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A Class of Conducting Polymers Having Nonconjugated Backbones[†]

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ABSTRACT: Having a *conjugated* backbone is usually considered to be a *necessary* condition for a polymer to be electrically conducting.[1] This paper will demonstrate that, in association with appropriate substituents, a *nonconjugated* polymer system may also become electrically conducting. The chemical constitution, electrical transport, and optical properties of the conducting complexes of a specific class of such nonconjugated systems are discussed in this paper. The details of the origin of conductivity for such nonconjugated systems are studied for a specific example, 1,4-*cis*-polyisoprene, which is considered to be a prototype for this class. This is the first time that conducting complexes having isolated double-bond structurs are reported.

In the last 10 years extensive research has been performed on conducting polymers.[1-3] "Conducting polymers" is the unique area of research that has received equal attention from chemists and solid-state physicists as well as theoreticians. A substantial data base has been acquired from various experimental standpoints, and many novel theoretical concepts have emerged in relation to conducting polymers. The analyses and observations, so far, have identified conducting polymers as possessing fully conjugated backbones that are capable of undergoing charge transfer in association with appropriate electron acceptors or donors.[1] The structure and properties of such charge-transfer complexes have been studied in significant detail in the light of theoretical models such as solitons, polarons, bi-polarons, etc.[1-5] Overall "conducting polymers", at present, is considered a relatively mature area of research from the points of view of structural synthesis, experimental measurements, and theoretical understanding.[1]

At the conceptual level the prevailing assumption in this subject area has been that a *conjugated* backbone is a prerequisite for a polymer to become electronically conducting.[1] Although the significance of interchain processes has been recognized in the charge-transport mechanism of conducting polymers, the possibility of tailoring systems that are amenable purely to interchain charge-transport processes was not explored. In the earlier literature, the subject of charge-transfer complexes has been treated in detail for many smaller organic molecules and the effect of substituents in the charge transfer processes has been exemplified.[6] As it has been demonstrated, the basic molecular characteristics such as electronegativity, inductive effect, etc. of any substituent have major influences on the electron-donating or -accepting properties of any adjacent unsaturated bond.[7,8] In principle, given appropriate substituents and dopants, significant charge transfer may be expected even for isolated double-bond structures. Thus the charge-transfer capability should not be limited to conjugated systems alone. It is the degree and ease of charge transfer that may distinguish a conjugated system from a nonconjugated one. In a nonconjugated system, subsequent to charge transfer the conduction process may follow the interchain mechanism since the intrachain mechanism may be unfavorable. Thus under appropriate conditions specific nonconjugated systems may display electronic conductivity to a similar level as π-conjugated polymers. In this paper, this possibility will be exemplified with a specific class of organic polymers.

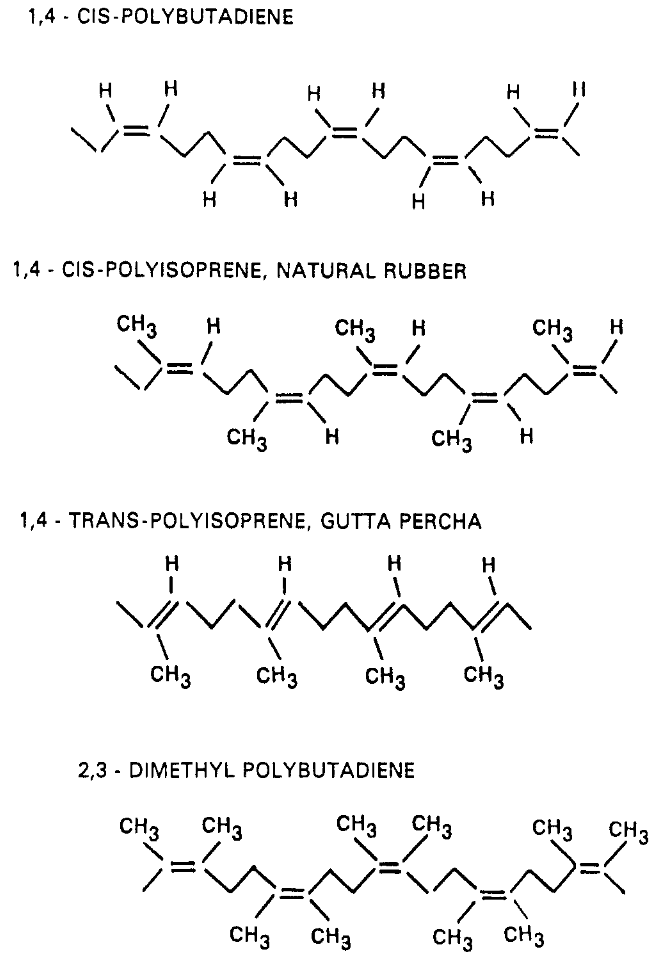
Experimental Section

The polymers that were investigated include 1,4-polyisoprene (synthetic and natural rubber, cis and trans), 1,4-polybutadiene, and poly(2,3-dimethylbutadiene), all of which possessed a substituted polybutadiene-type backbone (Figure 1). The samples were obtained from Firestone and Good Year Chemical companies, in the form of latex, pellet, and films. Standard electron acceptors such as I_2, Br_2, etc. have been utilized for doping of these polymers via established procedures.[1-3] The conductivities of the doped products were measured by the well-known four probe method at different dopant concentrations (Figure 2). Specifically the 1,4-*cis*-polyisoprene (natural rubber) was studied in more detail since that was a prototype for this class of materials. The dopant concentrations were measured gravimetrically. In order to determine whether there was any ionic contribution to the conductivity, an ion-bleaching test was utilized. A specific electrical current ($\sim 5\ \mu A$) was passed (N_2 atmosphere) through the samples for a long period of time (>1 month) amounting to the passage of a large quantity of charge so as to cause complete depletion of any existing ionic carrier. Since that did not lead to any decrease of the conductivity, it was concluded that the conductivity of these doped polymers was predominantly electronic. The sign of the carriers was determined by "hot probe" technique and was found to be p-type for the case of I_2 doping, as would be expected. The temperature dependence of conductivity was measured for a range of temperatures as displayed in Figure 3. In order to confirm the site of charge transfer, FTIR spectroscopy on thin-film samples was utilized at different doping levels. Optical absorption measurements before and after doping were accomplished by using a Cary spectrophotometer with thin-film samples on quartz substrates.

Results

Upon treatment with iodine, polybutadiene (hydrogen substituted, Figure 1) did not undergo any appreciable color change. The conductivity also remained as low as it was before treatment ($\sim 10^{-13}\ \Omega^{-1}\ cm^{-1}$). Polyisoprene (synthetic and Natural rubber, cis and trans), on the other hand, turned black upon complete doping with iodine. Poly(2,3-dimethylbutadiene) also underwent a similar change of color upon doping. These results clearly show that substituents have remarkable influence on the charge-transfer property of a polymer. The electrical conductivity of I_2-doped polyisoprene was in the range of 10^{-2}–$10^{-1}\ \Omega^{-1}\ cm^{-1}$ which is more than 10 orders of magnitude higher than what was observed at the pristine state ($\sim 10^{-13}\ \Omega^{-1}\ cm^{-1}$). For any given condition the rate of doping was faster in the case of poly(2,3-dimethylbutadiene) compared to polyisoprene, presumably because the former is disubstituted by the electron-donating methyl groups. This point will be discussed in more detail in the next section. Measurements of the electrical conductivity of polyisoprene as a function of the dopant concentration (Figure 2) showed that the conductivity saturates at a concentration of approximately 0.65 of iodine per repeat unit at room temperature. Thus the doped complex can be represented as $-(C_5H_8I_{.65})-$. In comparison with polyacetylene for iodine doping the carbon to iodine ratio at saturation was found to be similar.

[†] Part of this work done prior to joining AT&T Bell Laboratories.


1,4 - CIS-POLYBUTADIENE

1,4 - CIS-POLYISOPRENE, NATURAL RUBBER

1,4 - TRANS-POLYISOPRENE, GUTTA PERCHA

2,3 - DIMETHYL POLYBUTADIENE

Figure 1. Polymers that were used in this study.

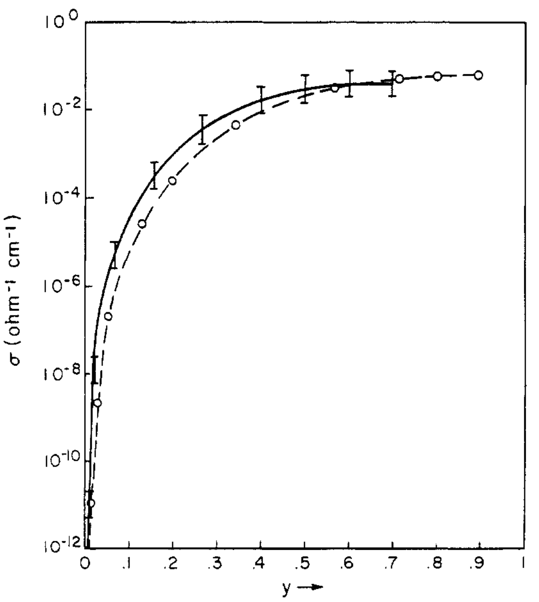


Figure 2. Electrical conductivities of doped *cis*-polyisoprene, *trans*-polyisoprene, and poly(dimethylbutadiene) as a function of molar concentration (y) of iodine. The data of *cis*- and *trans*-polyisoprene lie on the curve shown with the error bars. The other curve (dashed) corresponds to poly(dimethylbutadiene).

Measurements of the temperature dependence of the resistivity (Figure 3) showed that log ρ (ρ = resistivity) had a linear dependence on $1/T^{1/4}$ where T is the temperature in kelvin. This implies that the conduction mechanism in these systems includes primarily the hopping processes, as expected.[9,10]

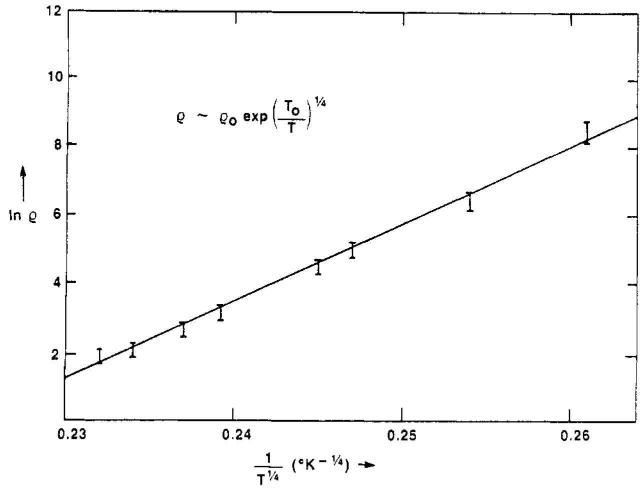


Figure 3. Variation of conductivity with temperature for doped ($y \simeq 0.65$) *cis*-polyisoprene.

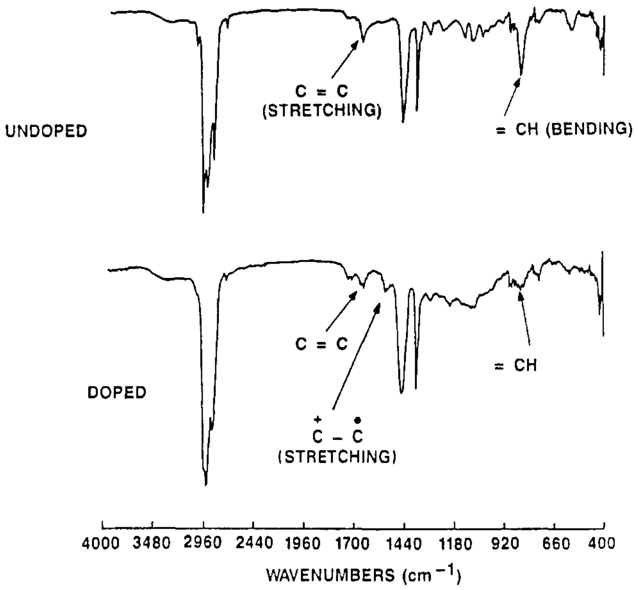
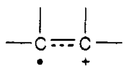


Figure 4. FTIR spectra of *cis*-polyisoprene before and after doping ($y \simeq 0.50$).

The site of the charge transfer upon doping was suggested by the FTIR spectra as shown in Figure 4. The absorption coefficients of the bands corresponding to –C=C– vibration modes (stretching, bending, etc.) decreased continuously as the dopant concentration was increased. Specifically the band at 836 cm^{-1} which corresponds to the bending mode of =CH decreased rapidly above a dopant concentration of $\sim$0.3. This is consistent with the fact that the material (e.g. natural rubber) loses flexibility upon doping. Another interesting feature one may note is that a new band began to appear at 1545 cm^{-1} while the –C=C– stretching mode at 1673 cm^{-1} was disappearing as a consequence of doping. This new band may very well be due to the radical cation



$$-\underset{\bullet}{\overset{|}{\mathrm{C}}}\cdots\underset{+}{\overset{|}{\mathrm{C}}}-$$

that is formed upon charge transfer. The increase of rigidity that was noted subsequent to doping may be caused by an interchain cross-linking mediated by the radical species that are generated. The FTIR results attested to the fact that no detectable dehydrogenation was caused by the iodine treatment. Thus the possibility of formation of any conjugation through dehydrogenation was ruled out.

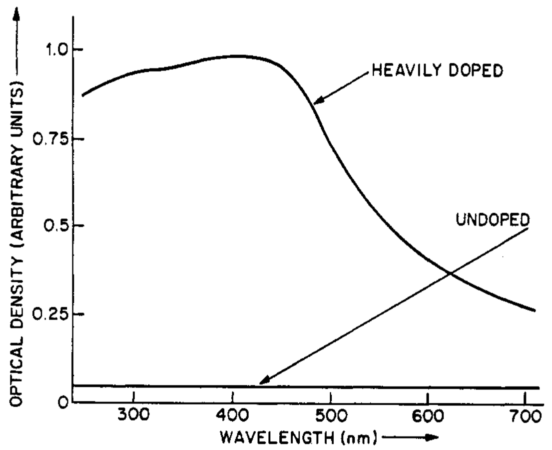


Figure 5. Optical absorption spectra of doped ($y \simeq 0.67$) and pristine natural rubber.

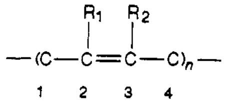
Treatment of the doped samples with NH_3 resulted in a reduction of the conductivity to the pristine level. Redoping with I_2 restored the conductivity to original value ($\sim 10^{-2}$–10^{-1} Ω^{-1} cm^{-1}). This reversibility of doping process implies negligible chemical bond formation of I_2 with the backbone.

The optical absorption spectra of 1,4-*cis*-polyisoprene before and after doping are shown in Figure 5. As stated earlier, for 1,4-polybutadiene no change in color was observed upon iodine treatment. However, as Figure 5 shows, polyisoprene absorbs strongly throughout the visible domain, upon complete doping with iodine. In the undoped state all the polymers in this class are colorless as would be expected for such isolated double-bond structures. The details of the evolution of absorption characteristic of polyisoprene as a function of the dopant concentration is presently under study and will be reported separately.

Discussion

The results presented above bring about some very intriguing conclusions regarding conducting polymers. First of all, a *conjugated* backbone is *not* a prerequisite for conducting polymers. However, some unsaturation along the backbone is required, along with appropriate substituents adjacent to the unsaturated sites. Without an appropriate substituent a backbone having an isolated double-bond structure may not become conducting. This is nicely demonstrated in the result that 1,4-polyisoprene forms a conducting complex with iodine whereas 1,4-polybutadiene does not. The inductive effect of the methyl substituent on the double bond in polyisoprene remarkably enhances the electron-releasing tendency of the backbone. Therefore the charge-transfer complexation becomes favorable for polyisoprene in association with the electron acceptors. Looking back on smaller organic molecules, such an inductive effect is also reflected in the higher reactivity of higher alkenes such as propylene compared to ethylene toward acid reagents.[11] Because of two methyl substituents around the double bond, poly(2,3-dimethylbutadiene) possesses even higher electron-releasing tendency (Table I). Consequently the rate of doping was higher in the case of poly(dimethylbutadiene) compared to polyisoprene. For the same reason the conducting complex of poly(dimethylbutadiene) with iodine was less stable toward partial iodination of the backbone as evidenced by a gradual loss of conductivity with time without any significant reduction of the iodine content. To look into the problem in some more detail, it was an interesting exercise to calculate the partial charges on the backbone carbon atoms for polybutadienes with different substituents using a standard chemical modeling routine (CNDO/2). CHEMLAB routine developed by Pearlstein and co-workers was used for this calculation.[12] As Table I shows, the carbon atoms on the double bonds of polyisoprene and other alkyl-substituted polybutadienes have much larger partial charges relative to unsubstituted polybutadiene. The accumulation of a negative partial charge is caused by the inductive effect of the substituents and is a measure of the electron-releasing tendency and therefore presumably the dopability of the backbone. Thus according to these calculations ethyl, propyl, and phenyl substituents would also be effective for the charge transfer.

Table I
Partial Charges at the Unsaturated Sites of Polybutadiene for Different Substituents[a]



$$-(\underset{1}{C}-\underset{2}{\overset{R_1}{C}}=\underset{3}{\overset{R_2}{C}}-\underset{4}{C})_n-$$

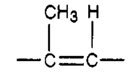
substituents		partial charges (electrons) at	
R_1	R_2	C_2	C_3
H	H	-0.005	-0.005
CH_3	H	+0.034	-0.031
CH_3	CH_3	-0.031	-0.031
C_2H_5	H	+0.027	-0.028
C_3H_7	H	+0.024	-0.027
C_6H_5	H	+0.035	-0.031

[a] The calculations were performed by CNDO/2 method.

Since these materials are predominently amorphous and the backbones nonconjugated, the charge transport must include an intersite hopping mechanism without any dimensional constraint. Therefore the temperature dependence of conductivity that was observed was as expected.[9,10]

The optical absorption spectrum of heavily doped polyisoprene is quite broad, presumably because of inhomogeneous donor–acceptor separations. For heavily doped charge-transfer complexes such a broad spectrum is not unexpected. The details of the origin of the optical states for these doped nonconjugated systems are not fully elucidated at present. Qualitatively the optical absorption can be explained as originated from a charge transfer (CT) excitation, modified by strong intersite Coulomb interactions.[13] A detailed quantitative analysis is underway.

On the basis of the FTIR analyses, the sequence of events during the doping process can be sketched as in Figure 6. In the first step the iodine atoms interacted with the



$$-\overset{CH_3}{C}=\overset{H}{C}-$$

groups and the charge transfer took place to generate the radical cation species. The FTIR results seem to indicate the absorption frequency of such radical cations. Subsequently, as more iodine atoms began to interact, the =CH bending mode started to decrease in intensity and also there was a gradual increase in the rigidity of the material indicating a partial cross-linking between chains as it has been observed for other conducting polymers upon doping.[14]

The magnitude of conductivity of iodine doped polyisoprene appears somewhat larger when compared to that of iodine-doped poly(methylacetylene), poly(phenylene sulfide), etc. However, this may be attributed to the difference in the morphology and flexibility of the rubber and the other systems. Overall, the experimental results seem to be explainable by simple and straightforward arguments. Electron-releasing groups other than those

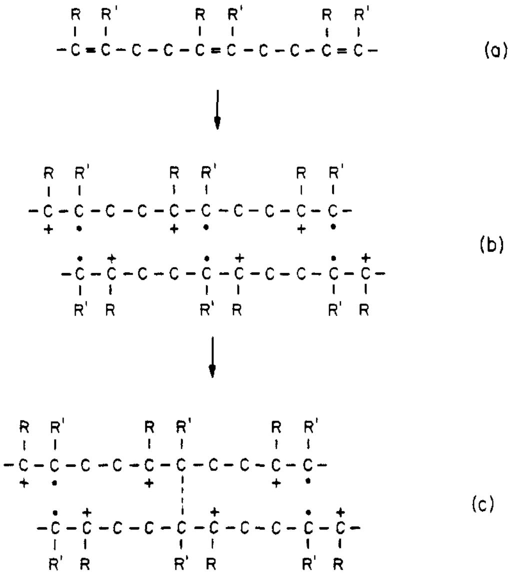


Figure 6. Schematic of the doping and partial cross-linking processes in the substituted polybutadiene systems: a, undoped; b, radical cations, generated by doping with electron acceptor; c, cross-linking via radical mechanism.

which were discussed in this paper (such as alkoxy, phenyl, etc.) might also lead to similar conducting properties. It should be pointed out that some rubbery systems including polyisoprene were previously utilized as binder materials for polyacetylene.[15] However, the inherent conductivity of polyisoprene was not identified.

Summary

Conducting polymers are not limited to conjugated systems alone. Through the influence of appropriate substituents, nonconjugated polymers may also form conducting complexes. This is exemplified with a class of polymers having substituted polybutadiene-type backbones. The significance of a methyl substituent as an electron-releasing group is clearly demonstrated by comparing 1,4-polyisoprene and 1,4-polybutadiene systems under identical doping conditions. The presence of electron-releasing substituents is proposed to be a key factor in the generation of conducting complexes for nonconjugated systems. The electrical transport in such complexes was shown to involve predominantly intersite hopping processes as might be expected. The site of charge transfer was identified to be the carbon–carbon double-bond position of the isolated double-bond structures. These results open up the scope of conducting polymers by including many other isolated double-bond structures and substituents for consideration as possible candidates for conducting polymers.

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Registry No. I_2, 7553-56-2; polybutadiene, 9003-17-2; poly(2,3-dimethylbutadiene), 25034-65-5.

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