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"SCIENCE AND TECHNOLOGY OF CONDUCTING POLYMERS"

by

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SCIENCE AND TECHNOLOGY OF CONDUCTING POLYMERS

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ABSTRACT

The applicability of the concept of "doping" is the unifying theme which distinguishes a certain class of organic polymers - "conducting polymers" - from all others. Doping results in dramatic electronic and magnetic changes with a concomitant increase in conductivity to, or approaching, the metallic regime. Doping phenomena and the chief types of dopable organic polymers are described with particular emphasis on polyaniline which is presently being commercialized on a relatively large scale and is the leading conducting polymer for technology, although closely followed by polythiophene derivatives. Polyaniline shows considerable promise for electromagnetic interference (EMI) shielding and is already used in commercial rechargeable batteries. Leading potential technological applications utilize polyaniline film membranes for gas separations and polyphenylenevinylenes as light-emitting diodes. Additional potential applications of conducting polymers such as electrochromic windows, redox capacitors, chemical sensors, etc. are also described briefly.

INTRODUCTION

An intrinsically conducting polymer (ICP), more commonly known as a "synthetic metal," is an organic polymer that possesses the electrical, electronic, magnetic and optical properties of a metal while retaining the mechanical properties, processibility, etc., commonly associated with a conventional polymer,[1]. These properties are intrinsic to the doped material. This class of polymer is completely different from "conducting polymers" which are merely a physical mixture of a non-conductive polymer with a conducting material such as metal or carbon powder. They are synthesized by "doping" an organic polymer, either an insulator or semiconductor, having a small conductivity, typically in the range 10^{-10} to 10^{-5} S/cm, to a material which is in the "metallic" conducting range (~1 to 10^4

S/cm). The concept of doping is the unique, central, underlying and unifying theme which distinguishes conducting polymers from all other types of polymers. The controlled addition of known, small (≤ 10%) non-stoichiometric quantities of chemical species results in dramatic changes in the electronic, electrical, magnetic, optical and structural properties of the polymer. Doping is reversible to produce the original polymer with little or no degradation of the polymer back-bone. Both doping and undoping may be carried out chemically or electrochemically. By controllably adjusting the doping level, a conductivity anywhere between that of the undoped (insulating or semiconducting) and that of the fully doped (highly conducting) form of the polymer may be easily obtained. Conducting blends of a (doped) conducting polymer with a conventional polymer (insulator) whose conductivity can be adjusted by varying the relative proportions of each polymer can be made. This permits the optimization of the best properties of each type of polymer.

The "classical" method of doping involves the redox doping, i. e. chemical or electrochemical partial oxidation ("p-doping"), or partial reduction ("n-doping") of the π backbone of the polymer,1. More recently, non-redox doping which neither adds nor removes electrons from the polymer backbone has been discovered.

Since the initial discovery in 1977,2 that polyacetylene, $(CH)_x$, now commonly known as the prototype conducting polymer, could be p- or n-doped, either chemically or electrochemically to the metallic state, the development of the field of conducting polymers has continued to accelerate at an unexpectedly rapid rate. This rapid growth rate has been stimulated not only by the field's fundamental synthetic novelty and importance to a cross-disciplinary section of investigators - chemists, electrochemists, experimental and theoretical physicists and electronic and electrical engineers - but to its actual and potential technological applications.

In the "doped" state, the backbone of a conducting polymer consists of a delocalized π system. In the undoped state, the polymer may have a conjugated backbone such as in trans-$(CH)_x$, which is retained in a modified form after doping, or it may have a non-conjugated backbone, as in polyaniline, (leucoemeraldine base form), which becomes conjugated only after p-doping. More recently it has been observed that a form of polyaniline (emeraldine base) can be doped by a non-redox process,3. This is accomplished by simply protonating the imine nitrogen atoms of the polymer to produce a polysemiquinone radical cation in which both charge and spin are delocalized along the polymer backbone. Protonic acid doping has subsequently been extended to systems such as poly(heteroaromatic vinylenes),4.

For several years after their discovery conducting polymers were regarded as materials whose properties were "answers waiting for the correct question" in so far as technological applications were concerned! This is, however, no longer the case as will be described in a later section. Technological applications may be divided into two classes - (i) that in which a conducting polymer is presently used in, and sold for a given purpose, and (ii) that in which it is not presently being used and sold but which has technological potential ranging from very high to the more exotic cases, where specific applications, if any, may be in the distant future. Some of these will be described in a later section.

At the present time polyaniline is without doubt the most important conducting polymer from the point of view of large scale technological use; however, derivatives of polythiophene and poly(phenylenevinylene) and indeed, polypyrrole, polyacetylene and polyparaphenylene show considerable technological promise as specialty polymers, as described later.

The polyanilines are probably the most rapidly growing class of conducting polymers as can be seen from the number of papers and patents published (1237) during the last five years, viz., 1986 (108); 1987 (221); 1988 (236); (1989 (383); and 1990 (289) (to June 3, 1991),5. These figures are due in large part to the very considerable industrial interest in polyaniline. This is highlighted by the 1987 manufacture and sales of novel rechargeable batteries by Bridgestone Corp. (Japan) based on polyaniline,6. In February of 1990 Lockheed Corp. (USA) and Hexcel Corp. (USA) announced a joint venture to manufacture polyaniline and its blends with conventional polymers. This was followed in April, 1991,[7,8] with an announcement by Neste Oy (Finland) of the start-up of pilot plant production of polyaniline and polythiophene derivatives to support application development of conducting polymers. In the same month Uniax Corp. (USA) and Neste Oy reported a joint venture for research and development of polythiophenes and polyanilines,[7,8]. In the following month Allied-Signal Inc. (USA), Americhem Corp. (USA) and Zipperling Kessler and Co. (Germany),[9] announced a joint venture to manufacture large quantities of polyaniline and its blends with conventional polymers such as polyvinylchloride and the Nylons, especially for use in electromagnetic interference shielding. Large quantities of these materials are currently available from these companies. In view of the technological importance of polyaniline, its synthesis and properties will be emphasized in this review.

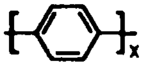
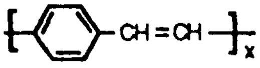
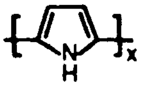
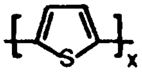
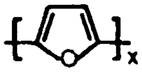
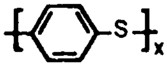
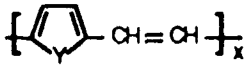
TYPES OF CONDUCTING POLYMERS

Following the discovery of the doping of both cis- and trans-$(CH)_x$,[2], other polymer systems (Table I), such as polyparaphenylene, poly(phenylenevinylene), polypyrrole, polythiophene, polyfuran, etc., and their ring- and N-substituted derivatives were found to undergo redox p-doping and/or n-doping,[1]. Polyphenylene sulfide upon doping with AsF_5 undergoes a chemical reaction to give a doped derivative of polythiophene,[1]. These discoveries were followed by the synthesis of dopable systems involving poly(heterocycle)vinylenes where Y = NH, NR, S and O which proved to be of very great importance to the whole field since, for the first time, they provided processible conducting polymers, some in the doped form, by virtue of their solubility in a number of different organic solvents; furthermore, several of them showed most promising environmental stability in the doped form,[1].

A number of other redox-dopable conducting polymer systems are also known such as those made by doping covalently-linked siloxane-phthalocyanine complexes, $[Si(Pc)O]_x$, but the above systems and their derivatives have been the most extensively investigated,[1].

Although "polyaniline" has been known for about 150 years, it was not until the mid-1980's that intense interest in it and its derivatives, as a completely different type of conducting polymer, really began,[1]. This resulted not only from its ease of synthesis and derivatization, but also from its novel non-redox doping properties and from its potential technological importance.

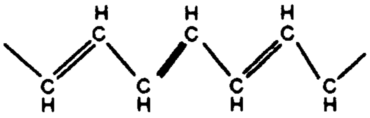
Table I. Selected Examples of Redox Dopable Organic Polymers.

Polyparaphenylene	
Poly(phenylenevinylene)	
Polypyrrole	
Polythiophene	
Polyfuran	
Polyphenylene sulfide	
Poly(heterocycle)vinylenes	

REDOX DOPING

Trans-$(CH)_x$, the most extensively investigated conducting polymer, is representative, in a broad sense, of all those conducting polymers which are dopable by redox processes,[1,2]. Its chief features will therefore be outlined below.

Free-standing films of cis-$(CH)_x$ can be synthesized from gaseous acetylene at -78°C in the presence of a $Al(C_2H_5)_3/Ti(OC_4H_9)_4$ catalyst and can subsequently be isomerized at ~150°C to yield lustrous, silvery, films of the more thermodynamically stable trans-$(CH)_x$,



The bonding π system of the polymer can be readily partially oxidized, "p-doped" by a variety of reagents such as iodine vapor or a solution of iodine in CCl_4, e.g.,

$$[\mathrm{CH}]_x + 1.5(xy)\mathrm{I}_2 \longrightarrow [\mathrm{CH}^{+y}(\mathrm{I}_3)^-_y]_x \qquad (y \leq \sim 0.07) \qquad (1)$$

with a concomitant increase in conductivity from $\sim 10^{-5}$ S/cm to $\sim 10^3$ S/cm. If the polymer is stretch-oriented 5 to 6 fold before doping, conductives parallel to the direction of stretching up to $\sim 10^5$ S/cm can be obtained,[1].

Analogously, the polymer backbone can be partially reduced, "n-doped" by, for example, a solution of sodium naphthalide, in THF, viz.,

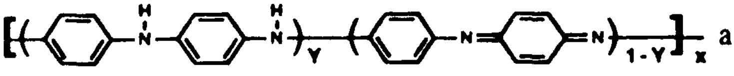
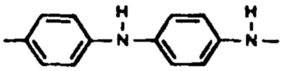
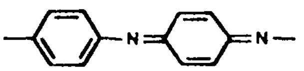
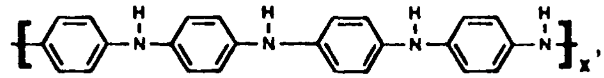
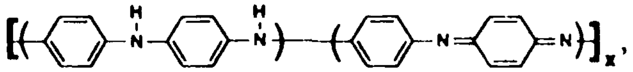
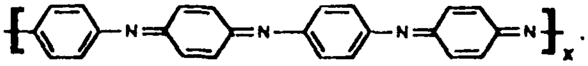
$$[\mathrm{CH}]_x + (xy)\mathrm{Na}^+(\mathrm{Nphth})^- \longrightarrow [\mathrm{Na}^+_y(\mathrm{CH})^{-y}]_x \qquad (y \leq \sim 0.1) \qquad (2)$$

with a very large increase in conductivity although values as large as those reported for iodine p-doping have not been obtained. The antibonding π^* system is partially populated by this process.

THE POLYANILINES

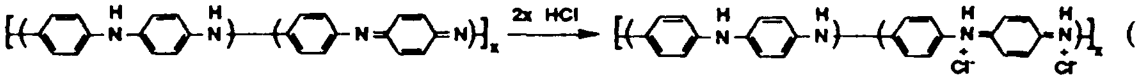
The polyanilines,[3] refer to a large class of conducting polymers which exist in three different discrete oxidation states at the molecular level, both in their doped and undoped forms. Physical mixtures of these oxidation states are also readily obtained. One of these discrete oxidation states can be doped by a non-redox process which neither adds nor removes electrons from the polymer π backbone. Until very recently, it was unique amongst all conducting polymers when similar effects, which have not yet been fully investigated, were discovered for some of the poly(hetrocyclovinylenes),[4]. The reduced form of polyaniline can also be doped by a conventional oxidation process,[3].

The interest in this conducting polymer stems from the fact that many different ring- and nitrogen- substituted derivatives can be readily synthesized and that each derivative can exist in a number of different average oxidation states (composed of the three discrete oxidation states) which can in principle be "doped" by a variety of different dopants either by non-redox processes or by partial chemical or electrochemical oxidation,[3]. These properties, combined with the relative low cost of several polyanilines, their ease of processing and satisfactory environmental stability indicate strongly their significant potential technological applicability.

The polyanilines refer to a class of polymers which can be considered as being derived from a polymer, the base form of which has the generalized composition:  and which consists of alternating reduced,  and oxidized,  repeat units,[3,10,11]. The average oxidation state, (1-y) can be varied continuously from zero to give the completely reduced polymer, , to 0.5 to give the "half-oxidized" polymer, , to one to give the completely oxidized polymer, . The terms "leucoemeraldine", "emeraldine" and "pernigraniline" refer to the three different discrete oxidation states at the molecular level where (1-y) = 0, 0.5 and 1 respectively, either in the base form, e.g. emeraldine base or in the protonated salt form, e.g. emeraldine hydrochloride,[3,10,11]. In principle, the imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts, the degree of protonation of the polymeric base depending on its oxidation state and on the pH of the aqueous acid. Complete protonation of the imine nitrogen atoms in emeraldine base by, e.g. aqueous HCl, results in the formation of a delocalized polysemiquinone radical cation,[3,11,12] and is accompanied by an increase in conductivity of ~10^{10}.

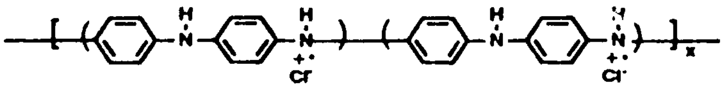
The partly protonated emeraldine hydrochloride salt can be synthesized easily as a partly crystalline black-green precipitate by the oxidative polymerization of aniline, $(C_6H_5)NH_2$, in aqueous acid media by a variety of oxidizing agents, the most commonly used being ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, in aqueous HCl,[3,10-12]. It can also be synthesized electrochemically from aniline,[3]. It can be deprotonated by aqueous ammonium hydroxide to give an essentially amorphous black-blue "as-synthesized" emeraldine base powder with a coppery, metallic glint having an oxidation state as determined by volumetric $TiCl_3$ titration corresponding approximately to that of the ideal emeraldine oxidation state,[13]. The ^{13}C ,[14] and ^{15}N NMR ,[15] spectra of emeraldine base are consistent with its being composed principally of alternating oxidized and reduced repeat units.

The emeraldine base form of polyaniline was the first well established example,[3,11,16-18] of the "doping" of an organic polymer to a highly conducting regime by a process in which the number of electrons associated with the polymer remain unchanged during the doping process. This was accomplished by treating emeraldine base with aqueous protonic acids and is accompanied by a 9 to 10 order of magnitude increase in conductivity (to 1 - 5 S/cm; 4 probe; compressed powder pellet) reaching a maximum in ~1M aqueous HCl with the formation of the fully protonated emeraldine hydrochloride salt, viz.,



(3)

If the fully protonated i.e. ~50% protonated emeraldine base should have the above dication i.e. bipolaron constitution as shown in equation 3, it would be diamagnetic. However, extensive magnetic studies,[3,19] have shown that it is strongly paramagnetic and that its Pauli (temperature independent) magnetic susceptibility increases linearly with the extent of protonation. These observations and other earlier studies,[11,16-18] show that the protonated polymer is a polysemiquinone radical cation, one resonance form consisting of two separated polarons:



It can be seen from the alternative resonance form where the charge and spin are placed on the other set of nitrogen atoms that the overall structure is expected to have extensive spin and charge delocalization resulting in a half-filled polaron conduction band.

Molecular Weight of Polyaniline

As-synthesized,[12] emeraldine base in NMP solution, containing 5 wt.% LiCl exhibits a monomodal symmetrical molecular weight distribution curve by G.P.C. The monomodal symmetrical peak obtained,gives values of M_p = 38,000, M_w = 78,000 and M_n = 26,000; polydispersity, M_w/M_n = ~3.0. Recent light scattering results, which give absolute M_w values, show that M_w values obtained from G.P.C. studies vs. polystyrene standard are approximately double the correct value. In one study a solution of emeraldine base in NMP/LiCl was passed through a preparative G.P.C. column and six separate fractions were collected, the lowest molecular weight fraction ($M_p < 5000$) being discarded, since in a separate study it was shown that it contained oxygen-containing impurities,[20]. Each of the six fractions (Table II) were shown to be pure emeraldine base by elemental analysis, infrared and electronic spectral studies and by cyclic voltammetry,[21].

The conductivity of the doped (1M HCl) polymer rises monotonically with molecular weight up to a value of ~150,000 (~1,600 ring-nitrogen repeat units) after which it changes relatively little. The reason for the change in dependency of conductivity on molecular weight is not clearly apparent; however, it is not caused by a change in the degree of crystallinity, since all fractions exhibited approximately the same crystallinity by x-ray diffraction studies.

Relationship Between Crystallinity and Conductivity of Polyaniline

It has been known for some time that emeraldine base is readily solution-processible,[22-24] and that it may be cast as free-standing, flexible, coppery-colored films from its solutions in NMP. These films can be doped with ~1M aqueous HCl to give the corresponding flexible, lustrous, purple-blue films (σ ~1-4 S/cm) of emeraldine hydrochloride,[22] which are partly crystalline.

Aligned Films: As will be seen below, the intrinsic properties of a conducting polymer can only be approached through processing. Uniaxially oriented, partly crystalline emeraldine base films are obtained by simultaneous heat treatment and mechanical stretching of films formed from "as-synthesized" emeraldine base containing ~15% by weight plasticizer such as NMP,[3,25]. Samples are observed to elongate by up to four times their original length when stretched above the glass transition temperature [> ~110°C], [3,25]. The resulting films have an anisotropic X-ray diffraction and optical response, with a misorientation of only a few degrees,[3]. The unstretched films are essentially completely resoluble in NMP. The solubility decreases with stretching (increased crystallinity) four-fold stretched films are completely insoluble in NMP. However, their crystallinity can be destroyed by repeated doping with aq. HCl and undoping with aq. NH_4OH whereupon they become completely re-soluble in NMP.

Table II. Characterization of Fractions of Emeraldine Base From Preparative G.P.C. Studies (a)

Fraction	M_p	M_n	M_w	M_w/M_n	Conductivity (b) (S/cm)
1	15,000	12,000	22,000	1.8	1.2
2	29,000	22,000	42,000	1.9	2.4
3	58,000	40,000	73,000	1.8	7.9
4	96,000	78,000	125,000	1.6	13.1
5	174,000	148,000	211,000	1.4	17.0
6	320,000	264,000	380,000	1.4	14.9

(a) Molecular weights relative to polystyrene standard (NMP solution).
(b) Compressed pellet; 4-probe; after doping with 1M aq. HCl for 48 hours.

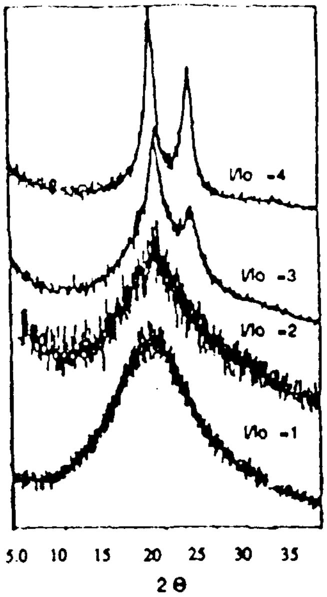


Fig.1. X-Ray Diffraction Spectra of Ribbons of Emeraldine Base of Increasing Draw Ratio, (l/l_o; l = final length; l_o = original length before stretching.)

Lustrous, copper-colored ribbons of uniaxially oriented emeraldine base film up to 1.2 meters (4 feet) in length and 2.5 cm in width (thickness ~20mm) of various draw ratios can be readily fabricated by stretch-orienting emeraldine base films cast from NMP solution at ~140° C between two metal rollers rotating at different speeds,[26]. As can be seen from Figure 1 the apparent degree of crystallinity is greatly increased by processing of this type.

The tensile strength of the ribbons also increases significantly with an increase in draw ratio (and crystallinity) as shown in Table III. As expected, biaxially oriented film exhibits significantly greater tensile strength than uniaxially oriented film for the same draw ratio ($l/l_o = 2$) (Table III). The conductivity of the HCl-doped uniaxially oriented ribbons increases on stretching ($l/l_o = 1$, σ ~5 S/cm; $l/l_o = 4$, σ ~80 S/cm). It should be noted that the conductivity of the oriented films is greatly dependent on their method of drying; conductivities of ~300 S/cm can be obtained for films which have not been dried to any great extent,[26].

The above observations show that polyaniline can be processed by methods used for commercial polymers. Even at this very early stage, its tensile strength overlaps the lower tensile strength range of commercial polymers such as Nylon 6. Unstretched Nylon 6 has tensile strengths ranging from 69 to 81 MPa, [27].

Aligned Fibers: Fibers (~30-70mm) of emeraldine base can be formed by drawing a ~20% by weight "solution" of emeraldine base in NMP in a water/NMP solution,[23,28]. If

Table III. Tensile Strength (MPa)[a] of Emeraldine Base Ribbons as a Function of Draw Ratio (l/l_o)

		Uniaxial Orientation:				Biaxial Orientation[b]:
		$l/l_o=1$	$l/l_o=2$	$l/l_o=3$	$l/l_o=4$	$l/l_o=2$
Tensile Strength	(Av.)	54.4	53.2	75.9	124.1	122.4
	(Best)	59.9	62.1	82.8	144.8	131.6

(a) gauge length = 3 inches (b) l/l_o = 2 in both directions desired, the emeraldine base "solution" in NMP may also be drawn in aqueous HCl which results in direct formation of the doped fiber. Fibers can also be spun from NMP solution. The drawn fibers (containing NMP as plasticizer) can be thermally stretch oriented at ~140°C up to four times their original length in a similar manner to emeraldine base films,[23]. X-ray diffraction studies show directional enhancement of the Debye-Scherrer rings. A monotonic increase in apparent crystallinity with draw ratio is observed. Doping with 1M aqueous HCl results in a significant increase in the conductivity parallel to the direction of stretching (σ ~40-170 S/cm) as compared to the conductivity of the polymer powder from which the fibers are prepared (σ ~1-5 S/cm).

As can be seen from Figure 2, the conductivity of the HCl-doped drawn fibers increases monotonically with draw ratio, (l/l_o). Since the crystallinity also increases with draw ratio, it is apparent that the conductivity increases with increase in crystallinity.

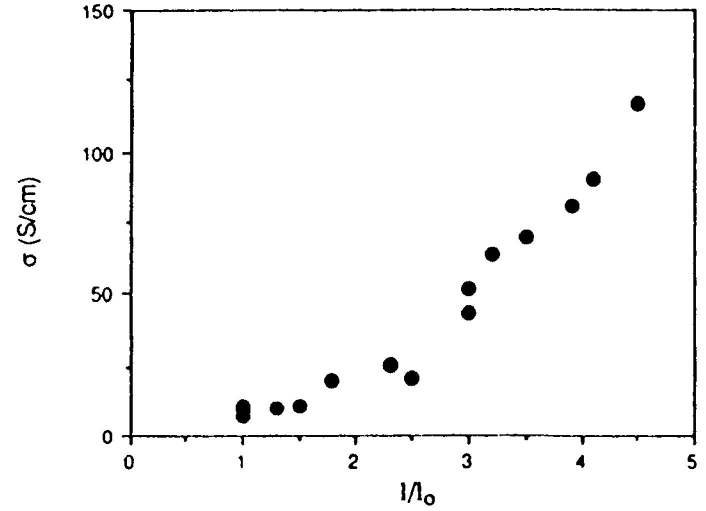


Fig.2. Conductivity of the HCl-doped Drawn Fibers vs. Draw Ratio (l/l_o); l = final length; l_o = original length before streching.

It should be stressed that the above data were obtained using "as-synthesized" emeraldine base containing low molecular weight polymer and low molecular weight impurities,[23]. Since l/l_o in general will increase with increasing molecular weight, e. g. by gel spinning, it is apparent that use of higher molecular weight polymer should result in greater l/l_o ratios and hence in even higher conductivities.

Preliminary studies show that emeraldine base fibers both before and after doping with 1M aqueous HCl exhibit promising mechanical properties,[1,23]. Values for one inch gauge length (tensile strength, MPa; initial modulus, GPa) for emeraldine base fibers stretch-oriented (l/l_o ~ 3-4) at ~140°C after drawing are: 318(Av.); 366(Best) and 8.1(Av.); 8.6(Best). After doping, corresponding values are: 150(Av.); 176(Best) and 4.6(Av.); 5.0(Best). X-ray diffraction studies show some reduction in crystallinity after doping, consistent with the reduction in tensile strength. As expected, the tensile strength of the oriented emeraldine base fibers are greater than those of oriented films. As can be seen on comparing the above tensile strengths with those of, for example, fibers of Nylon 6 (200-905 MPa),[29] the mechanical properties of polyaniline fibers, considering the early stage of development, are most encouraging.

TECHNOLOGY

Technological uses of conducting polymers may be classified as follows: (1) Use based on bulk conductivity of the pure conducting polymer or a blend of the conducting polymer with a conventional polymer; (2) Use based on the electrochemical redox properties of the polymer; (3) Use based on the formation of an excited state of the polymer; (4) Use based on the morphology/microstructure of the polymer. Each of these categories will be summarized below.

(1) Use Based on Bulk Conductivity

It is most unlikely that a conducting polymer will ever be used as a substitute for copper as an electrical conductor unless its conductivity and mechanical properties can be appropriately increased. However, the unique combination of properties which can be displayed by a conducting polymer or its blends with conventional polymers appear to show great promise for a variety of uses. A remarkable feature of several conducting polymers which has recently been brought to light is their ability to undergo percolation at very low loading levels when incorporated as a blend into an insulating polymer. When an electrically conducting material - metal or carbon powder or filaments - is mixed with an insulating polymer, essentially no increase in conductivity is observed until particles of the conducting material first touch each other and thus form a conducting pathway throughout the mixture. At this loading level "percolation threshold" (~16 vol.% for a three-dimensional network of conducting globular aggregates in an insulating matrix) the conductivity increases extremely rapidly. The percolation threshold is greatly dependent on the size and aspect ratio of the particles - whether, for example, spheres or long needles - and can vary from a few volume percent up to 30% to 40% or more in industrial composites depending on the efficiency of mixing and uniformity of size. However, in blends of doped polyaniline and also in blends of derivatives of certain substituted polythiophenes[30] in conventional insulating polymers either no or only very low (< 5%) percolation thresholds are observed. For example, a (5 wt. %) blend of doped polyaniline in Nylon 12 shows that percolation has already commenced and that the conductivity at ~ 20% loading is essentially the same as that of the pure conducting polymer,[9]. Thus the most desirable features of both the conducting and non-conducting polymers can be combined. At least in some cases it is believed that percolation commences at a very low level since the host (non-conducting) polymer forms a network upon which a very thin film of the conducting polymer is deposited, thus forming a continuous conducting film throughout the bulk material.

Doped polyaniline and blends of doped polyaniline are now commercially available in large quantities,[9]. The blends are easier to process than metal flake- or fiber-filled polymers and are non-abrasive and exhibit uniform and higher conductivities than is possible with carbon black fillers. They show superior electromagnetic (EMI) shielding properties to previous materials,[9] and have use in static dissipation. It seems highly likely that the polythiophene blends presently being developed,[7,8] may be used for similar purposes.

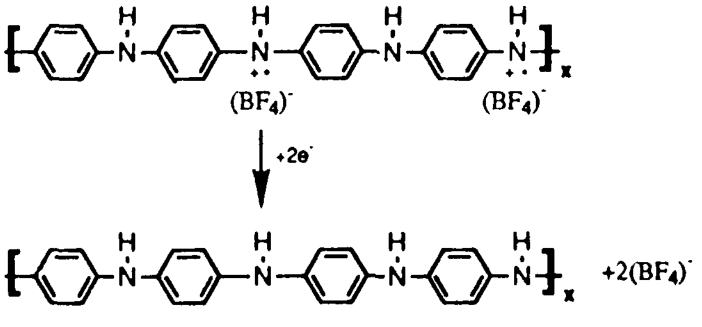
The bulk conductivity of films or powders of conducting polymers has also been utilized in a variety of chemical sensing devices whereby a conducting polymer is either doped or undoped by a specific chemical species whose presence is to be detected with a concomitant large change in electrical conductivity which can be recorded electronically,[31].

(2) Use Based on Electrochemical Redox Processes

The use of conducting polymers as a cathode material (with alkali metal anode) in novel rechargeable batteries is well established,[6]. Button-cell batteries containing polyaniline have been on sale since 1987. They are based on the concept of electrochemical oxidation and reduction. This is illustrated below for polyaniline/Li batteries, the fundamental electrochemical processes involved being:

Discharge Reactions

Cathode:



(4)

The electrons taken up by the polyaniline polysemiquinone radical cation come via an external wire from the anode.

$$\text{Anode:} \quad 2\,Li \longrightarrow 2\,Li^+ + 2\,e^- \qquad (5)$$

The charge reactions are the reverse of the above. These batteries show superior qualities for use as a back-up power source for personal computers and for portable solar-powered calculators, etc. Somewhat similar industrial prototype rechargeable batteries involving polypyrrole have also been announced,[32,33]. Rechargeable, completely packaged batteries using a polyacetylene or polyparaphenylene/alkali metal cathode have also been developed,[34]. These have approximately twice the energy density of nickel/cadmium batteries.

Many electrochemically dopant-induced structure-property changes in conducting polymers have been described for use in, for example, electrochromic windows and displays, electrochemically controlled chemical separation and delivery systems, redox capacitors, electromechanical actuators, etc.,[31]. Some of these are apparently close to commercial application.

(3) Use Based on the Formation of an Excited State of the Polymer

The evaluation of conducting polymers for use in non-linear optical (NLO) devices has aroused and continues to arouse a very large amount of scientific activity throughout the world. Although promising properties and prototype devices have been described,[30,35] commercial use in the immediate future does not seem likely.

An extremely exciting, very recent development,[7,36] reports the use of polyphenylenevinylene and derivatives as light-emitting diodes (LED) whereby their electroluminescent properties are utilized. Relatively intense visible light is emitted with reasonable efficiency. Considering the large number of conducting polymers and their derivatives it appears that this discovery may open up a whole new technology whereby flexible, large area diodes emitting a wide range of colors may be possible.

(4) Use Based on the Morphology / Microstructure of the Polymer

Another very recent exciting development involves the use of lightly-doped polyaniline film membranes for the separation of gases,[37]. Separations far exceed the selectivity of all known gas separation membranes for many simple gas mixtures, e.g. O_2/N_2. The process by which this occurs is not yet clear although it appears that protonic acid doping of emeraldine base films, followed by complete undoping and then followed by light doping may open up molecular-sized channels previously occupied by dopant anions, within the films. This type of use of conducting polymers opens up new unexpected avenues for research and development.

CONCLUSIONS

Undoubtedly, many important potential applications of conducting polymers have been omitted in this brief summary. The next decade will certainly bring forth new basic science and applications in the field that are logical extensions of what is already known, as well as completely new unexpected fundamental science and technology.

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