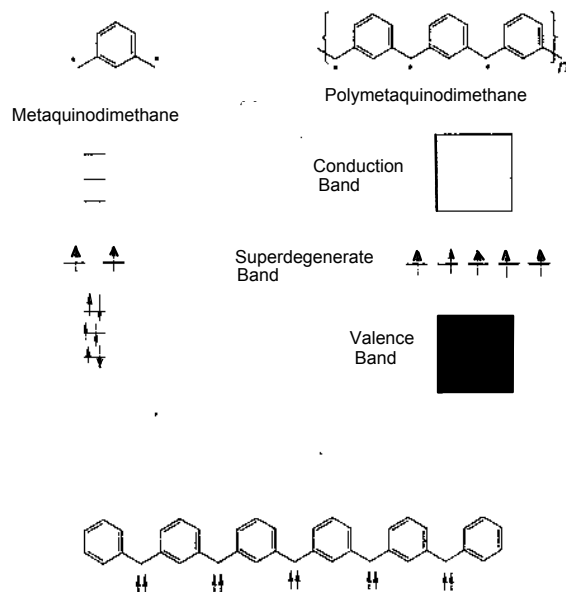


Figure 1

Representation of pi-molecular structure of metaquinodimethane, the associated spins, and an oligomer^{1,2}

ferromagnetic coupling in charge transfer complexes. This is best served by having the centers covalently bonded together, namely, a polymer system made up of repeating molecular segments sharing the framework of the high-spin systems, quinodimethanes based on the benzene, naphthalene, and biphenyl nuclei.

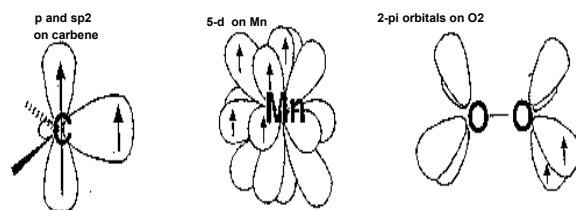


Figure 2

Possible model for magnetic spin coupling^{1,2}

Figure 2 shows a possible model for magnetic spin coupling where spins align in orthogonal orbitals in a small spatial region.¹ A description of the materials (six possible configurations of parallel and anti-parallel spins, along with canted ones for reference, to describe paramagnetic, ferromagnetic, antiferromagnetic, Ferromagnetic canted ferromagnetic, and correlated spin glass (disordered structure)) is given in reference 13.

The Experiments

Prerequisite Knowledge: There are three laboratory exercises described in this paper. They have been given both as in-class demonstrations and as student laboratories. The student should be familiar with the basics of materials science, metallography, and chemistry. Levels at which these experiments are performed are second semester junior year and either semester senior year. The students are first given lectures the properties of materials including polymers and magnetic,

luminescent and conductive polymeric materials (see paper in reference 15 for pre-lab tutorial). They should have already had a laboratory experiment on metallography and sample preparation.

Learning Objectives: The objectives of these three experiments are to show how the unique properties of polymers lend themselves to applications involving electrical, magnetic, and optical properties and how they are incorporated in a variety of devices. These experiments contain all of the elements of good design, with the caveat that a novelty in structure is sometimes a part of design. The students learn the process of designing materials for the world of device applications, analyze those already used, and suggest possible solutions to the problems involved with present technology.

Equipment and Supplies:

- (1) Metallurgical preparation and polishing apparatus (e.g. Buehler Co., Port Washington, NY).
- (2) Varieties of monomers (Roche Chemical Div., Hoffmann-LaRoche Inc., Nutley, NJ; Baker Chemical, U. of Utah Materials, Salt Lake City. National Starch (Beta Cyclodextrin).
- (3) Low voltage d.c. and 60Hz power supply (Edmund Scientific)
- (4) Miscellaneous graduates, glassware, ovens (Fisher Scientific),
- (5) Indium-tin oxide (ITO)coated glass and plastic (Tecknit Corp., Cranford, NJ)
- (6) Miscellaneous meters and power supplies.
- (7) Metallurgical microscope (Olympus, Zeiss, etc.).
- (8) Small photoresist spinner (Fisher Scientific).

Experiment 1. Making and testing magnetic polymers

Time: 3-4 hours, dependent on complexity.

Cost: \$15/student group

The work described here involves a formulation of a solution, the mechanism definition, and results for this formulation. These materials are deposited on a variety of surfaces from alumina to modified vinyl. This method enables the user to deposit a magnetic polymer on a wide variety of surfaces and topographies. These polymers retain the electrically insulating properties, while exhibiting ferromagnetic behavior. *Cyclodextrins*, cyclic oligosaccharides, were discovered approximately 100 years ago. In the pharmaceutical industry, Cyclodextrins have mainly been used as complexing agents to increase the aqueous solubility of poorly water-soluble drugs, and to increase their bio-availability and stability. Cyclodextrins are produced by a highly selective enzymatic synthesis consisting of six, seven, or eight glucose monomers averaged in a donut shaped ring, which are denoted alpha, beta or gamma Cyclodextrin respectively. The specific coupling of the glucose monomers gives the Cyclodextrin a rigid conical molecular structure with a hollow interior of a specific volume. This internal cavity, which is hydrophobic in its nature, is a key structural feature of the Cyclodextrins, providing the ability to complex and contain a variety of “guest” molecules (e.g. ferromagnetic ions, etc.). The guests must satisfy the size criterion of fitting at least partially into the Cyclodextrin internal cavity, resulting in an **inclusion complex**. The Empirical Formula is $(C_6H_{10}O_5)_7$ and is basically a carbohydrate as shown in Figure 3.

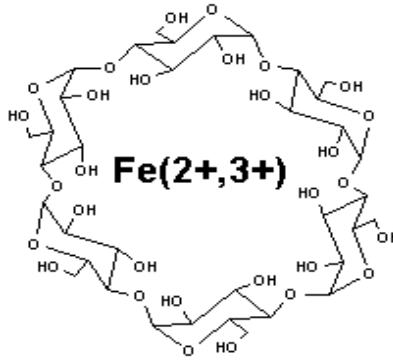


Figure 3. β -cyclodextrin with central hole which can filled with magnetic material¹⁵.

Table I shows the important parameters associated with the β -cyclodextrin used in this work. As can be seen, the size parameters fit very well with the size of the iron ion (1.17Å).

Table I: Important molecular parameters of β -Cyclodextrins (CD)

	b-CD	
glucose residues		7
molecular weight		1135
cavity diameter (Å)		6-6.6
cavity height (Å)		7.9
cavity volume (ml/mol)		262

Discussion

Procedure

A. General

The purpose of the process is to treat and polymerize a ferromagnetically modified cyclodextrin polymer and cast it into solid shapes for use in high-speed magnetic devices (inductors, transformers). This is done in aqueous solutions, with alcohol added as a dispersant.

B. Materials Needed

Substrates (alumina, printed circuit G-10, modified, ceramic-filled vinyl, and glass), FeCl₃, Beta Cyclodextrin, isopropyl alcohol.

C. The solution and polymerization

The solution is prepared by mixing 1 mole of FeCl₃

With 1 mole of β -cyclodextrin in an aqueous solution. By weight, the amounts are: 26.9 g FeCl₃, 16.2 g β -cyclodextrin, added to 50 g water. Alcohol is added, drop by drop, until the solution becomes homogeneous in appearance. The material is condensation polymerized by pouring onto the glass substrates and heating to 85° C until a thick film of the material is

formed. This material has a degree of polymerization (d.p.) of about 5000 and is capable of being thermally compression molded into shapes at 150 °C.

A electron photomicrograph of sample of the solution dried at 85 °C onto a glass substrate is shown in Figure 4. The voids are due to shrinkage and lack of wetting. This morphology differs, dependent on time at temperature.

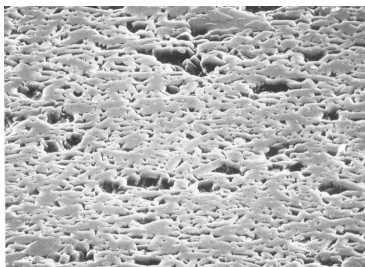


Figure 4. β -cyclodextrin:Fe condensation polymerized and baked at 85 °C on glass. 1000x.

The properties of the films as measured at 250MHz at room temperature were:

Resistivity : $>10^9$ ohm-m

Permeability (μ_r): 20-80

Loss tangent: $<10^{-3}$

Coils can be wound on the shapes fabricated and relative permeability can be deduced from the inductance measured on a non magnetic core of the same dimensions.

Conclusions (magnetic)

This process offers many advantages over conventional polymerization methods. The process is simple, low-cost, and effective. The materials used are not toxic, no special procedures need be used, and multiple applications can be made with great accuracy. The surface need not be a plane. Marking, drilling, and deposition can be done on a variety of substrate topologies. The polymer used must be non-hydrated, in order to avoid loss in the material at high frequencies due to water. Further studies are being performed on other metal/substrate systems with other polymer systems as well.

Luminescent Polymers

Introduction

Electroluminescent devices are showing promise for applications in future flat panel displays. Current flat panel display technology depends on inorganic light emitting diodes, backlit liquid crystal displays, and vacuum fluorescent displays with field electron emission onto phosphors. The problem for manufacturers lies in how to reduce the cost of illuminated displays, while increasing their capacity and efficiency. Organic/molecular films may hold the solution to this problem.

Observation of light emission has been observed in various polymers and copolymers of arylene vinylene, Polyphenylene vinylene (PPV) being the most efficient to date. However, a number of conjugated homopolymers, copolymers, and polymer blends have been investigated. These materials have light emission over the entire visible range.¹⁰⁻¹³ Though imbalances in the injection and carrier charge transport properties are partially responsible for low efficiencies in polymer light emitting devices, there is hope of overcoming these drawbacks with the use of

separate transport layers, electron withdrawing groups, and electron accepting additives and modifications. In addition to PPV, there are other materials which show promise. These are: poly (2,6-quinoline vinylene) (PQV), poly (phenylene vinylene-co-quinoline vinylene) (PPVQV), poly(p-pyridine) (PPP), poly(phenylene vinylene) (PPV), cyano-poly(phenylene vinylene) (CNPPV), and poly(2,3-diphenyl-5-hexyl-p-phenylene vinylene) (DP6-PPV). Two of these compounds are shown in Figure 5.¹⁴ A detailed description of electroluminescent polymeric materials and structures is given in reference 13.

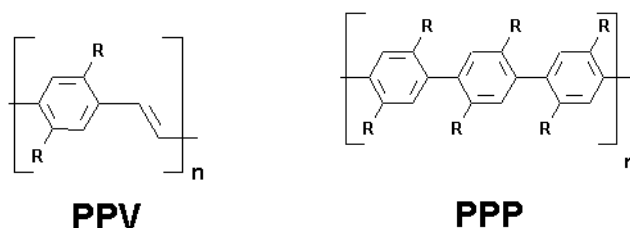


Figure 5. PPV and PPP¹³⁻¹⁵

Experiment 2. Making and testing luminescent polymers

Time: 2-4 hours, dependent on complexity.

Cost: \$25/student group

The experimental setup is shown in Figure 6. The transparent electrodes are the same as those shown in the experiment on Liquid Crystals (NEW Update 2000, ASEE 2002). The layers are spun onto the conductive glass using the solvents shown below. Electrodes may either be evaporated or “painted” on with conductive silver epoxy. Construction can also be of the AC variety as described in reference 14.

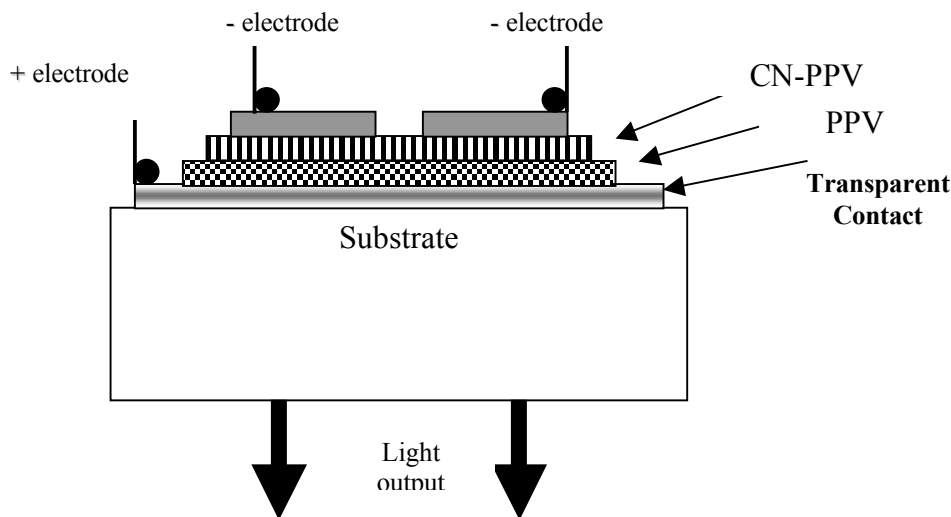


Figure 6. Light emitting polymer diode construction

Some materials which can be used are shown below.

Violet: Oxydodecyl poly(paraphenylene) (DDO-PPP)

- π -π * absorption band maximum at 340 nm
- PL band in the violet; 0-0 transition at 400 nm
- Soluble in toluene or THF for processing

Green: unsubstituted Poly(paraphenylenevinylene) (PPV)

- π - π * absorption band maximum at 400 nm
- PL band in the green; 0-0 transition at 520 nm
- Available as the precursor in aqueous solution for ease of processing

Red: Oxydodecylmethoxy-poly(paraphenylenevinylene) (DOO-PPV)

- π - π * absorption band maximum at 510 nm
- PL band in the red; 0-0 transition at 570 nm
- Soluble in toluene

The cyano-layer can be fashioned on any of these materials by adding potassium cyanide (1% solution) to the monomer. The cure cycle is 110 °C for 20 minutes. Measurements of current vs. voltage can be made and log I vs V can yield the activation energies and effective bandgap of the materials.

Conductive Polymers

The conductive and semiconductive polymers have properties which allow device, cost, and interconnection attributes not available with conventional inorganic materials¹⁶. It should be noted that there are no polymers based on carbon backbones that are intrinsically conductive to the extent of metallic or carbon/graphite loaded polymers. These polymers are usually made electrically conductive by adding either electron donors or acceptors to the host polymer, either by charge transfer complexes or dopant atoms (as in semiconductors)^{17,18}. Though silver and copper are, in reality, an order of magnitude higher than polyacetylene, the organic materials have certain electrical, electrochemical, and optical properties that make their use preferred. Some of the methods for making polymers conductive are shown in Figure 7. The proposed model for charge transfer is called percolation and is shown schematically as chain-like pathways for conduction.

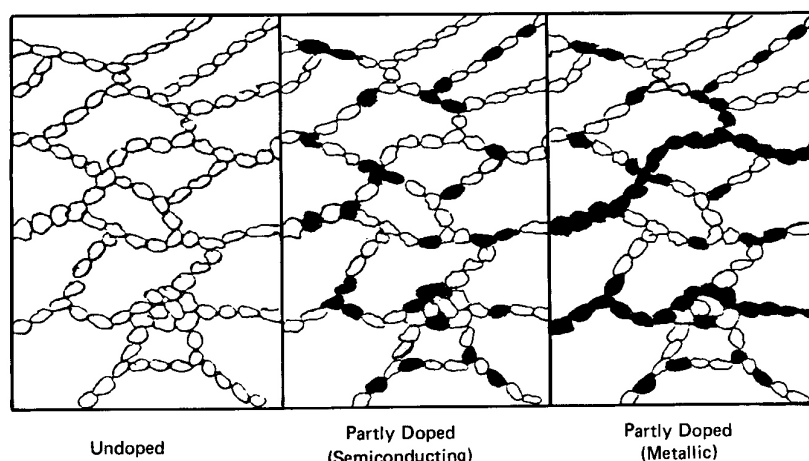


Figure 7. Percolation through polymers causing conduction¹⁶

A scanning electron micrograph of trans-polyacetylene is shown in reference 16. The chain-like structure is quite visible in SEM photos and supports, at least visually, the model of conductive pathways.

Some of the uses for these semiconductive and conductive polymers are: battery electrodes, polymer electrolytes for batteries, solar cells, compatible contacts for light emitting polymers, and high frequency window filters for microwaves, to name a few. Some of the conductive polymers presently in use are described in reference 16.

As newer materials are synthesized and new properties develop, applications will, as for most new materials, finally find uses for these emerging polymers.

Experiment 3: Fabricating conductive polymers

Time: 1.5-3 hours, dependent on complexity.

Cost: \$12/student group

Polyaniline (PANi)¹⁵

-Available as emeraldine hydrochloride or as emeraldine base. This experiment is extremely easy and simplistic, but it provides the student with a new vision of polymeric properties not given in a classical materials science class. This material is easily spun onto a conductive glass substrate or an insulative substrate. The graph of resistivity vs. $1/T$ should be made using either a 4-point probe or silver epoxy contacts. By using an ITO substrate and silver epoxy on the rear of the sandwich, a photovoltaic cell can be shown to give approximately 0.35 volts at 1 mA/10 sq. cm. Resistivities of these materials ranged from 0.1-10 Ω -m, dependent on baking temperature (80-125 °C). The activation energy measured (conductivity vs. $1/T$) for the samples ranged from 1-1.3 eV. PAN is probably the safest material to work with in the laboratory. Other conductive polymers that can be used are polyacetylene, polypyrrole, and certain cyanopolymers.

Conclusions (General)

The future of magnetic materials using molecular/organic substances as their basis will be dictated by the ability of scientists to find new materials or modifiers which force high, coupled electron spin densities into 1-, 2-, or 3-D network bonding using cooperative phenomena. The potential for modifying the physical properties through conventional organic synthesis techniques makes this class of materials very attractive to the magnetism community. The polymer light emitting devices are well on their way to impacting the industry as easily produced, low cost devices. They have the present drawback of having lifetimes shorter than those demanded by the telecommunications industries and the industry as a whole. The conductive and semiconductive polymers have properties that allow device, cost, electrochemical, electro-optic, electronic, and interconnection attributes not available with conventional inorganic materials. This may lead to their use in photonic, electronic, and magnetic devices to make lower cost, high performance telecommunications, electrical, and electronic systems. These experiments provide an introduction to students of materials science or engineering, in general, which can open pathways to materials selection previously unavailable in "classical materials science courses.

Acknowledgments

It is important to recognize the efforts of pioneering researchers and the efforts that they expended in bringing this science to the level mentioned in this overview. Drs. J. Miller and A. Epstein of Ohio State University have taken polymeric formulations and turned them into working devices, both magnetic and luminescent. Dr. A. Heeger of the University of Santa Barbara and Dr. A. McDiarmid of the University of Pennsylvania pioneered many of the early conductive polymer efforts, especially the advances in polyacetylene and other electrically active polymers. Dr. T. Skotheim has advanced the understanding of conjugated polymer structures and allowed many other efforts to be published through his comprehensive treatise on conducting polymers. For all of these and many more whose efforts have made a substantial difference, but are not mentioned here (including students who have performed these experiments), we are forever grateful.

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