Conductive Polymers

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When polymers were first developed, their most obvious characteristics were their mechanical and chemical properties. The onset of World War II and the need for synthetic rubber and natural product substitutes determined the course of development of the polymer industry. Almost in parallel with this development, the exploitation of solids in electronics centered on elemental inorganic materials such as silicon and germanium and subsequently on inorganic compound semiconductors. As a consequence, only scattered studies of the electronic properties of organic solids in general, and polymers in particular, were made up to 1970. Thus, although the origins of a definable plastics technology can be traced back about 50 years, it was not until very recently that polymers have been viewed as a potential source of electronic materials.

Summary. Recent research has shown that polymers, normally thought of as being insulators, exhibit a wide range of electrical conductive properties.

In the 1970's there has been increased attention to disordered materials and organic solids. One reason for this is interest in the effects of disorder on solid-state properties of solids and in the crystalline and amorphous forms of molecularly bonded or organic solids (*1*, *2*). A second motivation has been a growing need for large-area, low-cost elements in electronic and photoelectronic devices. The need of the electrophotography industry for such elements provided opportunities for the use of amorphous inorganic and polymeric materials. This is now a multibillion-dollar industry, at the technological heart of which are amorphous materials.

Work in the past few years has included substantial studies of the electronic properties of polymers, since they combine a number of advantageous features such as good mechanical properties, ease and diversity of synthesis, and the potential for molecular engineering. These studies have utilized and coordinated the skills of chemists, materials scientists, and physicists. Sophisticated experimental and theoretical approaches are being applied to establish a firm understanding of the basic phenomena and to elucidate structure-property relationships (*3*, *4*).

Although significant progress has been made, there is much that is still not understood. My purpose in this article is to review our present understanding of the electronic properties of organic polymers and their actual or possible technological applications. The discussion will be limited to key phenomena and materials involving bulk transport of charge and thus excludes interesting phenomena such as triboelectricity and materials such as electrets whose properties are determined by bound charge.

Conduction Processes

It is convenient here to take a broader than usual interpretation of the concept of conductivity. The strong interaction between the atomic building blocks and their ordered arrangement on a three-dimensional lattice in a crystalline, covalently bonded solid lead to the existence of bands of allowed energy. The bandwidths are related to the strength of the interaction between the building blocks, which in organic and molecular solids are molecules. In this class of solids intermolecular interactions are typically weak, so bandwidths even in crystals are generally very much smaller than for covalently bonded solids. Within the bands, electrons are not identified with a particular site, but have an equal probability of being associated with any site. This phenomenon of delocalization, in which the electronic wave function is extended in space, has led to the states in these energy bands being called extended or conduction states. The bands of interest correspond to the highest fully occupied states (valence band) and lowest empty states (conduction band). These energy bands are separated by a range of forbidden energies which defines the band gap, E_g, characteristic of a particular solid.

In such an idealized crystal, the material at the absolute zero of temperature is an insulator since all states in the valence band are occupied and all states in the conduction band are empty. As the temperature is raised, there is an increasing probability (defined by Fermi-Dirac statistics and the position of the Fermi level) that some electrons in the valence band can acquire sufficient thermal energy to make the transition to states in the conduction band. Partial occupation of the conduction band can occur, and in an applied electric field the electrons can accelerate and move into higher energy states within the conduction band. Since the valence band is also no longer full, electrons in this band can experience a similar effect, although this is visualized as being associated with the motion of the vacated states, called holes.

The conductivity σ is proportional to $ne\mu_e + pe\mu_h$, where n and p are the equilibrium concentrations of free electrons and holes and μ_e and μ_h are the electron and hole mobilities or velocities per unit field. The mobility therefore determines the facility with which the carriers can move through the crystal lattice and for a material such as crystalline silicon is about 1000 square centimeters per volt per second. Such motion is hindered by collisions or interactions with the vibrating atoms of the crystal at finite temperatures. Thermal vibrations of the lattice are termed phonons. The electrical conductivity is thermally activated and, because of the increasing free carrier population, increases with temperature. This type of solid, where the electrons and holes are produced in equal numbers, is called an intrinsic semiconductor. In the case of metals the conduction band is already partially occupied because of the number of valence electrons per atom and the filling of available states. Since the number of free carriers is therefore essentially temperature-independent, the conductivity of metals decreases as the temperature rises because the carrier mobility is reduced by enhanced scattering of electrons by lattice imperfections or phonons.

A major advance in the field of semiconductors was the discovery that the

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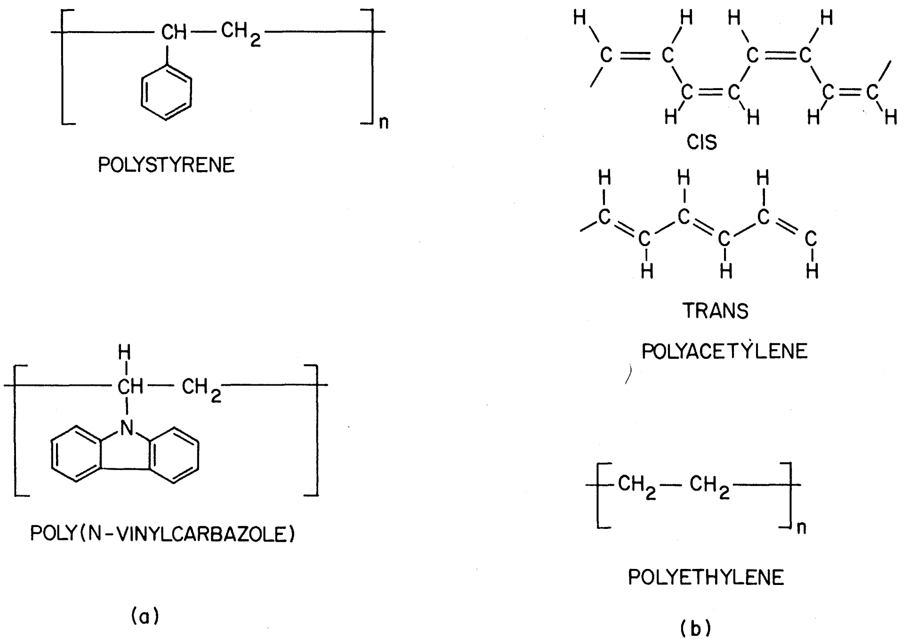

Fig. 1. (a) Structures of two pendant-group polymers, polystyrene and poly(*N*-vinylcarbazole). (b) Structures of a saturated-backbone polymer, polyethylene, and a non-pendant-group polymer with an unsaturated chain, polyacetylene.

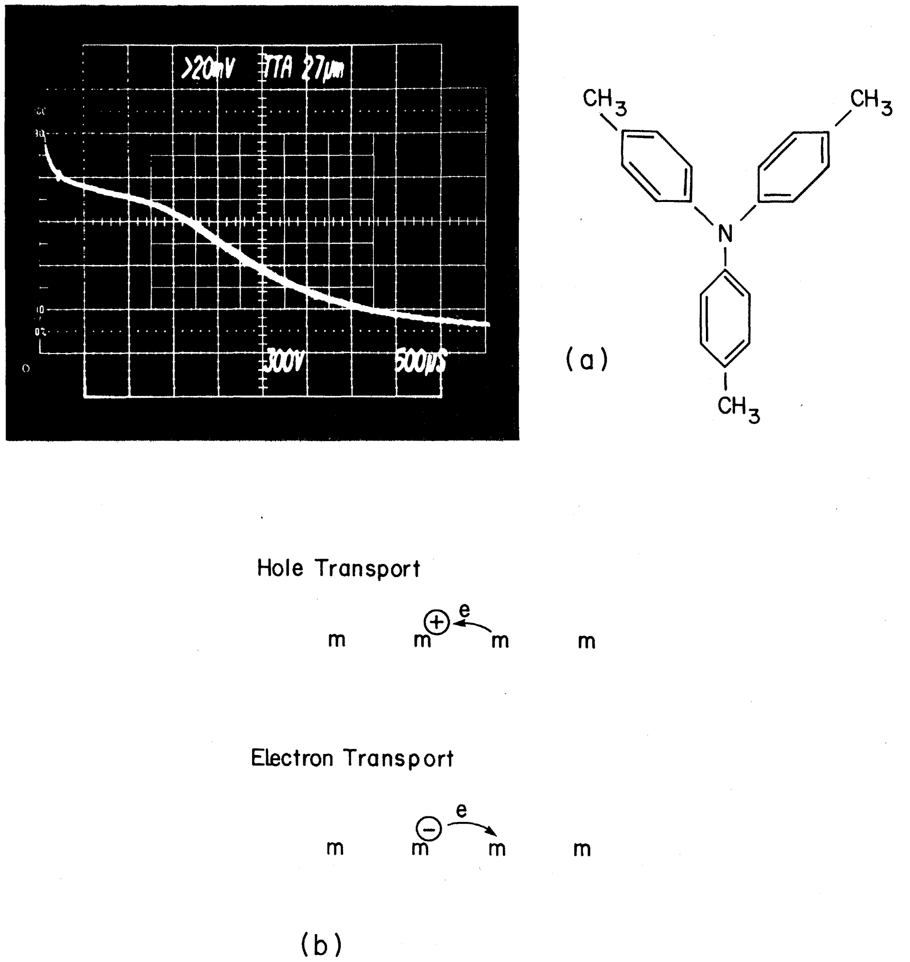

Fig. 2. (a) Current transit pulse in a molecularly doped polymer, polycarbonate Lexan doped with molecules of tri-*p*-tolylamine (TTA), shown at the right. The transient photoconductivity is induced by a 10-nanosecond 3371-Å flash strongly absorbed by the TTA molecules. The motion of the induced charge sheet across the sample exhibits considerable dispersion, as discussed in the text. Undoped Lexan exhibits no electronic activity under these conditions. (b) Schematic representation of the basic transport process; *m* stands for molecule, *e* for electron.

addition of a small concentration of impurities could drastically modify the electrical conductivity at room temperature. Such doping can lead to *n*-type extrinsic or impurity-controlled conduction since the excess electrons can be thermally excited out of a localized or donor level, resulting from the introduction of the impurity, into the conduction band. Similarly, certain impurities can lead to localized states in the forbidden gap just above the valence band. These unoccupied states can accept electrons and lead to an increase of holes in the valence band. This type of doping gives *p*-type material (the Fermi level lies closer to the valence band). By controlled doping of materials in this manner, it is possible to form contiguous regions of *p*- and *n*-type materials, which results in a *p*-*n* junction.

There are solids with sufficiently large band gaps that the thermal generation rate and equilibrium carrier concentration are so low that the material is an insulator even at room temperature. This can be the case even though any thermally excited carriers would move with high mobility in the available conduction states. This quiescent, low, dark conductivity can be changed by photoexcitation of carriers into the high-mobility states (photoconductivity) or by injection of carriers from contiguous solids such as metal electrodes (*5*). In either case, the introduction of nonequilibrium carriers leads to their transport in already existing transport states, and the solids can be highly insulating although electronically active. Some materials remain insulating and electronically inactive because their insulating nature is associated with a lack of adequate accessible transport states. In this case doping can transform an electrically inactive material into an electronically active but insulating material by the provision of otherwise absent transport states. Additional chemical modification can make these materials semiconducting. All of these approaches lead to conductivity in polymers, and the remainder of this article will be devoted to representative examples.

Electronic States of Polymers

Figure 1 shows examples of two classes of polymers that have quite different optical properties—a difference that is reflected in their electrical properties. These are (i) polymers with saturated backbones and appended aromatic chromophores (Fig. 1a), of which polystyrene and polyvinylcarbazole are examples, and (ii) non-pendant-group polymers (Fig. 1b) with saturated or unsaturated backbones, such as polyethylene and polyacetylene. A third class of polymers with unsaturated backbones and appended chromophores has not received much attention and will not be discussed further.

It is characteristic of the pendant-group polymers (the first class) that they are remarkably similar in their electronic states to the isolated pendant aromatic molecule. Their electronic interactions are essentially those of a random and therefore disordered ensemble of the constituent pendant molecules. This led to the concept of molecular engineering of electronically active polymers. In non-pendant-group polymers, the electronic properties are very much controlled by the states associated with the strong intrachain covalent bonding. As with inorganic covalent solids, one expects wide conduction bands because one-dimensional order is substantially maintained along the chain even in otherwise largely amorphous polymers. Indeed, this is the most unusual aspect of such polymers. By analogy with the inorganic solids, appropriate doping with donors and acceptors should lead to extrinsic semiconductors. Although this has been observed, recent studies suggest that the analogy cannot be drawn too closely and the situation is more complex than was first thought.

The electronic absorption spectra of pendant-group polymers are similar to those of the polymers in solution or of effectively isolated chromophores in the gas phase (*6*). It has long been recognized intuitively that this is evidence that the weak interaction between the pendant molecules leads to small exchange energies and bandwidths much smaller than the energy fluctuations associated with the disorder. In general, such electronic states will be localized. The pendant molecules have a much lower ionization potential than the saturated polymer backbone and are expected and observed to dominate the low-energy transitions and to play an integral role in their electrical properties. The energy required to separate a negative and a positive charge for an isolated molecule (as in gas-phase ionization) is $I_g - A_g$, where I_g is the gas-phase ionization energy and A_g is the energy gained by binding the ionized electron to a neighboring homolog molecule. In a solid the energy ΔE to produce these ion states is diminished by the existence of the molecules within a polarizable medium; thus $\Delta E = I_g - A_g - 2P$, where P is the polarization energy of the "free electron" and, to a good approximation, is the same for electrons and holes. In this sense, one can speak of conduction states for electrons and holes separated by a band gap ΔE.

Polyethylene is a non-pendant-group polymer with a saturated backbone which has been extensively studied over the past decade (see Fig. 1b). The early studies were of its ultraviolet absorption, and the dominant feature is an absorption threshold extending from 7.2 to 11 electron volts. Energy band calculations for a single polyethylene chain predict a large energy gap between filled and vacant states. The strong covalent intrachain bonding leads to energy bands of considerable width with mobility estimates of ~25 cm²/V-sec. In this picture, the photoconductivity edge should coincide with the absorption edge; that is, the solid-state properties would be expected to be similar to those of a covalent inorganic semiconductor. In fact, the photoconductivity measurements show a threshold at 8.8 eV, which is significantly higher than the optical absorption threshold at 7.2 eV. Inclusion of the effects of highly localized excitons (electron-hole pairs bound by their mutual Coulomb attraction), which dominate the absorption threshold, helps to reconcile the photoconductivity results with the broad energy bands dictated by the structure of the polyethylene chain.

The most studied polymer with an unsaturated backbone is polyacetylene, $(CH)_x$, whose two possible structural forms are shown in Fig. 1b. It is the simplest unsaturated organic polymer, having a backbone composed of a linear chain of carbon atoms alternately singly and doubly bonded (*7*). The π electron is in a p orbital perpendicular to the plane of the chain. Within each C_2H_2 unit, the p orbitals combine to form a filled π and empty π^* orbital. In an extended polyene chain such as $(CH)_x$, these molecular orbitals broaden into filled and unfilled bands. If the π electron delocalization was complete and the carbon-carbon bond length was constant, the separation between the π and π^* bands would be zero and intrinsic metallic behavior would be observed. In practice, however, bond alternation persists and results in a finite gap between the π and π^* bands. Band structure calculations indicate that conduction and valence bandwidths are essentially the same for the *cis* and *trans* forms. The general feature of the alternating conjugation is the appearance of an absorption threshold in the visible region of the spectrum, and $(CH)_x$ at room temperature behaves as a semiconductor. It is this absorption that

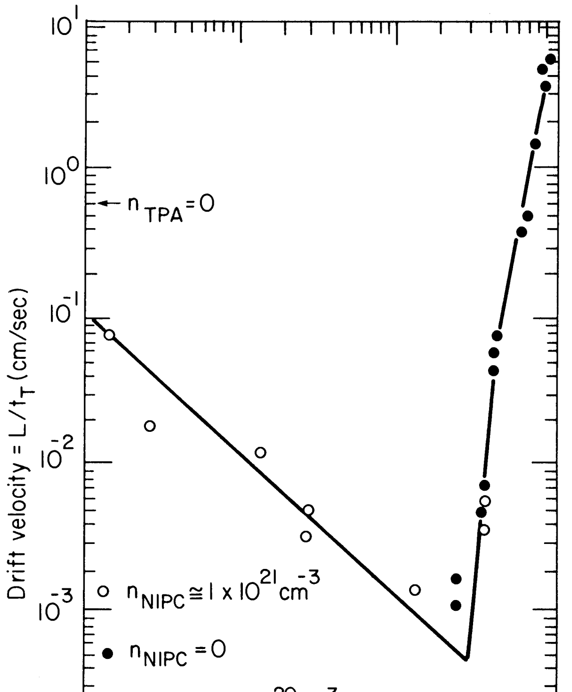

Fig. 3. Concentration dependence of the velocity of holes in a mixed doped polymer. The NIPC concentration was fixed at the values indicated; the points correspond to samples with varying concentrations of TPA, which has a lower ionization potential than NIPC (*14*).

is responsible for the dichroism of the K polarizer invented by Land (*8*); this is formed by the dehydration of oriented polyvinyl alcohol, which results in oriented polyene chains.

Conduction in Pendant-Group Polymers and Molecularly Doped Polymers

A few highly insulating pendant-group polymers do exhibit significant conductivity when excess carriers are produced—for example, by light. Poly(*N*-vinylcarbazole), PVK, is a well-known example (see Fig. 1a). The facility with which charges move through such an insulator has been measured by a technique, widely applied to insulating solids, called time of flight (*5*). A sheet of charge, defined both spatially and temporally, is produced by a short pulse of light strongly absorbed in the film. The drift of the resultant photocarriers across the sample can be timed electronically to determine their velocity or mobility. The transport in PVK, in common with inorganic amorphous solids (*9*), is dispersive in the sense that although all the carriers begin to move simultaneously, they have a wide spread of arrival times at the other side of the sample. In addition, the mobilities, which are only observable for holes, are typically many orders of magnitude smaller than those in inorganic crystals.

Although initially this dispersive transport was thought to be due to ionic drift or impurity effects, results in the past few years have proved that it is associated with basic intermolecular electronic transfer interactions (*10, 11*). The hole transport in PVK is now known to involve electron hopping from one carbazole chromophore to another without involvement of the vinyl backbone. Since films of PVK are amorphous, the pendant carbazole units are in effect randomly oriented in space. The random distribution of distance and relative orientation between the planar carbazole chromophores results in a wide distribution of hopping probabilities between molecular sites and thus a wide distribution of effective velocities.

These ideas are also involved in the molecular doping of polymers—an approach that can be accurately described as molecular engineering of electronically active, insulating polymers. Otherwise electrically insulating and inactive polymers such as polycarbonates or polyesters can be doped with organic molecules such as *N*-isopropylcarbazole (NIPC), tri-*p*-tolylamine (TTA), or trinitrofluorenone (TNF) (*11-13*). It is possible to form solid solutions with dopant polymer concentrations of about 10^{21} per cubic centimeter. In such a molecular dispersion, the molecules are separated on the average by ~10 angstroms from their nearest neighbors. Figure 2a illustrates the transport of holes produced by photoexcitation of the dopant molecules by a 10-nanosecond ultraviolet light pulse in a polycarbonate film doped with TTA. The dispersive nature of the transport is evident, with the transit time indicated by the shoulder corresponding to a hole drift mobility of $\sim 2 \times 10^{-5}$ cm^2/V-sec.

Figure 2b indicates schematically the basic transport process. A neutral dopant molecule is photooxidized to produce a molecular cation, followed by electron transfer from a nearby neutral molecule to this cation. The "free hole" propagates through the film by successive reversible oxidation-reduction (electron loss–electron gain) reactions. Transport is therefore typically unipolar: hole transport occurs if the neutral dopant molecule is donor-like (for example, NIPC or TTA), electron transport if it is acceptor-like (TNF) (*11, 13*). (Thus, in an interesting conjunction of physics and chemistry, an effect that a solid-state physicist perceives to be macroscopic electrical conductivity could be described by a chemist as reversible solid-state chemistry.)

Detailed aspects of the transport process have been unraveled by changing the concentration of the dopant molecules in predetermined ways. This results in controlled, variable intermolecular separations, and shows clearly that the transport process is governed by electronic wave function overlap between neighboring molecules with any excess charge being highly localized on the host molecule. The high degree of localization is the determinant of the electronic properties of these systems and of the analogous pendant-type polymers. As a consequence, electronic transport in these systems is decidely non-bandlike and proceeds by an intermolecular hopping process. Concomitantly low mobilities with values $\lesssim 10^{-3}$ cm^2/V-sec are expected. This imposes considerable and definable constraints on the range of potential technological applications of these systems, although the applications that remain, as will be discussed later, can be of major consequence.

In principle, the broadest objective of science is that of harnessing nature's properties through understanding. In this

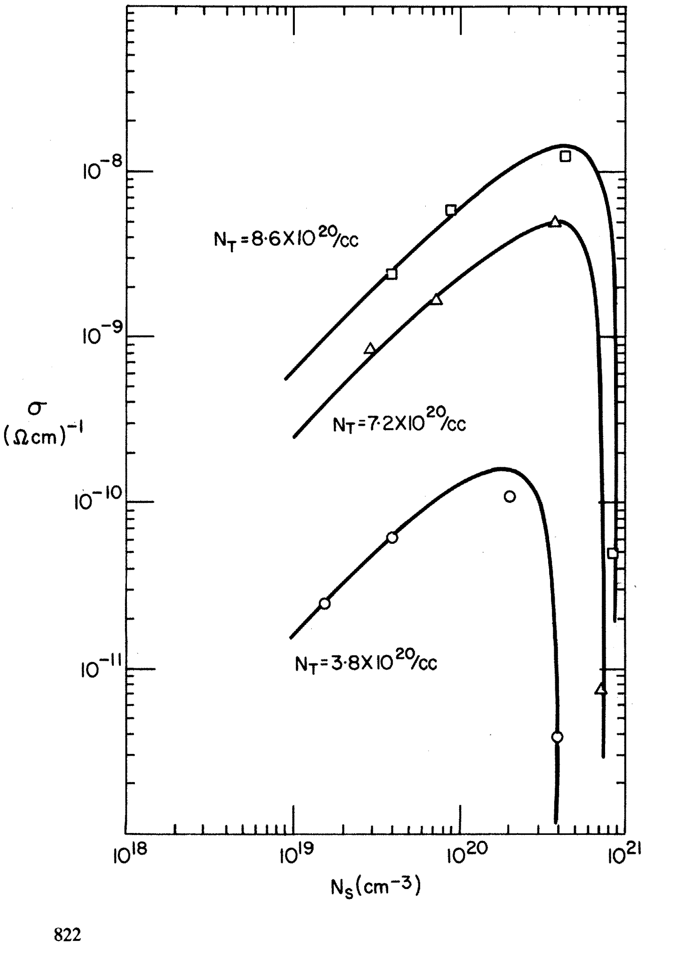

Fig. 4. Plot of the logarithm of the d-c conductivity of Lexan doped with three different concentrations (N_T) of TTA molecules against spin density, N_s. The spin density measures the concentration of the paramagnetic molecular cation TTA$^+$ (*15*).

respect, doped polymers provide a model system in which to test our understanding of the basic electronic properties of systems involving electron transfer between molecules. Such processes are basic to many phenomena both in nature and in potential technical applications, ranging from photosynthesis to photochemical photovoltaics. Figure 3 shows the results of experiments that confirm intuitive expectations of how admixtures of different molecules will act. In these experiments (*14*) controlled small quantities of a molecule, triphenylamine (TPA), with a lower ionization potential than a second molecule (NIPC), present in very high concentrations, are introduced. In the absence of TPA, the holes normally propagate by hopping between the closely spaced NIPC molecules. The introduction of TPA, with its lower ionization potential, results in the trapping of a hole and its temporary removal from the transport channel. As the concentration of TPA rises, the average carrier velocity falls. This is an unambiguous example of a trap-controlled hopping process. A concentration of TPA is ultimately reached at which (because of sufficient overlap between TPA molecules) it becomes an alternative and preferred transport channel, so the carrier velocity rises again.

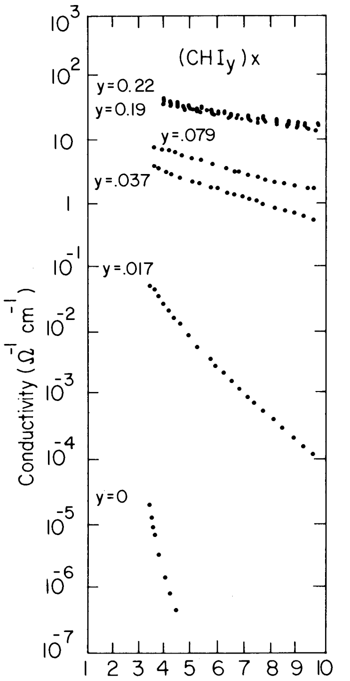

Fig. 5. Plot of the logarithm of conductivity against the reciprocal of temperature for polyacetylene for various concentrations (y) of iodine. The sharp rise in conductivity and related decrease to a weak activation energy is clearly seen (*16*).

In an extension of these ideas, chemical control of dark conductivity by the introduction of finite equilibrium concentrations of free carriers has been demonstrated (*12*). (The carriers are free in the sense that in an applied field they determine the conductivity; they are, of course, highly localized on the constituent molecules and are not free in the sense of carriers in a metal or a crystalline semiconductor.) The concept employed here can be understood in the following way. As discussed before, transport in electronically active but otherwise insulating systems is observed and measured by the transient photooxidation of some of the dopant molecules by suitable exposure to light. This photoinduced conductivity is nonequilibrium in that it decays with the removal of the illumination. By analogy, it is possible to effectively chemically oxidize a controlled, equilibrium fraction of the neutral molecules.

Figure 4 shows results of a study where, in addition to doping the polymer matrix with the molecule TTA, variable amounts of the molecular cation TTA^+ are incorporated so that the total number of molecules, neutral and oxidized, is constant. The TTA^+ is in the form $TTA^+SbCl_5^-$ ($SbCl_5^-$ is the average composition), prepared by reacting neutral TTA with the strong oxidizing agent $SbCl_5$. In this way different fractions of the TTA molecule can be oxidized to the molecular cation TTA^+ and constitute free carriers. The conductivity thus initially increases as the fraction of oxidized species is increased. Since the transport process requires electron transfer from a neighboring neutral molecule, if all the molecules are oxidized no transport can occur and the conductivity must go through a maximum, as observed. The maximum value of the dark conductivity achieved is $\sim 10^{-7}$ (ohm-cm)$^{-1}$, reflecting the intrinsically low mobility associated with hopping between localized states; the maximum also shows that in this system free carriers are ultimately formed at the expense of transport states. Interestingly, these molecular ion states that play an important role in the dark conductivity are, in the case of TTA, also paramagnetic, so opportunities exist to study correlations between electrical conductivity and magnetic phenomena. Recent coordinated studies (*15*) have revealed that in such systems exchange between two paramagnets (TTA^+ species) can be mediated by the presence of a diamagnetic, neutral TTA molecule; this effect is called superexchange.

Conduction in Non–Pendant-Group Polymers

This class embraces polymers with saturated backbones, such as polyethylene, which exhibit no significant electronic activity either intrinsically or after photoexcitation or chemical doping, and those with unsaturated backbones, such as polyacetylene. Recent work (*16*) on doping such an unsaturated polymer indicates that materials can be produced with conductivities close to those of conventional metals and with intermediate conductivities by controlling the doping concentrations. In fact, a remarkable range spanning 12 orders of magnitude in conductivity is possible. The materials have been known for several years, but the systematic study of their electrical properties is a relatively recent development, which has been made possible by advances in the production of high-quality materials and films. Thus the production of high-quality polyacetylene films of useful thickness and good mechanical flexibility by catalytic polymerization of acetylene gas (*17*) has led to extensive studies of their electronic properties. Much of this work is current, and so many of the mechanisms are not fully understood. Some general features do seem clear, however. In contrast with the pendant or doped polymers, the electronic states in these systems are associated with the in-chain bonded atoms. In this sense, within the single dimension of the chain the strong covalent bonding between the constituent atoms results in extended or bandlike states. Thus, con-

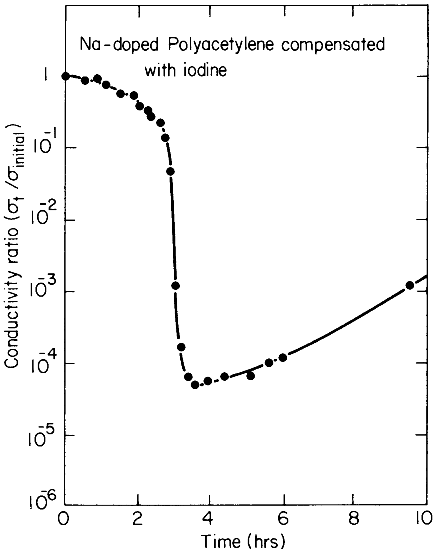

Fig. 6. Compensation curve for Na-doped polyacetylene, showing the conductivity ratio versus time. The sample was initially doped n-type and subsequently exposed to iodine vapor (*18*).

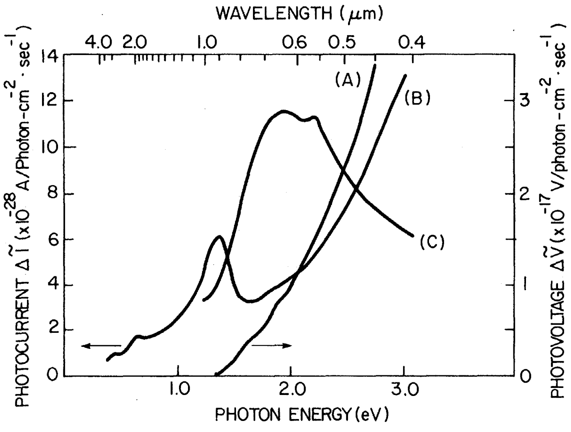

Fig. 7. (Curve A) Open-circuit photovoltaic response of a Schottky barrier junction formed between p-type polyacetylene and a metal with a low work function, normalized to the incident photon flux density and the transmittance of the indium contact. (Curve B) Photoconductivity similarly normalized. (Curve C) Absorbance spectrum of undoped $(CH)_x$ measured at room temperature (*19*).

ceptually one-dimensional order exists in an otherwise disordered or amorphous polymer.

As polymerized, undoped polyacetylene is a semiconductor with a conductivity of $\sim10^{-5}$ to 10^{-6} (ohm-cm)$^{-1}$. Thermopower measurements indicate that the conductivity is p-type. The activation energy of the conductivity is much lower than the band gap deduced from optical absorption—0.3 versus 1.4 eV. By doping with the electron acceptor AsF_5 or with halogens, p-type conductivities as high as 1000 (ohm-cm)$^{-1}$, comparable to that of mercury, have been achieved in unoriented films. Doping with electron donors such as sodium naphthalide results in n-type material with comparable conductivity. The concentration dependence of the doping indicates that an abrupt semiconductor-metal transition occurs at ~1 to 3 atomic percent (Fig. 5). Below the transition the conductivity is strongly thermally activated, as expected for a semiconductor; above the transition, the conductivity approaches a temperature dependence like that for a metal. In the regime of high dopant concentrations, additional strong electronic absorption is observed in the infrared that is interpreted as being due to free carrier absorption. The ability to control conductivity by compensation, analogous to the technique familiar in inorganic semiconductors, has also been demonstrated. This is illustrated in Fig. 6, where the n-type conductivity produced by sodium doping is reduced by incorporation of acceptor-type states due to iodine (*18*). In addition, recent measurements by workers at IBM (*19*) indicate the onset of a photovoltaic response at ~1.48 eV in $(CH)_x$ (Fig. 7). The photoconductive quantum efficiencies reported to date are extremely low, of the order of 10^{-8} carriers per absorbed photon.

One of the more remarkable aspects of the work on polyacetylene is the fact that such high conductivities are observed experimentally. The films consist of highly disoriented fibers (average diameter, 200 Å) and are reported to have a density only one-third the theoretical density determined from x-ray diffraction studies. Indeed, orientation of the films by stretching does result in further significant increases in the conductivity.

Considerable debate is taking place about the detailed interpretation of the observations in polyacetylene, particularly with respect to the semiconductor-metal transition. There are various possible explanations for this effect, but only two will be mentioned as illustrative of the kinds of ideas being considered. According to the first mechanism, the transition could be the result of a percolation phenomenon in which the segmented $(CH)_x$ chains constitute essentially unconnected metal wires as a result of doping. The problem is akin to dispersing small metal needles in an insulating medium and asking at what concentration sufficient interconnection will occur for the system to appear like a metal. Such a percolation phenomenon does exhibit a sharp conductivity threshold transition (*20*). A more fundamental explanation involves excitations known as solitons. In the case of polyacetylene, solitons are kinks in which domains to the left and right of the kink exhibit bond alternations that are out of phase with each other. Calculations (*21, 22*) suggest that at low doping levels, it is energetically more favorable for the charge from the dopant molecule to bind itself to the kink rather than enter the conduction or valence bands. In this model the precipitous drop in conductivity below the transition could be associated with a change in the transport mechanism (*22*). Carrier mobilities would therefore be highly concentration-dependent and would be relatively low in the semiconducting regime. The two effects discussed could both be involved, of course, since they are not mutually exclusive.

Work is also under way on other materials such as polyparaphenylene, polypyrrole, and pyrolyzed polymers. Polyparaphenylene is a polymeric chain of phenyl rings, which exists in the form of a thermally moldable powder but has not, to date, been produced in thin flexible films. The band gap in undoped polyparaphenylene lies in the near ultraviolet. Doping with alkali metals or AsF_5 results in broad absorption from the far infrared to the visible and n- and p-type conductivities with relatively high values, but significantly less than those achieved in polyacetylene (*23*).

Highly stable flexible films of polypyrrole with p-type conductivities of $\sim$ 100 (ohm-cm)$^{-1}$ have been prepared (*24*) by electrolytic oxidation of appropriate pyrrole monomers. The preparation of films by electrolysis of mixtures of pyrrole and N-methylpyrrole dissolved in acetonitrile, using tetraethylammonium tetrafluoroborate electrolyte, leads to conductivities that can be systematically varied over five orders of magnitude to the maximum of 100 (ohm-cm)$^{-1}$. This process avoids the diffusive and often nonuniform doping of films by exposure to oxidizing or reducing chemicals. Very little is known about the fundamental processes controlling the electronic properties of this material. The polymer is believed to be formed by the linkage of pyrrole units through α-carbon atoms and is therefore not a pendant-group polymer; Raman studies confirm the maintenance of the pyrrole rings in the polymer.

Technical Applications

The most extensive technological application of conductive polymers is in the electrophotographic industry. Polymers that are electrically insulating in the dark but can transport nonequilibrium carriers produced by light are well suited to function as photoreceptor elements (*25*). Polymers such as PVK or molecularly doped polymers have strong intrinsic optical absorption only in the ultraviolet, and since visible light is employed in practice, the polymer photosensitivity must be extended into the visible. This can be done by (i) formation of a charge-transfer complex with absorption in the visible, (ii) dye sensitization with an appropriately absorbing dye, or (iii) use of a thin contiguous sensitizing layer such as amorphous selenium. The ability to make large-area flexible polymer films at relatively low cost by solution coating accounts for the application of these materials in electrophotography. Although pendant-group polymers or polymers doped with aromatic molecules have very low mobilities $\lesssim 10^{-3}$ cm^2/V-sec, this is not a limitation for electrophotographic usage. In this process the most important parameter, within limits, is how far the carriers move before they are immobilized rather than how fast they travel (*26*). For most process speeds such mobilities are adequate provided the photogenerated carriers can transverse the total device thickness; that is, $\mu E\tau >$ sample thickness, where μ is the mobility, E the electric field, and τ the lifetime of carriers with respect to deep traps. Remarkably, such polymers do exhibit large carrier ranges because of their very large deep-trapping lifetimes.

For systems where the photogeneration occurs by photoexcitation within a polymer, such as the charge-transfer complexes or dye-sensitized systems, the photogeneration efficiency can be controlled by a geminate recombination mechanism. In such a process, the initial photoexcitation leads to electron-hole pairs, which diffuse within their mutual Coulomb well. There is a finite probability, which decreases with applied field, that the pair will recombine on the initial excitation site rather than thermally dissociate into a free electron and a hole (*27*). Carrier recombination in molecular systems can lead to quantum efficiencies for photogeneration that are substantially less than unity and are strongly field-dependent. This may result in a photosensitivity limitation, depending on the particular system, and can be overcome to some degree by increasing the light exposure in a machine.

For other electronic applications the magnitudes of the carrier mobilities are of paramount importance, since they determine the frequency response of devices or, through the related diffusion lengths, determine ultimate collection efficiencies in devices such as photovoltaic cells. Pendant-group polymers and disordered molecularly doped systems are not likely to find applications in these areas because of their low mobilities and the probable importance of geminate recombination processes. No such assessment can yet be made for materials such as polyacetylene or polyparaphenylene, since questions remain to be answered regarding many fundamental parameters. The ability to produce *p*- and *n*-type materials in these solids by appropriate doping holds some promise. Questions remain about the long-term chemical stability of individual and contiguous layers. Preservation of high mobility associated with the one-dimensional order along the chains in the semiconducting regime would be an enormously important feature, but thermopower and conductivity measurements suggest that this may not be the case. Very little information is available regarding localized gap states and minority carrier parameters. Initial photoconductivity studies (*19*) indicate extremely low quantum efficiencies for photogeneration in currently available materials, but it is not clear whether this is intrinsic to the materials.

Conclusion

The current status of investigations of polymers as electronic materials has been briefly reviewed. Despite many gaps in our understanding, some general codification of properties according to the electronic states of polymers is possible. The remarkable spectrum of conductive behavior observed should provide further stimulation for fundamental studies and the exploration of possible technological applications. This mutual interplay of scientific and technological motivation can be expected to lead to improved understanding, new materials, and new concepts.

The materials are quite complex, and the many questions concerning chemical reactivity and materials stability are further complicated by the morphological features of polymers. Eventual practical application will hinge on the tractability of materials from the perspective of materials processing. Offsetting such difficulties is the diversity of molecular and materials architectures inherent in organic chemistry which can be brought to bear on these problems. Thus the field, still very much in its infancy, poses experimental and theoretical challenges to experimentalists, theorists, synthetic chemists, and materials scientists alike.

Attempts to predict specific applications for the semiconductive and metal-like polymers are not warranted at this stage, since the definition of the full scope and limitations of the phenomena and materials has just begun. The situation is quite different for electronically active insulating polymers, which have already made the difficult transition from laboratory to marketplace. Electronically active polymers function as electronic materials with major industrial applications in the electrophotographic industry. As such, they constitute a tangible demonstration of the promise of appropriate polymers as electronic materials for specialized applications where low cost and large area are important.

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