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TITLE   ADVANCES IN INHERENTLY CONDUCTING POLYMERS

AUTHOR(S)   MAHMOUD ALDISSI, MST-7

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MASTER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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M. Aldissi

Los Alamos National Laboratory
P.O.Box 1663
Los Alamos, NM 87545

INTRODUCTION

Since their discovery, conducting polymers have generated an excitement about the possibility of combining some electronic and optical properties of semiconductors and metals with the attractive mechanical properties and processing possibilities of polymers. Polymers as plastic materials have numerous technological applications because of their low cost, lightness, and flexibility.

The main characteristic of a potentially conducting polymer is a conjugated backbone that can be subjected to oxidation/reduction by electron acceptors/donors resulting in a polycation/polyanion or what are frequently termed p-type/n-type doped materials. The conjugation of a polymer's backbone is necessary for conduction. This conjugation is also responsible for the environmental stability of most of these materials due to the high reactivity of the double bonds (or of the charge transfer complex obtained by doping) with oxygen, moisture, and light. Therein lies some of the research challenge.

The initial polymer systems were intractable and therefore, their characterization and a full understanding of their properties were difficult to obtain. It took a few years for progress to be made in that direction, resulting in the synthesis of a few solution-processable polymers. Most of the potentially conducting polymers possess an amorphous character with microstructures of various sizes and shapes and of a certain porosity that depends upon the nature of the polymer and its synthesis technique. The modification of the morphology of some of these materials toward a more ordered structure has been investigated, and earlier work showed that alignment of the polymer chains and their aggregates enhances the optical and electrical properties of the materials.

Processability, environmental stability and chair and/or aggregate orientation are the key elements in this discussion and will be explained based on recent and earlier work.

I. MATERIALS SURVEY

The initial polymer systems consisted of materials obtained by conventional techniques that had been known for a long time. A brief description of these earlier polymers and of the more recent ones is given in this section. Note that the material discussed here will be limited to organic polymers.

The polymer first discovered as a highly conductive material when doped is polyacetylene. The polymer is obtained in the cis and/or trans configuration as silvery cohesive films, of a fibrillar morphology, by Ziegler-Natta catalysis (1,2). Polyacetylene is known as the prototype material in this area of research. One attractive feature is that the polymer films can be stretched to form an anisotropic material (3).

The oxidative-coupling method (4) is one of the best methods to obtain a poly(p-phenylene), PPP, with a high molecular weight. The product consists of mostly uncrosslinked paralinkages. The powdery material can be annealed in an inert atmosphere up to 400°C for 24 hours, thus increasing its crystallinity by crosslinking toward a graphite-like structure. The annealing process results in an increase of the conductivity.

The first processable polymer known to be rendered conductive was poly(phenylenesulfide), PPS. The synthesis employed was generally step-growth condensation reactions (5). Films are prepared by melting the polymer powder (m_p = 270°C) or by casting it from a 10% solution in diphenylether at 220°C.

Electrochemical polymerisation (6) is a novel method of synthesis for some conducting polymers. The most-studied ones are polypyrroles and polythiophenes. Until recently, most highly conductive polymers obtained by using this technique were insoluble. The electrosynthesis of soluble conducting polymers of this type will be discussed in a subsequent section.

Another class of material of interest is that of ladder-chain polymers. They consist of mixed aromatic hetercocyclic backbones having rigid, planar, ladder-chain structures that are melt-processable. These materials are usually obtained by condensation polymerisations. Polyquinolines and polyquinoxalines are known examples of high-temperature polymers that could be rendered conductive (7).

Polyanilines (8-10) are examples of intrinsically conducting polymers that do not involve doping in the same way as do the other polymers. The polymer can be obtained in various forms and structures, the conductivity of which varies from the insulating regime to the conducting regime, depending upon the pH of the synthesis medium (11). Polyaniline can also be synthesised electrochemically in an aqueous medium that consists of 48% HBF_4.

II. ELECTRONIC STRUCTURE

A. Pristine (Undoped) Polymers

In order to understand transport in conducting polymers it is essential to examine their electronic structure in terms of band structure and excitations. Trans-polyacetylene is unique among conducting polymers in having a degenerate ground state (12), i.e., two geometric structures having the same energy. The two structures differ by the alternation of the single and double bonds. This degeneracy results in the formation of the neutral soliton excitation (radical) having a spin 1/2 that separates the two ground states (Fig. 1a) and can propagate freely on a one-dimensional basis along the chain (13,14). The ground state in polyaromatics is nondegenerate (15). The ground state corresponds to an aromatic structure with a single-like bond

between rings. The quinoid structure (Fig. 1b) has a much higher energy, and therefore, it is not possible to have a soliton in this type of polymer in the undoped state.

B.   Lightly Doped Polymers

Doping in polyacetylene means on the one hand that the neutral soliton is ionized, resulting in a spinless, negatively or positively charged soliton (16-18), i.e., polymeric anion (n-doping) or polymeric cation (p-doping), which corresponds to a localized electronic state near the midgap (Fig. 2). On the other hand, doping can be viewed as the formation of a polaron (Fig. 3a), which is a radical anion or a radical cation with a spin 1/2, as for neutral solitons (19-22). Two adjacent polarons can, however, recombine leaving two charged solitons on the chain (22). The result is a soliton band that is empty for p-doping or fully occupied for n-doping. Light doping in polyaromatics is believed to provoke a geometry relaxation toward the quinoid structure and the formation of radical ions (polarons), thus introducing two sub-gap states, one above the valence band edge and the other below the conduction band edge (23).

C.   Heavily Doped Polymers

In polyacetylene, the charge carriers can be viewed on the one hand as charged solitons that form a soliton band overlapping with the valence and conduction bands (13,17). This picture does not explain the carrier hopping between the chains. On the other hand, two charged solitons can form a soliton pair or a bipolaron that can hop between chains with a low activation barrier (23) (Fig. 3b). In polyaromatics, the two polaron states in the gap formed by light doping are pushed farther away from the band edges by further doping, resulting in the recombination of polarons to form bipolarons, which are spinless charge carriers (22,24). In conclusion, charged solitons (in trans-polyacetylene) or polarons (in polyaromatics) are viewed as radical ions which are the charge carriers in the lightly doped state. Bipolarons, however, seem to be the spinless entities responsible for transport in the metallic regime in the various systems.

III. MATERIALS PROPERTIES

A.   Electrical Conductivity

When conjugated polymers are doped with an electron acceptor or donor, their electrical conductivity increases by several orders of magnitude at low dopant concentrations. The conductivity increases by further doping until it reaches a maximum at the saturation level of doping. A semiconductor-to-metal transition is observed around 1-2 mol% of dopant for all doping species (25,26). The temperature dependence of conductivity is usually linear between the liquid nitrogen and room temperature except for very low levels where a slight curvature at low temperatures is observed due to doping inhomogeneities. The activation energy of conduction is of the order of few meV for highly conducting polymers.

B. Optical Absorption

1. Undoped Materials: The maximum absorption for cis-polyacetylene is at 2.0-2.1 eV and at 1.77 eV for the trans isomer. The latter is characteristic of a semiconductor and constitutes the perfect example of an infinite polyene. In its benzoid form, PPP has a much more localized π system than does polyacetylene (27). The bond connecting phenyl rings is close to that of a single bond, and the resulting band gap is about 3.5 eV. The linkage of the sulfur atom in PPS provides for a continuous overlap of orbitals along the chain. The band gap is similar to that of PPP (3.6 eV). Polythiophene and polypyrrole absorb at intermediary values of energy between polyacetylene and PPP. These polyheterocycles share the aromatic property with PPP and involve an extended D system similar to that of cis-polyacetylene. Note that the linkages between the heterocycles occur at the α-carbon positions (26). Their band gap is in the range 2.5-3.2 eV.

2. Doped Polymers: The evolution of the optical absorption of polyacetylene upon electrochemical doping (29) is shown at various stages [1-5] in Fig. 4. When cis-polyacetylene [1] is lightly doped [2], a decrease in the intensity of the interband transition is observed, and a new band that corresponds to the soliton is formed near the midgap, at approximately 0.7 eV. Further doping [3] results in a further decrease of intensity of the interband transition, and heavy doping [4] leads to an absorption characteristic of a metallic behavior due to the formation of a large band of charged soliton pairs or bipolarons. The spectrum of trans-polyacetylene [5] is obtained by undoping or by a thermal treatment of the cis structure. Optical absorption spectra for increasing doping levels in polypyrrole (Fig. 5) exhibit several absorption maxima that correspond to the various excitation states (30). For the almost fully reduced form, the maximum at 3.2 eV is characteristic of the interband transition. For low doping levels, the intensity of the interband transition (E_g) decreases and several bands appear that are characteristic of the sub-gap states (Fig. 6),

o   0.7 eV, valence band to lower polaron level, $\hbar\omega_1$
o   1.4 eV, lower to upper polaron level, $\hbar\omega_2$
o   2.1 eV, valence band to upper polaron level, $\hbar\omega_3$

At higher doping levels, the 1.4 eV band disappears indicating the recombination of polaron states to form bipolarons, as discussed earlier, and the interband transition disappears in favor of the bipolaron transitions (1.0 eV and 2.7 eV).

IV. PROCESSABILITY

A. Overview

Because of the rigid nature of their backbones, crosslinking, and the aggregated character of their morphology, processing of most of the initial undoped polymer systems was unsuccessful. For doped polymers, the difficulties were greater because doping causes further aggregation and certain local

geometry changes of the chain, i.e., chain relaxation to accommodate the formation of the charge transfer complex. The first processable, highly conductive polymer was PPS. When it is doped, it becomes intractable owing to structural changes (31). It was found later that only by doping the polymer in AsF_3 solution with AsF_5 could a blue solution of the doped polymer be formed (32). However, this technique was not successful with other polymers. Only by direct polymerisation (oxidative coupling) of acetylenic and aromatic monomers, using a similar combination of AsF_3 and AsF_5, could soluble polymers be obtained (33,34).

B.   Poly (3-alkylthiophenes)

Homopolymers of 3-alkylthiophenes have been prepared yielding highly conductive materials. It was found that the chemically prepared polymers become readily soluble in common organic solvents when the alkyl substituent is equal to or larger in size than butyl (35). The optical absorption spectra of the various polymers indicated that in spite of the large substituents, these polymers are highly conjugated. In fact, the maximum absorption is not shifted by varying the size of the alkyl group (~ 460 nm). Molecular weights in the range 3,000-8,000 were measured. Conductivities of 1-10 S/cm were obtained for the doped materials. High molecular weights (M_w ~ 40,000) were reported on the electrochemically prepared ones and conductivities ranging from 10 to 100 S/cm were measured on the doped materials (36). Optical absorption studies of poly (3-hexylthiophene) in its doped and undoped states showed that the electronic structure and the charge storage mechanisms are unchanged upon dissolution and are similar to those of polythiophene. The weak interchain interaction resulting from substitution of the thiophene ring by large alkyl groups and the high conductivity suggest that the electronic motion along the chain is predominant and therefore, conduction is anisotropic.

C.   Copolymer Systems

1)   Random Copolymers: Copolymers of acetylene and methylacetylene or phenylacetylene were synthesised. The materials were soluble below an acetylene mole fraction of 30% (37) or 25% (38) respectively, but at this point, their conductivity is very low. Later, synthesis of soluble random copolymers of alkylthiophenes was reported (38). For example, when a 1/1 mixture of 3-methylthiophene and 3-butylthiophene are copolymerised chemically, soluble materials are obtained and the molecular weight is approximately 35,000. Doping of the polymers in solution led to materials with conductivities of about 50 S/cm, measured on the solution-cast films.

2)   Graft Copolymers: The polymerisation of methyl methacrylate using sodium doped polyacetylene led to a graft copolymer with poly(methyl methacrylate) blocks grafted on polyacetylene chains (39). The process resulted in a small blue fraction soluble in THF. Other process that consisted of grafting polyacetylene chains onto either a polystyrene or polyisoprene chain (40), were reported to result in graft copolymers. No real proof for the

distinction between copolymers and a mixture of two homopolymers was reported. The determination of their physical properties was difficult owing to the impossibility of separating the excess of the initial homopolymer; therefore, no conductivity was reported.

3) <u>Block Copolymers</u>: Block copolymers have an advantage over other copolymers because the various steps in block copolymerisation can be controlled easily, and therefore the products can be tailored. Also, their properties can generally be predicted because block copolymers have properties close to the average weighted properties of their two components. The first diblock copolymer was that of styrene and acetylene in which the styrene component consisted of extremely long blocks, compared with those of polyacetylene, which,therefore, was insulating (41,42). A variety of polyacetylene copolymers were prepared by varying the nature and the concentration of the copolymer components as well as the experimental conditions of the reaction (43-45). As a result of the change in morphology when the composition of the copolymer is varied, the electrical conductivity of the doped materials is also varied. The electrical properties are strongly dependent upon the the relative amount of polyene segments. Conduction occurs by percolation with a threshold at approximately 16% volume fraction of polyacetylene.

4) <u>Alternating Copolymers</u>: The first alternating polymers to be synthesised are poly(arylpyrroles) (46). The difference between this type of monomer and pyrrole or thiophene is that the monomer structure of the former contains a higher π-electron density and therefore, the delocalisation of these electrons causes the polymerisation to occur easily, i.e., at a lower applied potential than needed for polypyrrole or polythiophene. One important feature of these polymers is their solubility in the organic medium in which they are prepared. Conductivities of the polymer films are in the range 1-10 S/cm.

D.   Precursor Polymers

     The synthesis of precursor polymers constitutes a neat route for the preparation of conducting polymers. The precursor systems of interest can be easily handeled in solution and purified to a high extent before they are converted to the intractable conjugated material. The first example was that of the Durham route to polyacetylene (47-49) which resulted in highly dense polyacetylene films. A variety of precursor homopolymers and copolymers were synthesised using this route and the reaction kinetics were studied for optimisation purposes of polyacetylene synthesis. Similarly, the synthesis of poly(phenylenevinylene) from its water-scluble sulfonium salt precursor polymers was reported (50,51). Conductivities of approximately 100 S/cm were measured on the doped polymer.

E.   Water-Soluble Conducting Polymers

     It was found recently that conducting polymers can be made water-soluble by attaching a surfactant or soap molecule to the structure of the polymer (35,53). In this process alkyl-

sulfonates and-carboxylates are substituents on the β carbon atom of a thiophene or a pyrrole monomer. The water-soluble polymers are synthesized chemically or electrochemically by known procedures. The dopant is covalently bonded to the chain. Therefore, intrinsic or self-doping occurs when a charge is ejected from the π system, leading to the formation of a charge transfer complex between the anion and the defect on the conjugated chain. Conductivities of about 10^{-2} S/cm are obtained for the various materials. The conductivity can be increased by doping the polymers, up to 10^2 S/cm, with oxidizing agents such as AsF_5 or H_2SO_4. When the alkyl chain length (m) is in the range 10-20, a liquid crystalline polymer is obtained in the lyotropic phase (52). Therefore, by combining liquid crystalline properties and conductivity in conjugated polymers, a new class of polymers is born which presents a real challenge in this area of research.

F.   Use of Surfactants and Lattices in Polymerization

Surfactant anions, such as alkylsulfate and alkysulfonate electrolytes were used in the anodic oxidation of pyrrole (54). This led to the formation of air-stable and more flexible insoluble films of polymer. This technique was extended to the use of polymeric anions in the electropolymerization, in the form of lattices such as acrylates, methacrylates, etc. (55). The conductivities of these samples are in the range 10^{-3}-5 S/cm for polypyrrole contents in the range 3-30%. Coatings can be made by dipping, spin coating, and spraying. Optical transmission of 55-60% in the uv-visible region is obtained, and the material has the appearance of a grey filter and seems to have the appropriate characteristics of an antistatic material.

V. STABILITY

A.   Overview

Stability has been an important issue in the research on conducting polymers and one of the major drawbacks toward their use in technological applications. Some of the pristine, undoped polymers are air-stable, but for the doped polymers, stability is a more complex issue because it involves an additional parameter, which is the nature of the charge transfer complex formed by doping. In general, n-type polymers are very reactive in air and p-type polymers are relatively more stable. Several stabilization techniques have been used, and some of them are described briefly here.

B.   Use of special dopants

When polypyrrole is synthesized electrochemically using p-toluenesulfonate and similar salts, it remains stable in air for several years (56). The reactivity of n-type polymers in air can be decreased by use of complexing agents. When the appropriate crown ether is added to an n-type dopant such as $Npht^-Na^+$ (Npht = naphthalene) in THF, a stable complex is formed with the alkali metal. When polyacetylene or other polymers are immersed in such a solution, the polymer is doped with the alkali

metal complex and the stability of the resulting material is enhanced (57). The choice of the crown ether depends upon the size of the alkali metal.

C.   Use of Antioxidants

The role of antioxidants is that of a free-radical scavenger such as that coming from oxygen or from radical species formed by oxidation of the polymer. Use of certain antioxidants such as substituted phenols and quinones was examined with polyacetylene (45a,58). The results indicated that the induction period is lengthened up to a year with a gradual conductivity loss.

D.   Encapsulation

Because oxidation is a diffusion-controlled process, the choice of the protecting material is crucial. For example, PVC is known to be one of the best oxygen barriers among conventional polymers, and its use with conducting polymers such as polyacetylene proved to be effective (45b). Other good oxygen barriers are coated on conducting polymers by vacuum deposition. A good example is the use of fluorinated parylene, which is an excellent oxygen barrier (59). The film's flexibility stays intact with no measurable conductivity loss.

E.   Stabilization Effect of Multicomponent Systems

Composites can be obtained by electrochemical polymerization of, for example, pyrrole onto a platinum electrode coated with a few-micron-thick film of PVC (60,61). The polymerization time determines the extent of mixing of the two polymers. In general, a few minutes of polymerization results in a surface coating of polyvinylchloride, which leads to the possibility of making conducting patterns on an insulating flexible substrate (62). The composite material obtained when long polymerization times are used exhibits an enhanced stability compared with polypyrrole.

The results on doped diblock polyisoprene/polyacetylene copolymers showed that the materials were less stable than polyacetylene, the homopolymer (45). This was explained by the decrease in the chain-chain interaction, which is an important stability parameter of the polymer structure. In another example, the copolymerization of methyl- and butyl-substituted thiophenes yielded a stable material in the doped state (35).

When doped polyacetylene is used as the anode in the electrosynthesis of polypyrrole (63,64) or polyaniline (49a), composites can be formed if the electrolyte/monomer mixture is allowed to diffuse completely in the bulk of polyacetylene film. Polypyrrole or polyaniline, which are relatively more stable in their conducting form than polyacetylene add to the latter an improved but not long-term stability.

VI. MOLECULAR AND SUPRAMOLECULAR ORIENTATION

Intrinsic anisotropy in the optical and electrical properties of conducting polymers has been one of the important aspects in this area of research. Anisotropy in these systems results from the existence of an extended π system on parallel

chains and a weak interchain interaction. Several techniques have been applied to obtain oriented polymers with success.

Stretch-alignment of a polyacetylene film to a maximum of three times its original length resulted in a modest optical and electrical anisotropy ($\sigma_{\parallel}/\sigma_{\perp} \approx 3-5$) (3). The stretch-orientation was improved later by improving the synthesizing method and the highest parallel conductivity resulting from that process was 1.5×10^5 S/cm, which is only five times less than that of copper (65). With a perpendicular conductivity of 100 S/cm, this constitutes the highest electrical anisotropy ever obtained. The resulting material is highly dense and consists of almost perfectly aligned fibrils.

Although the Durham technique for the synthesis of oriented polyacetylene yielded a highly oriented material by stretch-alignment of the precursor polymer, the highest conductivity reached at an ultimate draw ratio of 20 is comparable to that of the initial stretch-aligned Ziegler-Natta polyacetylene. However, the material exhibited a high optical anisotropy (66-68). A similar technique was used to synthesize highly oriented poly(phenylenevinylene). The electrical anisotropy was 100 at a draw ratio of 10 with a parallel conductivity of approximately 2.8×10^3 S/cm (50,51).

The polymerization of acetylene in a liquid crystal medium has become an area of interest. The first polymerization attempt was made using N(p-methoxybenzylidine)p-butylaniline which has a nematic range of 19-30°C in a magnetic field of ≥ 2.5 kgauss (69). The polymerization of acetylene using a catalyst concentration of 0.1 mol/l of Ziegler-Natta catalyst was carried out under a magnetic field of 4 kgauss. In these conditions, the liquid crystal molecules are oriented with respect to an externally defined axis and the dissolved catalyst is expected to be oriented in the same direction. This process resulted in a noncrosslinked material with an electrical anisotropy of more than 4. The liquid crystal alignment is generally affected by its purity and therefore, the amount of the catalyst was crucial to the alignment process. When the relative volume ratio of the catalyst to the solvent is kept under 10%, improved anisotropy is obtained. In fact, parallel conductivities higher than 1×10^4 S/cm are obtained when the oriented polymer is doped with AsF_5. Other experiments followed using 4-(trans-4-n-propylcyclohexyl)-ethoxy-benzene or -butoxybenzene as the nematic liquid crystal (70). Similar anisotropy was obtained. In other experiments (71), when the same two solvents were used for the polymerization of acetylene under a flow of the nematic catalyst solution in the absence of a magnetic field an oriented polymer resulted with electrical anisotropy and conductivities lower than those mentioned above for the polymers obtained under a magnetic field.

VII. APPLICATION AREAS

The electronic behavior of conducting organic polymers could be utilized in many ways in a wide range of conductivities. The potential application areas include organic conductors and semiconductors, elements in integrated electronic circuits, information storage systems, temperature sensors, gas and irradiation detectors, pressure indicators, rectifiers and electrochromic display devices. Electrochemistry and photoelec-

trochemistry are potential areas of interest, particularly for battery and fuel cell applications. Also, conducting polymers can be of use for static charge dissipation and electromagnetic interference shielding. A few examples are discussed below.

A. Heterojunctions

Several configurations can be envisioned for their utilization in junction devices:

1) Heterojunctions formed at the interface between an undoped polymer and an inorganic semiconductor. High band gap inorganic semiconductors were used (CdS, ZnS) with polyacetylene films (72,73). The cell is illuminated through the inorganic layer and most of the incident light is absorbed within the polymer layer. High V_{oc} is obtained but the photocurrent is poor due to the high series resistance of both components and recombination rate. A power efficiency of 1% was reported. Thin layers of poly(3-methylthiophene) deposited on n-GaAs with a thin gold layer to form ohmic contacts resulted in junctions with better characteristics (74). A power efficiency of 3.5% is obtained due to light absorption within the GaAs layer.

2) Schottky diodes in which the doped polymer acts as a metallic layer. Examples include polypyrrole on n-Si (75) and polyacetylene on CdS (72,73). Due to the high series resistance of the semiconductor the efficiencies were low.

3) Schottky diodes with the undoped polymer acting as a p-type semiconductor on which a metallic layer is deposited. Cells of this type with poor efficiencies were reported for polyacetylene (76) and poly(3-methylthiophene) (77).

A disadvantage of the various configurations is the high recombination rate that limits the collection efficiency of photogenerated electrons and holes.

B. Electrochromic Display Devices

The electrochromic effect in conducting polymers is the result of the change in the optical absorption coefficient in the visible range upon doping. This is generally accompanied by a color change. Polyheterocycles are good examples for the illustration of this process. The switching operation consists of a doping-undoping cycle under a monochromatic light such as a laser. Several polythiophenes and polypyrroles showed good switching characteristics (78). In the case of polypyrrole this cycle can be repeated up to 10^4 times in several tens of milliseconds for each cycle. The same device could be used as a memory element because the color and the conductivity of the polymer in each state remains the same for a long time.

C. Shielding Against Electromagnetic Interference

Some conducting polymers which combine the lightness and flexibility of plastics and the high conductivities of metals could offer the solution to problems of grounding, static dissipation and shielding against electromagnetic interference (EMI). The search for shielding materials continues as more and more noise fills the air. Conductive coatings on plastics housings and incorporation of conductive fillers in the resin are

two methods of en used. Shielding effectiveness and frequency range determine the methods and configuration of the shield. Very few tests have been performed in determining the shielding effectiveness of inherently conducting polymers. Examples of conducting polymers used in such tests are polyacetylene and polypyrrole. The preliminary tests indicate that the polymers act as shielding materials in both the RF and MW frequency ranges but with a lower effectiveness than conventional conductive coatings.

D. Electrochemistry

A variety of conducting polymers have been investigated for their possible use in secondary batteries. The most widely studied polymers are polyacetylene (79,80), poly(p-phenylene) (81), polypyrrole (82) and polyaniline (11). In general, conducting polymers can be oxidized or reduced electrochemically to form p-type or n-type materials suited for use as cathodes or anodes respectively. The power and energy densities obtained for the various systems are comparable or, in some cases, higher than commercially available systems.

CONCLUSIONS

The discovery of polyacetylene as the prototype material led to extensive research on its synythesis and characterization. The techniques that emerged as the most important and promising ones are those that dealt with molecular orientation and that resulted in conductivities almost as high as that of copper. The study of dozens of other materials followed. Interest in conducting polymers stems from their nonclassical optical and electronic properties as well as their potential technological applications. However, some of the factors currently limiting their use are the lack of long-term stability and the need to develop conventional low-cost techniques for easy processing. Therefore, research was extended toward solving these problems, and progress has been recently made in that direction. The synthesis of new materials such as stable and easily processable alkylthiophenes, water-soluble polymers, and multicomponent systems, including copolymers and composites, constitutes an important step forward in the area of synthetic metals. However, a full understanding of materials chemistry and properties requires more work in the years to come. Although, few small-scale applications have proven to be successful, long-term stability and applicability tests are needed before their commercial use becomes reality.

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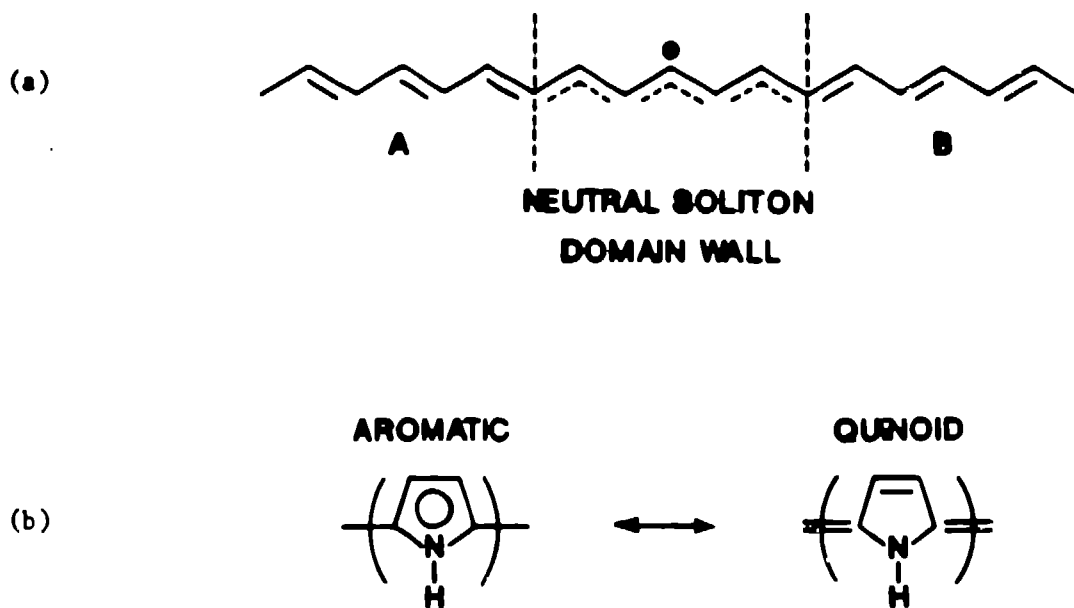
FIGURE CAPTIONS

Fig.1   Degenerate ground states and soliton representation in trans-polyacetylene (a) and nondegenerate ground states in polyaromatics (b).
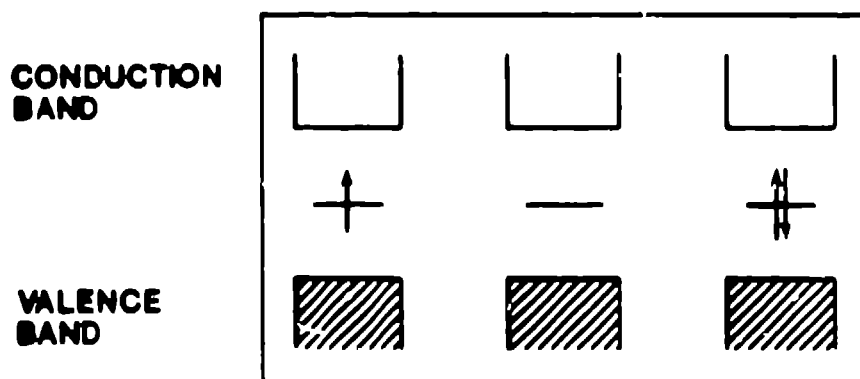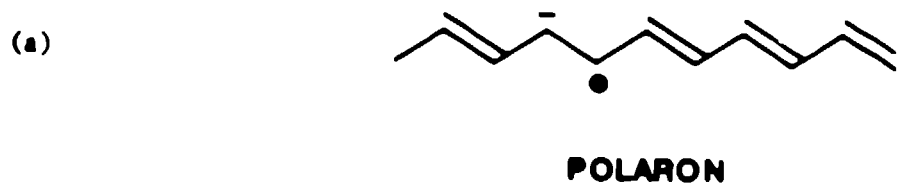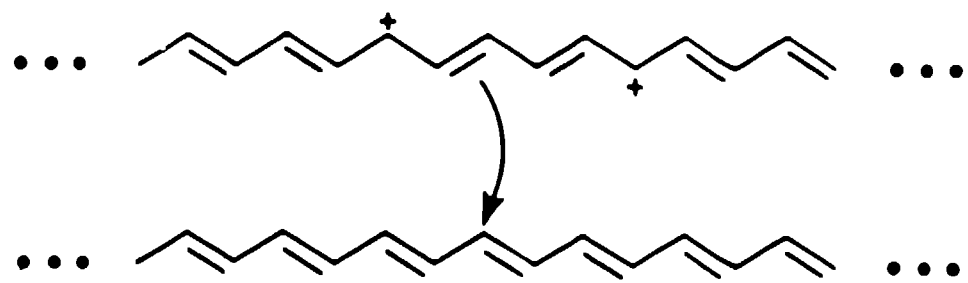
Fig. 2   Band structure of polyacetylene containing a soliton: neutral (left), positively charged (middle), and negatively charged (right).
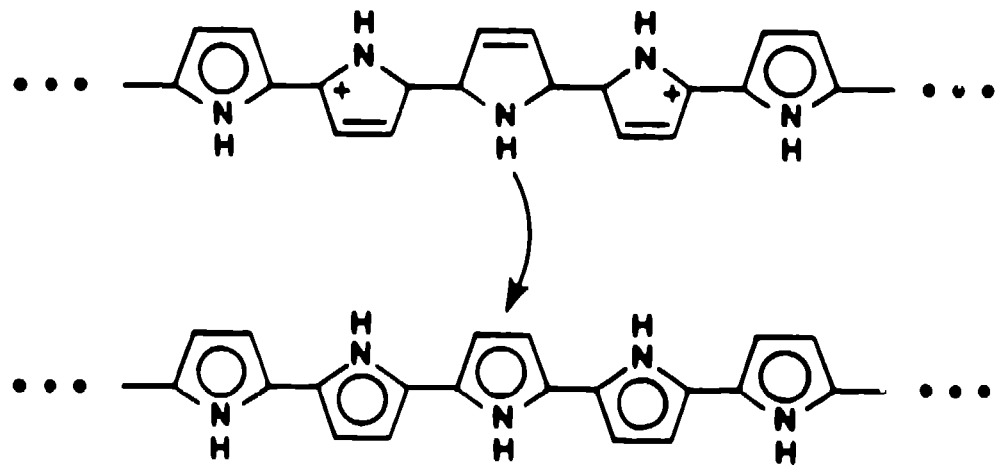
Fig. 3   Representation of a polaron on a trans-polyacetylene chain (a) and of bipolaron hopping (b).

Fig. 4   Optical absorption spectra of cis-polyacetylene (1), increasing doping levels (2, 3, and 4) and of trans-polyacetylene (5).

(a)

NEUTRAL SOLITON

DOMAIN WALL

AROMATIC   QUINOID

(b)

Fig. 1: Degenerate ground states and soliton representation in
trans-polyacetylene (a) and nondegenerate ground states
in polyaromatics (b).

CONDUCTION
BAND

VALENCE
BAND

Fig. 2: Band structure of polyacetylene containing a soliton:
neutral (left), positively charged (middle), and
negatively charged (right).

(a)

POLARON

(b) **POLYACETYLENE**

POLYPYRROLE

Fig. 3: Representation of a polaron on a trans-polyacetylene chain (a)
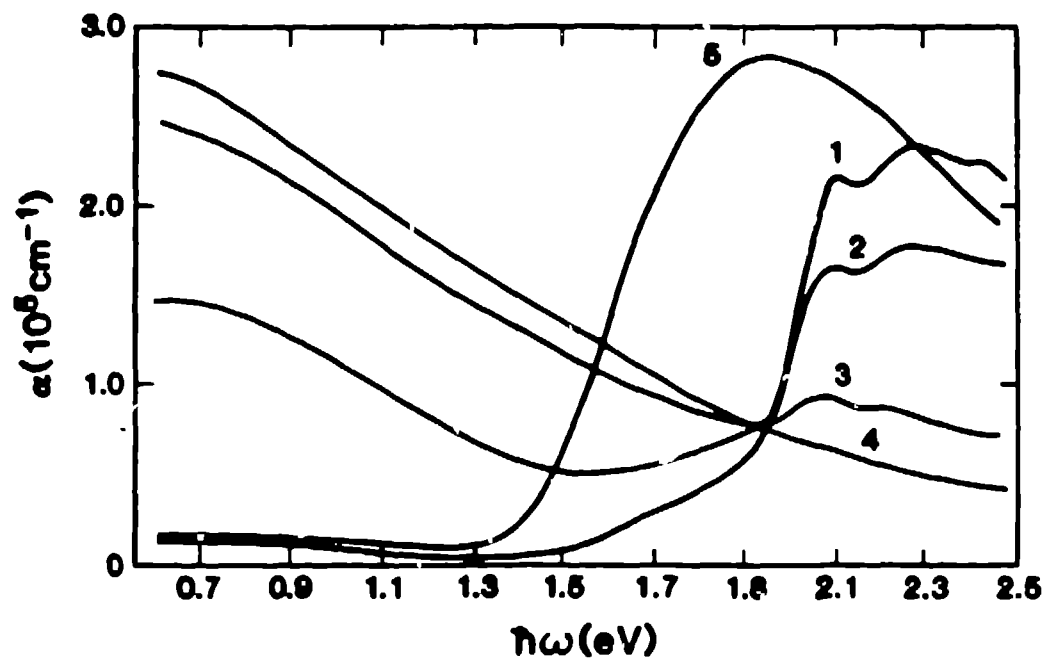and of bipolaron hopping (b).

Fig. 4: Optical absorption spectra of cis-polyacetylene [1],
increasing doping levels [2-4], and of trans-polyacetylene [5].
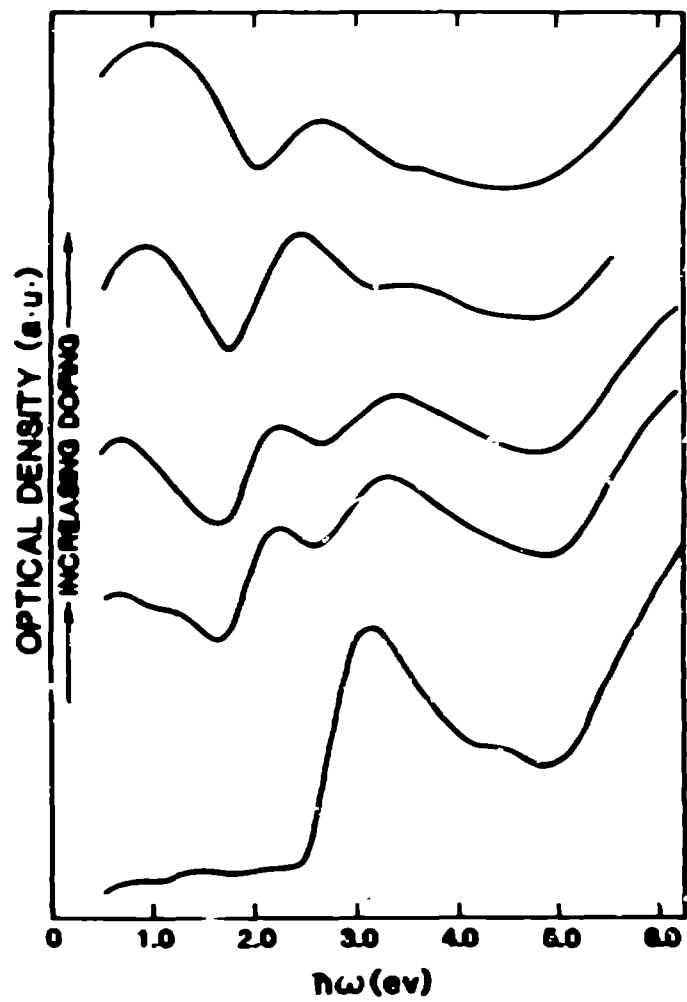
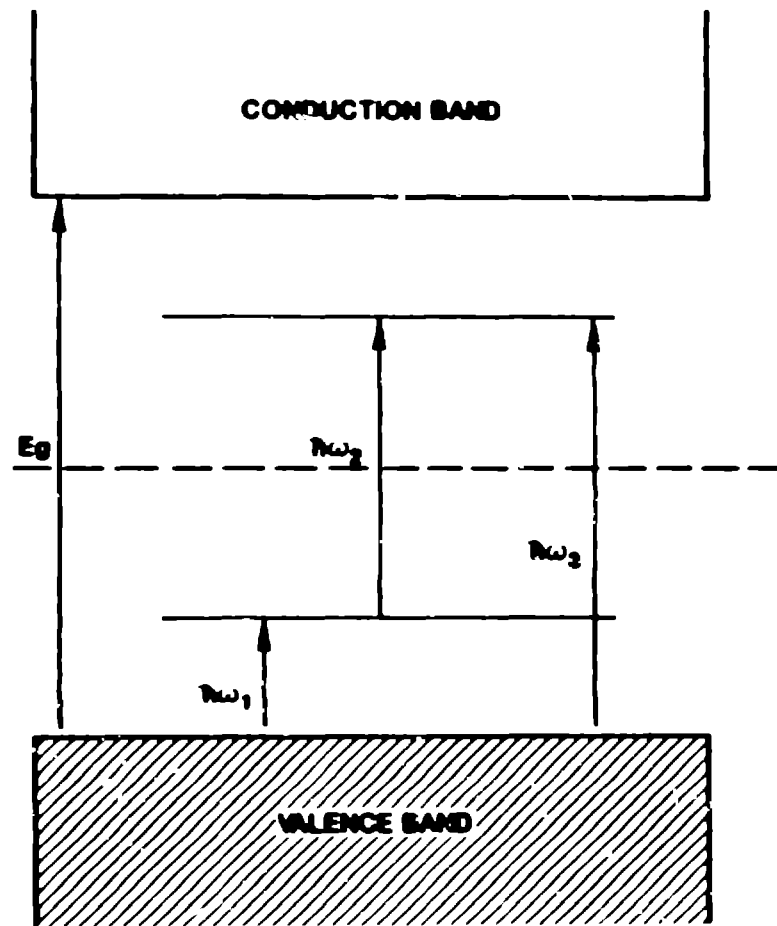Fig. 5: Optical absirption spectra for various
        doping levels of polypyrrole.

Fig. 6: Sub-gap states in polyaromatics.