NONCONJUGATED CONDUCTIVE POLYMERS

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Dedicated to the memory of Professor Sukant K. Tripathy.

ABSTRACT

Conjugation is not a prerequisite for a polymer to be conductive. A polymer must have at least one double bond in the repeat to become conductive. Interaction with a dopant (e.g., electron acceptor) causes transfer of an electron from the double bond to the dopant creating a hole at the double bond site. Electrical conduction occurs via intersite hopping of holes. Various spectroscopic methods (FTIR, optical absorption, solid-state ^{13}C NMR, etc.) along with electrical measurements have been used to elucidate the mechanism of conduction in specific nonconjugated conductive polymers. Examples of these polymers include 1,4-polyisoprene which has one double bond and three single bonds in the repeat. The conductivity of polyisoprene increases 100 billion times upon doping with iodine to a maximum value of 10 S/m. Polyisoprene (natural rubber) is used nonconjugated conductive polymers have a wide range of applications in antistatics, various sensors and optoelectronics.

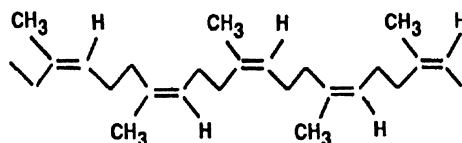*Key Words*:   Nonconjugated conductive polymers; Dopants; Polyisoproprene; FTIR; ^{13}C NMR

In 1977, Shirakawa *et al.* reported that the electrical conductivity of the conjugated polymer polyacetylene increased by a billion times upon doping with iodine [1]. This discovery has led to the 2000 Nobel Prize in Chemistry awarded to Heeger, Macdiarmid and Shirakawa. Subsequent to this discovery, many other
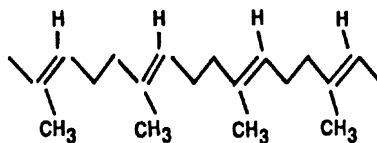
polymers with conjugated backbones have been shown to become conducting upon doping. Such conjugated polymers have been studied in great detail. A statement in the web page of the Nobel Foundation (www.nobel.se/laureates/2000/chemadv.pdf), goes as follows: A key property of a conductive polymer is the presence of *conjugated* double bonds along the backbone of the polymer. In conjugation, the bonds between the carbon atoms are alternately single and double. However, as reported in 1988, (Thakur, *Macromolecules*) [2], specific *nonconjugated* polymers with one double bond and three single bonds in the repeat also become conductive upon doping with iodine. The examples of such nonconjugated polymers include: cis-polyisoprene, trans-polyisoprene, and poly(dimethylbutadiene), etc. The material becomes colored (black) upon doping while it is colorless in the undoped state (Figure 1). The conductivities of these nonconjugated polymers increase by about 100 billion times to a value of 10 S/m compared to less than 10^{-10} S/m in the undoped state. Starting with this article [1] in *Macromolecules* (1988), through several subsequent reports [3-8, 11, 13], Thakur and others have elucidated the electronic structure and mechanism of electrical conduction in these nonconjugated polymers. While use of halogens (e.g., iodine) for enhancement of conductivity was known back in the nineteen sixties, [12] its use in conjugated polymers began with the report of Shirakawa.

Unlike polyacetylene, the nonconjugated polymers are soluble in common organic solvents, therefore can be easily formed as thin films. These films have
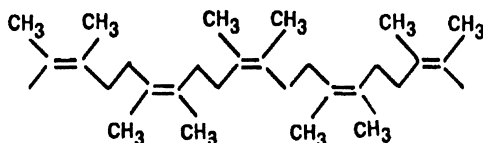

Figure 1. The molecular structures of the nonconjugated polymers that became conducting upon doping, reported in Reference 2 (Macromolecules **1988**).

been thoroughly characterized by various spectroscopic methods such as optical absorption, fourier-transform infrared and solid-state ^{13}C NMR before and after doping [2-5]. As these results have shown, the dopant interacts with the double bond in the polymer backbone and forms a polaronic state (radical cation) as an electron is transferred from the double bond to the dopant creating a hole or a positive carrier at the double bond site. These holes or positive carriers are responsible for the electrical conduction in these materials. The existence of holes as the carriers has been established by appropriate electrical measurements [2, 3]. Holes are the carriers in similarly doped conjugated polymers as well. The transport in the nonconjugated polymers occurs by hopping of these carriers across innumerable polaronic sites that are created upon doping (see Figure 4). The polaronic bond (radical cation) in doped nonconjugated polymer leads to a specific peak (~ 1545 cm^{-1}) in the fourier-transform infrared spectrum [2]. Subsequent theoretical calculation has justified that assignment [6]. The presence of I_3^- species has been identified by resonance Raman and Mossbauer spectroscopies [7, 8]. The I_3^- counterions are formed after an electron is transferred from the double bond to iodine (Figure 2). The same counterions are produced upon doping of conjugated polymers such as polyacetylene as well.
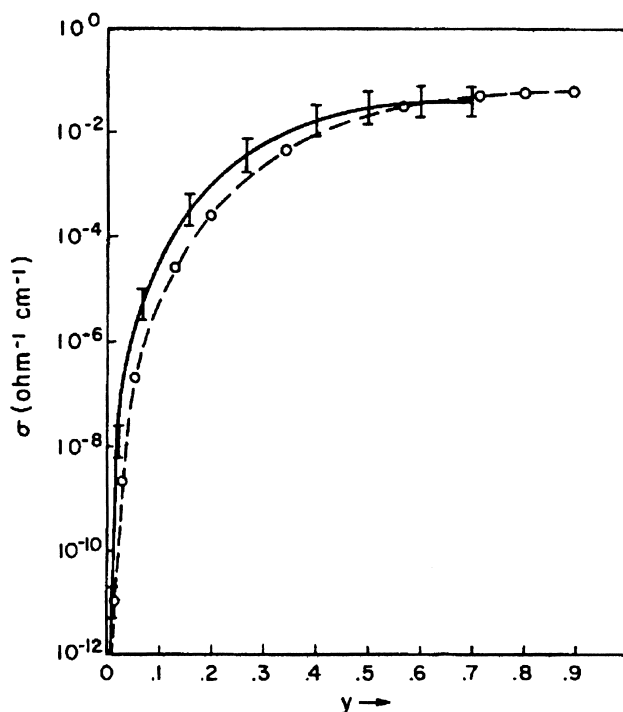

Figure 2. Electrical conductivities of *cis*-polyisoprene (natural rubber), *trans*-polyisoprene, and poly(dimethylbutadiene) for different molar concentrations (y) of iodine. The data for *cis*- and *trans*-polyisoprene lie on the solid curve and the data for poly(dimethylbutadiene) lie on the dashed curve. From Reference 2 (Macromolecules **1988**).

The optical absorption of polyisoprene as a function of doping level was studied for several different dopants [3, 5]. The absorption spectra for iodine doping are shown in Figure 3. The material is nonabsorbing in the pristine state. At low doping two major peaks are observed - one at about 3.3 eV and the other at about 4.27 eV. As the dopant concentration is increased, the overall absorption increases and the spectrum, in particular, the 3.3 eV peak becomes broader. The 4.27 eV peak has been interpreted as due to radical cation while the peak at 3.3 eV is attributed to the charge transfer between the donor and acceptor. The 4.27 eV peak has been correctly explained using a theoretical model involving Coulomb correlation in the cation radical which is similar to an ethylene ion [3]. The value of the Coulomb energy obtained from this analysis provides the correct and known optical gap of ethylene molecule. The broadening and the red-shift of the 3.3 eV band is due to an decrease in the average distance between the dopant (acceptor) and the radical cation (polaron) sites at higher doping levels. These results show that the electronic energy-band theory as applied to conjugated polymers is not appropriate for explanation of the electronic structure and electrical conduction in nonconjugated plastics. Interaction of the dopants at the molecular level producing localized charge-transfer sites provides the correct picture. The mechanisms of electron transfer (ET) reactions as previously modeled by Marcus is appropriate [9]. Besides radical cations, specific iodonium complexes have been considered as possible structures produced by iodine doping [2, 13]. However, the fact these polymers are equally responsive to dopants other than iodine such as $SbCl_5$ rules out iodonium complex formation as a potential mechanism
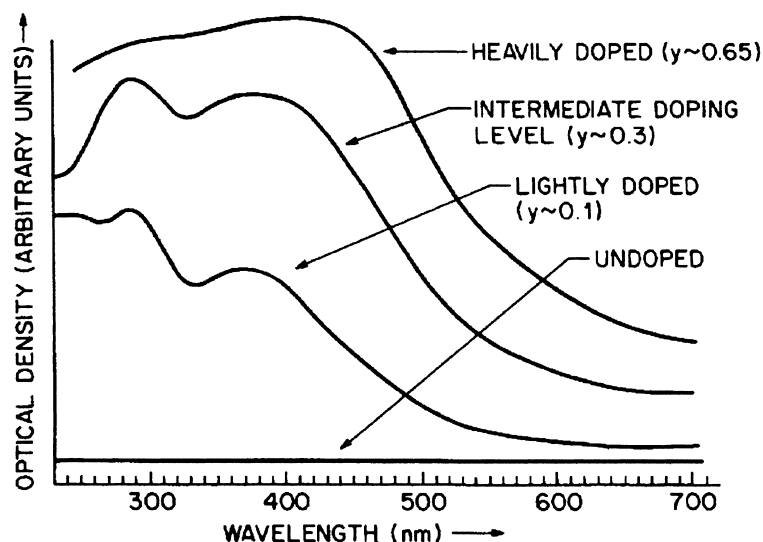

Figure 3. Optical absorption spectra of 1,4 *cis*-polyisoprene (natural rubber) for different molar concentrations (y) of iodine. From Reference 3 (J. Chem. Phys. **1989**).

[5]. All the experimental results as discussed above and in the following have shown that radical cation formation gives a consistent picture.

The solid-state ^{13}C NMR spectroscopic measurements (Cholli *et al*. *J. Chem. Phys.*, 1989) [4] have provided a clear and unequivocal insight regarding the effect of doping. The measurements have been made by detailed cross polarization and magic angle spinning (CP/MAS) techniques and the effects of doping on the backbone carbon atoms were elucidated. Some of the results of these measurements are shown in Figure 4. As Figure 4 shows, the intensity of the resonances for double-bond carbon atoms (α,β) decreases as the dopant concentration is increased. No new resonance appears in the downfield region (100–150 ppm) showing that new double bonds do not form or conjugation does not occur upon doping. FTIR results have also shown decrease of peak intensities of C=C stretching and =CH bending modes upon doping [2, 13]. The bands corresponding to the aliphatic region (b-d, Figure 4) have contribution from resonances of carbon atoms in the radical cations. The treatment of the doped polymer with a reducing agent such as ammonia leads to reformation of the double bonds. This has been confirmed by NMR measurements before and after treatment of the doped material with ammonia [4]. The color (black) of the doped material also disappears as it is reduced or dedoped. This reversibility of doping has not been studied in so much detail in the case of conjugated polymers. The abundant supply of natural rubber and ease of doping these materials has facilitated undertaking these detailed experiments. In addition, the detailed magnetic susceptibility and electron paramagnetic measurements have been made on this material (cis-polyisoprene) before and after doping and the generation of radicals (spin-1/2 species) with doping has been confirmed [3] Elemental analysis of the materials also showed that no conjugation resulted due to doping [5].

The electrical conductivity of the doped material has been measured as a function of temperature to elucidate the mechanism of charge transport [2]. The resistivity which is the reciprocal of conductivity has a specific temperature dependence: that is $\log\rho$ (ρ = resistivity) is linearly proportional to $1/T^{1/4}$, where T is the temperature in $^{\circ}K$. This result is consistent with the model of variable-range hopping of charge carriers between polaronic sites. The model of hopping conduction has been used in doped conjugated polymers such as polyacetylene as well [9]. A schematic of the conduction process in doped nonconjugated polymer is shown in Figure 5.

As observed by Thakur, a wide range of nonconjugated polymers becomes conducting upon doping provided those contain at least one double bond in the repeat. The final conductivity depends on the number fraction of double bonds in the repeat. The higher the number fraction of double bonds per repeat, higher is the conductivity since a larger number of charge carriers are created upon doping. For example, in polyisoprene, the number fraction is 1/4 (one out of four bonds is a double bond while three are single bonds). In the case of conjugated polymers, such as polyacetylene, the number fraction of double bonds is 1/2 (one out of two bonds is a double bond and the remaining one is a single bond) and consequently
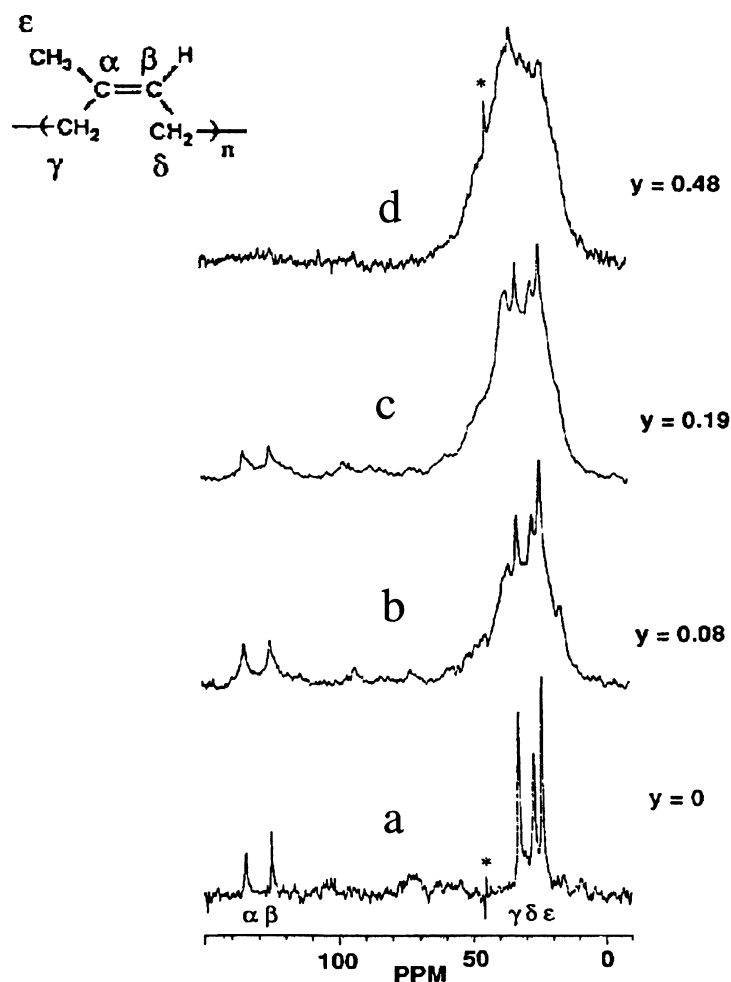
Figure 4. Solid state ^{13}C NMR spectroscopic results (from Reference 4) for 1,4-*cis*-polyisoprene with different doping levels (y = molar concentration) of iodine: (*a*) corresponds to undoped state; (*b*)–(*d*) correspond to polymer with increasing molar concentration of iodine. The spectra were recorded using cross polarization and magic angle spinning (67.9 MHz). The resonances corresponding to the double bonded carbon atoms (α,β) decrease in intensity with doping due to formation of radical cations. Formation of any conjugation upon doping is ruled out since double bond concentration decreases with doping. The carbon atoms in the radical cations contribute to the resonance peaks around the aliphatic carbons (γ, δ, ε).

polyacetylene has a larger electrical conductivity compared to polyisoprene. In contrast, a polymer having no double bonds such as polyethylene can not be conducting because there is no opportunity for a charge-transfer due to the lack of π-electrons (double bonds). Indeed, polyethylene can not be made conducting. Thakur's unpublished work has shown that the conductivity of polymers having number fraction of double bonds of 1/3 is higher conductivity than that of doped
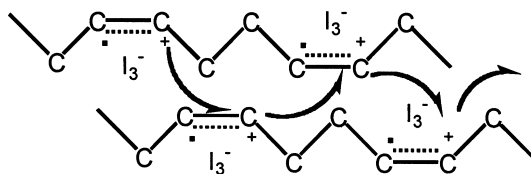
Figure 5. A schematic of electrical conduction in nonconjugated conducting plastic, doped natural rubber. The holes (positive charges) move by hopping between polaron sites as a voltage is applied.

polyisoprene. Thus, the invention of nonconjugated conducting polymers has provided a clear understanding of conductive plastics in general. Besides having a double bond in the backbone there are other requirements for a polymer to become conducting. These include crystalline and amorphous characteristics of the polymer. If the polymer is too rigid such that dopants can not penetrate then it can not be conducting whether it is conjugated or nonconjugated. The details of the effect of morphology on conductivity of conjugated and nonconjugated polymers are still to be fully understood. There have always been differences in views and opinions regarding mechanisms of conduction in conductive polymers since these are complex systems. The soliton theory in polyacetylene proposed by Heeger *et al.* was opposed by other groups [10].

A wide range of applications have been demonstrated using doped nonconjugated polymers. The nonconjugated polymers discussed above include natural rubber (1,4 *cis*-polyisoprene) which is naturally occurring (from plants), stable, inexpensive and far more easily processible than many polyacetylene. These plastics (e.g., *cis*-polyisoprene, natural rubber) have a broad range of commercial applications in household, industrial, transportation, medical and spacecrafts. About 15 billion pounds of elastomers is used in United States annually. Twenty percent of this total is *cis*-1,4-polyisoprene. The doped nonconjugated plastics have a wide range of technological applications. Examples of such applications include: antistatics, EMI shields, sensors, and specific optoelectronic devices. Antistatic applications do not require very high (metallic) conductivity, therefore, lightly doped nonconjugated plastics are appropriate. In addition, the material is suitable for corrosion-resistant paints and various other large volume applications in which the exceptionally low cost of the polymer and its processing is exploited. Specific doped nonconjugated polymers emit light in the visible wavelength range upon optical excitation implying applications in lasing. Field-effect transistors with p-channels formed by doped nonconjugated polymer films have been demonstrated.

In this article, a brief account of nonconjugated conductive polymers is presented. The author gratefully acknowledges the assistance he received from and the valuable discussions he had with Dr. Sukant Tripathy in some of the measurements discussed.

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