

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Polyalloocimene, a Novel Nonconjugated Conductive Polymer: The Correct Fundamental Basis for Conductive Polymers

M. Thakur^a; S. Khatavkar^a; E. J. Parish^a

^a Photonic Materials Research Laboratory, 201 Ross Hall, College of Engineering and Engineering Experiment Station, Auburn University, Alabama, USA

Online publication date: 10 July 2003

To cite this Article Thakur, M. , Khatavkar, S. and Parish, E. J.(2003) 'Polyalloocimene, a Novel Nonconjugated Conductive Polymer: The Correct Fundamental Basis for Conductive Polymers', *Journal of Macromolecular Science, Part A*, 40: 12, 1397 – 1406

To link to this Article: DOI: 10.1081/MA-120025318

URL: <http://dx.doi.org/10.1081/MA-120025318>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Polyalloocimene, a Novel Nonconjugated Conductive Polymer: The Correct Fundamental Basis for Conductive Polymers

M. Thakur,* S. Khatavkar, and E. J. Parish

Photonic Materials Research Laboratory, College of Engineering and Engineering Experiment Station, Auburn University, Alabama, USA

ABSTRACT

A polymer does not have to be conjugated to become electrically conductive. The correct fundamental basis for a polymer to be conductive is that it must have at least one double bond in the repeat. The magnitude of conductivity increases with the number fraction of the double bonds in the repeat. Polyisoprene, the first known nonconjugated conductive polymer has a double bond number fraction of 1/4 while polyacetylene, the first known conjugated conductive polymer, has a number fraction of 1/2. A new nonconjugated conductive polymer, polyalloocimene, has a double bond number fraction of about 1/3. Consequently, the electrical conductivity, the doping rate and the optical transition energies of polyalloocimene are intermediate between those of polyisoprene and polyacetylene. The magnitude of conductivity has a power law dependence on the number-fraction of double bonds. The optical absorption peak of the radical cation produced upon doping appears at lower energies as the separation between the double bonds decreases. The general mechanism of conductivity going from a nonconjugated structure involving isolated double bonds to a fully conjugated structure has been established.

Key Words: Nonconjugated conductive polymer; Polyalloocimene; Dopant; Radical cation.

*Correspondence: M. Thakur, Photonic Materials Research Laboratory, 201 Ross Hall, College of Engineering and Engineering Experiment Station, Auburn University, AL 36849-5351, USA; Fax: 334-844-3307; E-mail: mthakur@eng.auburn.edu.



INTRODUCTION

Conjugation is not a prerequisite for a polymer to be electrically conductive.^[1-5] Although a majority of the past research effort was focused on conjugated polymers, a broad range of nonconjugated conductive polymers offering unique advantages have been studied. The first conjugated polymer reported to become electrically conductive upon doping with iodine is polyacetylene having alternating double and single bonds in the backbone.^[6] The first nonconjugated conductive polymer is 1,4-*cis*-polyisoprene that has double bonds separated by three single bonds in the repeat along the backbone.^[1] Doping with iodine leads to about a billion times increase in conductivity of polyacetylene. In polyisoprene, a similar doping procedure with iodine leads to an increase of conductivity by about 100 billion times. The final levels of conductivity in the two polymers are different: for polyacetylene it is about 100 S/cm and for polyisoprene the magnitude is about 0.1 S/cm. The overall results show that the conductivity increases with the number fraction of the double bonds in the polymer repeat. In polyacetylene the number fraction of double bonds is 1/2 and in polyisoprene it is 1/4. In this paper, we will discuss another polymer that has a structure intermediate between polyisoprene and polyacetylene. This new polymer, polyalloocimene, has a number fraction of double bonds of about 1/3. Studies of this polymer in comparison with other nonconjugated and conjugated polymers provide a clear insight into the general mechanism of electrical conductivity in conductive polymers.

Studies limited to conjugated systems alone led to the incorrect conclusion that a band structural approach with specific details of excitations provides a general picture of the electrical conduction in conductive polymers. This incorrect conclusion inevitably leads to an incorrect prediction that a nonconjugated polymer having a large band gap (>6 eV) cannot be doped and should behave like an insulator. The experimental results from studies of polyisoprene and other nonconjugated conductive polymers prove this conclusion to be incorrect and nonfactual. In order to achieve a general understanding of conductive polymers we cannot rely on the band picture borrowed from inorganic semiconductors such as silicon. Interaction of the dopants at the molecular level is critical to consider to achieve a general and correct understanding of conductive polymers. The studies discussed in this paper involving polyalloocimene along with previous results on conductive polymers having isolated double bonds elucidate the general mechanism of electrical conduction in conductive polymers.

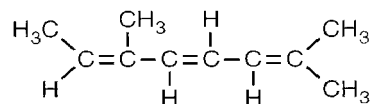
EXPERIMENTAL

Synthesis

Polyalloocimene was synthesized by polymerization of alloocimene (2,6-dimethyl-2,4,6-octatriene) in the presence of a metal catalyst dispersed in a substantially anhydrous ether component under an inert gas atmosphere. The details are described in the literature.^[7] Alloocimene was purchased from Aldrich Chemicals Corp. The reaction was undertaken using sodium as the catalyst in dry toluene and under nitrogen atmosphere. The polymer after purification and separation is a nearly clear solid. The chemical structures of alloocimene and the isomers of polyalloocimene are shown in Fig. 1.



2,6 - Dimethyl - 2,4,6-octatriene



Polyalloocimene (Isomers)

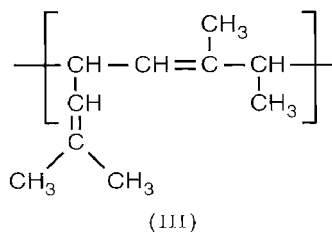
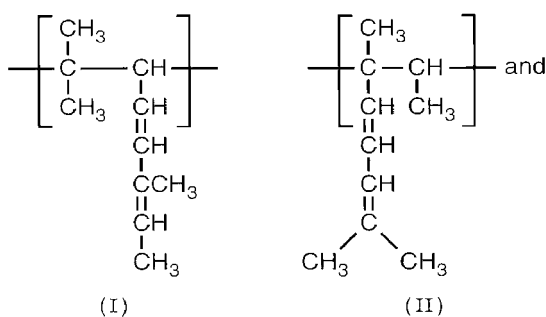


Figure 1. Monomer and polyalloocimene isomers.

Doping

A thin film of polyalloocimene on a quartz substrate was cast from a solution in tetrahydrofuran (THF). The film is colorless in the undoped state. The film was exposed to iodine vapor over various time periods and the corresponding weight uptakes were measured. The conductivity of the film for different dopant concentrations was determined by four-probe method. The maximum conductivity observed is about 1 S/cm for a doping level of about 1.2 iodine atoms per repeat. The concentration of iodine is consistent with the large chain-repeat of polyalloocimene. The doping rate of the polyalloocimene film was studied in comparison with that of a 1,4-*cis*-polyisoprene film of a similar thickness cast on a quartz substrate from a hexane solution. The polyalloocimene turned black within about 30 min of doping while polyisoprene needed a few hours to become black in appearance. Thus the doping rate of polyalloocimene is significantly higher than that of



polyisoprene. As reported earlier, the maximum electrical conductivity of polyisoprene is about 0.1 S/cm.

Optical Absorption Spectroscopy

Optical absorption spectra of the polymer film on a quartz substrate were recorded using a spectrophotometer for various dopant concentrations (Fig. 2). In the undoped state, the absorption is negligible in the visible domain. As the film was doped with iodine, absorption maxima appeared at 3.7 and 3.1 eV. At higher doping, the overall absorption increased and the absorption band of the lower energy peak became broader and shifted toward lower energy—thus covering the visible domain. The film turned black at high doping. This is similar to that observed for doping of polyisoprene. However, the overall absorption spectrum (peaks) for doped polyalloocimene appeared at lower energies than that observed in the case of doped polyisoprene. The peaks in the case of lightly doped polyisoprene^[2] appeared at 4.27 and 3.30 eV.

FTIR Spectroscopy

Polyalloocimene thin film on a sodium chloride substrate was used for FTIR spectroscopic studies. A Perkin Elmer spectrometer was used for these measurements.

Optical Absorption Spectra of Polyalloocimene

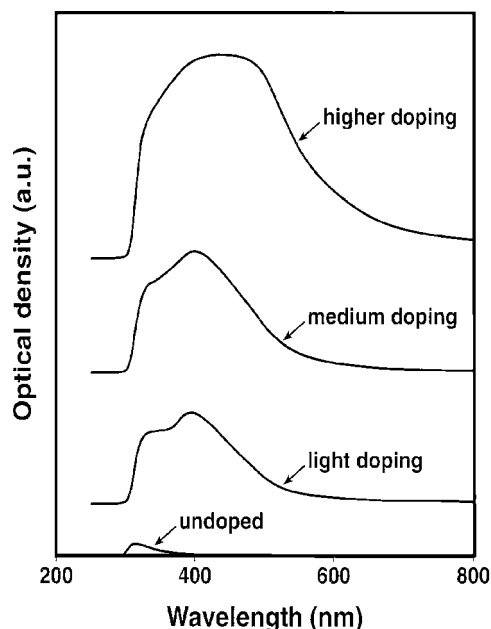


Figure 2. Optical absorption spectra of polyalloocimene for various doping levels.



The spectra were recorded for different dopant concentrations (Fig. 3). In the undoped film, peaks corresponding to the methyl vibrations (1447 and 1376 cm^{-1}) and the $=\text{C}-\text{H}$ bending mode (964 cm^{-1}) were pronounced. As the film was doped, the peak corresponding to the $=\text{C}-\text{H}$ bending mode rapidly reduced because of the charge transfer from the double bond to the dopant and consequent formation of radical cations. This result is similar to that observed for polyisoprene in which case also a reduction of the peak corresponding to the $=\text{C}-\text{H}$ bending mode was observed with the increase of doping. The peak corresponding to the symmetric vibration (1376 cm^{-1}) of methyl group attached to the double bond is also relatively reduced upon doping.

RESULTS AND DISCUSSION

As the absorption spectra show, the undoped film is essentially nonabsorbing in the visible with a small absorption in the ultraviolet. Upon doping, a peak similar to that observed in lightly doped polyisoprene but at a lower energy is observed. This is assigned

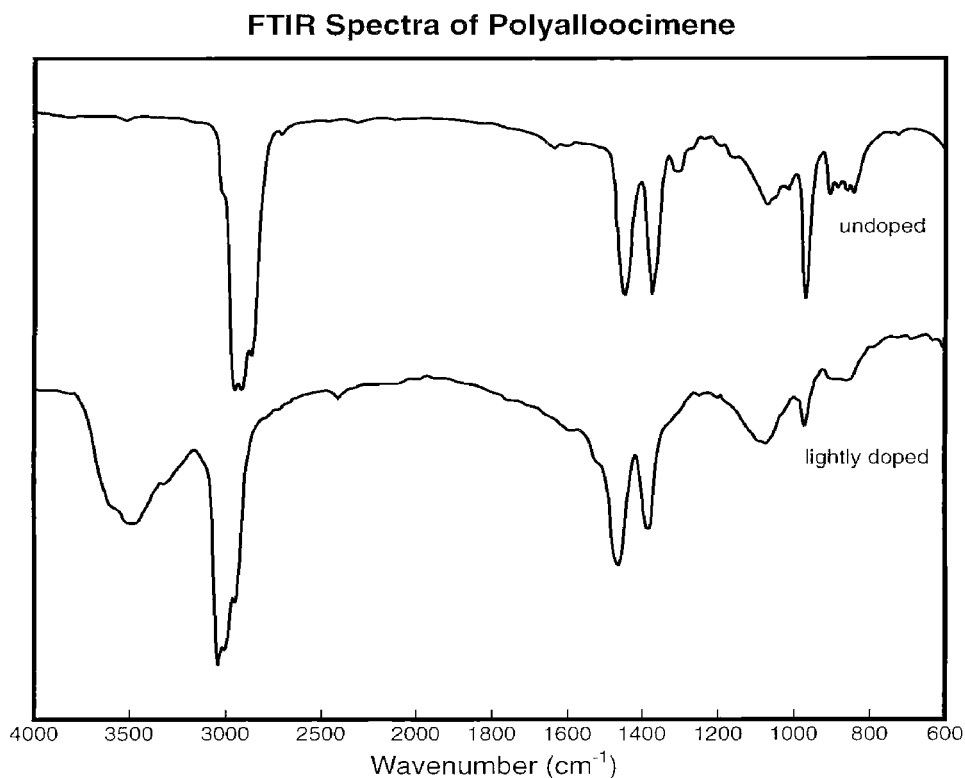


Figure 3. FTIR spectra of undoped and doped polyalloocimene.



to the optical transition of the radical cation formed upon doping and charge-transfer. The shift of this peak to a lower energy is explained as due to a reduction of the average distance between the double bonds in the repeat compared to that in polyisoprene. The peak at the lower energy corresponds to the charge-transfer state formed between the cation and the dopant. The reduction in the average distance between the double bonds in the repeat causes a slight red shift of this peak as well compared to that observed in lightly doped polyisoprene. This band becomes broader and stronger with doping because of the reduction in the average distance between the double bond and dopant molecules. The transition in the radical cation is explained using the valence band approach, which involves Coulomb correlation. The value of the hopping integral between the carbon atoms obtained from the experimental optical gap leads to the correct estimation of the optical gap in ethylene molecule in the valence band approach including the appropriate Coulomb term. This has been discussed in Ref.^[2].

The FTIR results show that double bonds decrease with doping and charge-transfer. A broad background-absorption appears in the infrared region due to the band-tail of the electronic absorption. This is a common characteristic of conductive polymers upon doping. As previously shown using solid-state ¹³C-NMR spectroscopy in the case of 1,4-*cis*-polyisoprene, doping does not lead to conjugation.^[3] No new double-bonded carbon resonance appears upon doping. The peaks corresponding to the double-bond carbon atoms decrease in intensity with doping as the radical cations are produced. This decrease is reversible (with dedoping using ammonia). The doped polymers (polyisoprene and polyalloocimene) become colorless again upon dedoping. Theoretical studies of the FTIR spectrum of radical cations of polyisoprene have been reported.^[8] Formation of I₃⁻ upon doping and charge transfer from the isolated double bonds in polyisoprene has been reported.^[9] Doping of conjugated polymers also leads to formation of I₃⁻.

The electrical conductivity of doped polyalloocimene film is higher than that of doped polyisoprene. The maximum conductivity of doped polyisoprene after saturation is about 0.1 S/cm. In doped polyalloocimene the conductivity reaches about 1.0 S/cm. As reported in the literature,^[6] the maximum conductivity in doped polyacetylene for iodine doping is about 100 S/cm. With these results, the final electrical conductivities can be correlated with the different number fractions of double bonds in the polymers. The chemical structures of the nonconjugated and conjugated polymers are compared in Fig. 4. In Table 1, the number fractions of double bonds, number of single bonds separating the double bonds in the repeat and the corresponding maximum electrical conductivities are compared. An approximate empirical correlation between the conductivity and the number fraction is as follows. $\sigma \sim 10^5 f^{10}$, where σ represents conductivity in S/cm and f represents the number fraction of double bonds. Another correlation that can be established involving the number of single bonds separating the double bonds and the conductivity is as follows: $\sigma \sim 3000 \exp(-3.5n)$, where n represents the number of single bonds separating the double bonds. These correlations are essentially empirical and should provide guidance regarding the expected level of conductivity for a given number-fraction of double bonds in a polymer. Besides the number-fraction of double bonds there are other critical factors to enhancement of conductivity in polymers upon treatment with a dopant. These include rigidity of the polymer chain—whether the polymer is glassy, crystalline, or flexible. In rigid polymers including polymer crystals, dopants cannot diffuse easily to interact with the unsaturated bonds. Therefore, even with a larger number fractions of double bonds



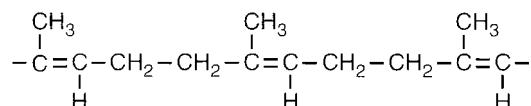
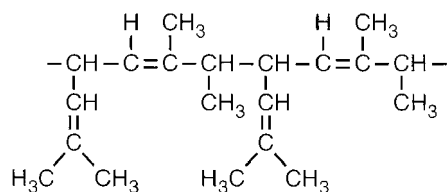
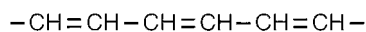
1) Polyisoprene2) Polyalloocimene3) Polyacetylene

Figure 4. Comparison of molecular structures of polyisoprene, polyalloocimene, and polyacetylene.

electrical conductivity may be small unless the polymer is flexible. For example, polystyrene which is glassy cannot be made conductive (maximum conductivity $\sim 10^{-6}$ S/cm) upon doping even though it has double bonds in the repeat. Polydiacetylene crystals cannot be made appreciably conductive (maximum conductivity $< 10^{-4}$ S/cm)

Table 1. Correlation between number fraction of double bonds and electrical conductivity.

Polymer	Number fraction of double bonds (f)	Number of single bonds between double bonds (n)	Maximum conductivity (σ) (S/cm)
Polyisoprene	1/4	3	0.1
Polyalloocimene	1/3	2	1.0
Polyacetylene	1/2	1	100



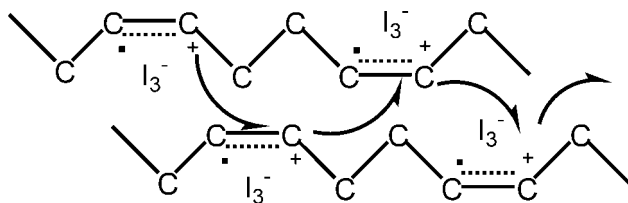


Figure 5. Schematic of the intersite hopping transport in a doped nonconjugated conductive polymer (polyisoprene).

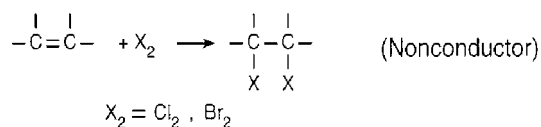
even though the chain contains fully conjugated bonds. The important conclusion of this work is that as long as a polymer is dopable, the conductivity will increase with the increase in the number fraction of double bonds or equivalently with a decrease in the number of single bonds separating the double bonds.

A seriously incorrect statement in the web page of the Nobel Foundation (www.nobel.se/chemistry/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." The press releases also make a similarly nonfactual statement: "For a polymer to be able to conduct electric current it must consist alternately of single and double bonds between carbon atoms." The semiconductor band model used to explain the mechanism of conduction in conductive polymers is consistent with such an incorrect conclusion. The present report clearly points out the error committed by most in the field in the basic understanding of conducting polymers. Conjugation is not a requirement. As long as charge-transfer is possible, electrical conduction will occur through hopping transport of carriers between charge-transfer sites involving isolated double bonds (Fig. 5). Higher the number of double bonds higher is the probability of charge-transfer and the number of carriers leading to a higher conductivity.

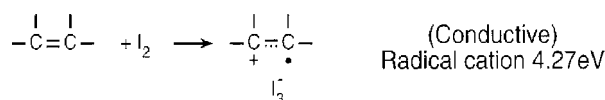
The interaction of a dopant such as iodine with the double bond can be explained as in Fig. 6. As is well known, halogens such as chlorine and bromine directly add to the double bond (electrophilic addition) due to their high electronegativities. In direct addition to the double bond, a single bond between the carbon atoms is produced, therefore, there is no increase in the electrical conductivity. This occurs for conjugated polymers as well. Thus, doping with chlorine and bromine does not lead to enhancement of conductivity. Iodine is not as electrophilic as bromine or chlorine, therefore its direct addition to the double bond does not lead to a stable product. Instead, iodine forms a charge-transfer complex via attracting an electron from the double bond. In the case of an isolated double bond, such a complex is localized compared to the conjugated double bonds. As the double bonds are brought closer that is the number of single bonds separating the double bonds is decreased, there is more overlap and greater statistical probability of forming a charge-transfer complex with the dopant. Therefore, the doping rate and the maximum electrical conductivity is increased with the double bond number fraction. The increased overlap between the double bonds at a higher number fraction leads a red shift of the radical cation peak that is formed upon doping and charge-transfer. The radical cation peaks for the nonconjugated polymers polyisoprene and polyalloocimene appear at 4.2 and 3.7 eV, respectively. Thus, there is a 0.5 eV red-shift



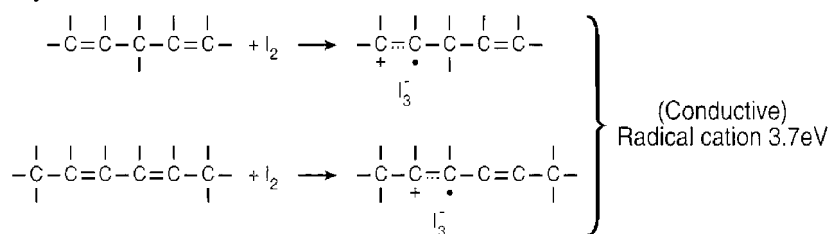
Electrophilic Addition



Polyisoprene



Polyalloocimene



Polyacetylene

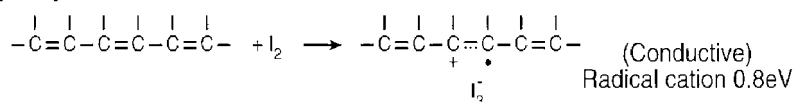


Figure 6. Effect of doping on conductive polymers with different double-bond number fractions.

with the increase of the double bond number fraction from 1/4 to 1/3. The radical cation peak of polyacetylene appears at 0.8 eV. A correlation can be established between the excitation energies and the number of double bonds in the repeat by using simple quantum chemical models such as the infinite potential well.

CONCLUSION

The general mechanism of electrical conductivity is best understood by starting with an isolated double system, and then adding more double bonds toward a fully conjugated chain. Consideration of the potential chemical reactions that may occur with the dopant provides an added dimension to the correct understanding of the fundamental basis of conductivity in polymers. The overall conclusion therefore, is that a polymer must have at least one double bond in the repeat to become conductive. The higher the number of double bonds in the repeat, the larger the conductivity and doping rate and the lower the



optical transition energy associated with the radical cation. These constitute the fundamental basis of conductive polymers in general.

REFERENCES

1. Thakur, M. A class of conducting polymers having nonconjugated backbones. *Macromolecules* **1988**, *21*, 661.
2. Thakur, M.; Elman, B.S. Optical and magnetic properties of a nonconjugated conducting polymer. *J. Chem. Phys.* **1989**, *90*, 2042.
3. Cholli, A.L.; Thakur, M. Structural investigation of a nonconjugated conducting polymer by solid state ^{13}C -nuclear magnetic resonance spectroscopy. *J. Chem. Phys.* **1989**, *91*, 7912.
4. Yu, G.-Q.; Thakur, M. Electrical conduction in a nonconjugated polymer doped with SnCl_4 and SbCl_5 . *J. Polym. Sci. Pol. Phys.* **1994**, *32*, 2099.
5. Thakur, M. Nonconjugated conductive polymers. *J. Macromol. Sci.—Pure and Appl. Chem.* **2001**, *A38* (12), 1337.
6. Shirakawa, H.; Louis, E.J.; MacDiarmid, A.G.; Chiang, C.K.; Heeger, A.J. Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, $(\text{CH})_x$. *J. Chem. Soc., Chem. Comm.* **1977**, 578.
7. Veazey, R.L. Terminally Functionalized Poly(alloocimene). US Patent, 4,690,979, September, 1987.
8. Orlandi, G.; Zerbetto, F. The infrared spectrum of a nonconjugated conducting polymer. *Chem. Phys. Lett.* **1991**, *187*, 642.
9. Myer, Y.P.; Chen, Z.J.; Frisch, H.L. Resonance Raman spectroscopic study of an iodine-doped pseudo-interpenetrating polymer network of natural rubber-poly(carbonate urethane). *Polymer* **1997**, *38*, 729.

