

A conductive polymer from *cis*-1,4-polybutadiene

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Abstract

This study reports that *cis*-1,4-polybutadiene can be converted into a semiconductor when doped with iodine. The conductivity achieved by iodine doping was about 10^{-6} S/cm. The products were characterized by elemental analysis, FT-IR, differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) techniques. Temperature dependence of electrical conductivity exhibits a semiconductor behavior.

Keywords: *cis*-1,4-Polybutadiene; Iodine doping; Semiconductors; Conductivity

1. Introduction

For many years there has been interest in the production of electrically conductive polymers. In 1906, photoconduction in organic solids was found for anthracene [1]. Later on, work on electrical conduction for organic solids was reported from the late 1940s to early 1950s for certain classes of organic compounds. Phthalocyanines have been found to show electrical conductivity [2]. Electrical conduction was observed for highly condensed polycyclic aromatic hydrocarbons whose molecular structure resembles that of graphite, which is known to be highly conductive [3]. In the mid 1970s Shirakawa and Ikeda [4] discovered that polyacetylene can be made into films having metallic luster and low level conductivity. This conductivity can be increased 9–13 orders of magnitude by doping with various donor and acceptor species to give p-type or n-type semiconductor and conductor complexes. Many modifications of polyacetylene have been prepared including substitutions [5] and conjugation length variations [6,7]. Most conductive polymer research has focused on conjugated polymers like polyacetylene which have long series of alternating single and double bonds. In order to have conductivity, conjugation was nonetheless thought to be necessary because the electrons have to be delocalized over a large distance to produce a small energy gap between valence and conduction bands.

In 1988 nonconjugated polymer conductivity was discovered by Thakur [8]. He found that conjugation is not neces-

sary for a polymer to be conducting. Thakur reported that when natural rubber, *cis*-1,4-polyisoprene (which has an isolated double bond with no conjugation), was treated with I₂ it becomes 10 orders of magnitude more highly conducting than native rubber. He also reported that this effect was also seen with *cis*-1,4-(2,3-dimethylbutadiene) but not with *cis*-1,4-polybutadiene. In 1990 Hudson and co-workers [9] reported that *trans*-1,4-polybutadiene becomes conducting upon treatment with I₂. In 1994 Dai et al. [10] reported that *trans*-1,4-polybutadiene becomes conducting but *cis*-1,4-polybutadiene does not become conducting when doped with I₂. Lastly, in 1996 Dai et al. [11] again reported that the conductivity of *trans*-1,4-polybutadiene can be increased by eight orders of magnitude upon conjugation and self-doping by I₂ at room temperature, whereas *cis*-1,4-polybutadiene cannot be conducting by reaction with I₂ under the same conditions.

In contrast to the previous reports the results in this paper show that *cis*-1,4-polybutadiene can be obtained as a semiconductor material when doped with I₂. Characterization and temperature dependence of conductivity are also studied.

2. Experimental

2.1. Materials

Samples of *cis*-1,4-polybutadiene were purchased from Yarpet Chemical Company. Crosslinked and linear samples of polybutadiene (PBD) contain 98% *cis* isomer as seen from

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the FT-IR spectrum. The *cis*-1,4-polybutadiene is doped with I_2 by two different methods: vapor phase doping and solution doping.

2.1.1. Vapor phase doping

Vapor phase doping was performed by exposure of polymer films to I_2 vapor.

2.1.2. Solution doping

The *cis*-1,4-polybutadiene was dissolved in chloroform. A weighed amount of I_2 was also dissolved in the solution. After evaporation of solvent, doped polymer was obtained as a dark brown film and it was dried by a dynamic vacuum.

2.1.3. Preparation of polymer films

Polymer films were cast from polymer solutions or polymer and I_2 solutions in chloroform in flat Teflon molds. After evaporation of the solvent, the cast films were dried under vacuum.

2.2. Measurements

FT-IR spectra of the samples were taken with a Mattson 1000 FT-IR spectrometer. Samples were prepared as films or as pellets in KBr. For thermal analysis, a TA-General V4 1C Dupont 2000 differential scanning calorimeter was used. Conductivity measurements were carried out by using standard two-probe and/or four-probe techniques. Mechanical measurements were carried out by using an Instron mechanical tester. Thermal gravimetric analysis (TGA) was performed by a Dupont 2000 TGA analyzer.

Table 1
Mole I_2 per mole BD unit used for doping reactions

Sample ^a	I_2 (mol)	BD unit (mol)	I_2 (mol)/ BD (mol)	Conductivity (S/cm)
1c	5.00×10^{-3}	4.68×10^{-3}	1.07	10^{-6}
2	4.98×10^{-3}	4.69×10^{-3}	1.06	10^{-6}
3	4.97×10^{-3}	4.68×10^{-3}	1.03	10^{-6}
4c	5.00×10^{-3}	4.68×10^{-3}	1.01	10^{-6}
5c	2.12×10^{-2}	2.12×10^{-2}	1.0	10^{-6}
6	5.24×10^{-3}	6.99×10^{-3}	0.75	– ^b
7c	3.00×10^{-3}	4.67×10^{-3}	0.64	10^{-6}
8	2.49×10^{-3}	4.68×10^{-3}	0.53	– ^b
9	4.73×10^{-3}	9.41×10^{-3}	0.50	– ^b
10	1.25×10^{-3}	4.68×10^{-3}	0.27	– ^b
11	3.47×10^{-5}	2.77×10^{-4}	0.13	– ^b

^a c: crosslinked samples.

^b Conductivity values less than 10^{-13} S/cm.

3. Results and discussion

Linear and crosslinked samples of *cis*-1,4-polybutadiene were studied. Both of them became conducting after I_2 doping by using vapor phase doping and solution doping methods.

In vapor phase doping, conductivity could not be achieved before about 2 weeks and it took about 2 months to reach the maximum conductivity (5.8×10^{-6} S/cm)

Different ratios of mole I_2 per BD unit were used for solution doping reactions. The doping ratios play an important role in conductivity (Table 1). For crosslinked samples when the doping ratio of I_2 (mol)/BD unit (mol) was more than 0.64, *cis*-1,4-polybutadiene became conducting. The maximum ratio of I_2 (mol)/BD unit (mol) was nearly 1.00 (in

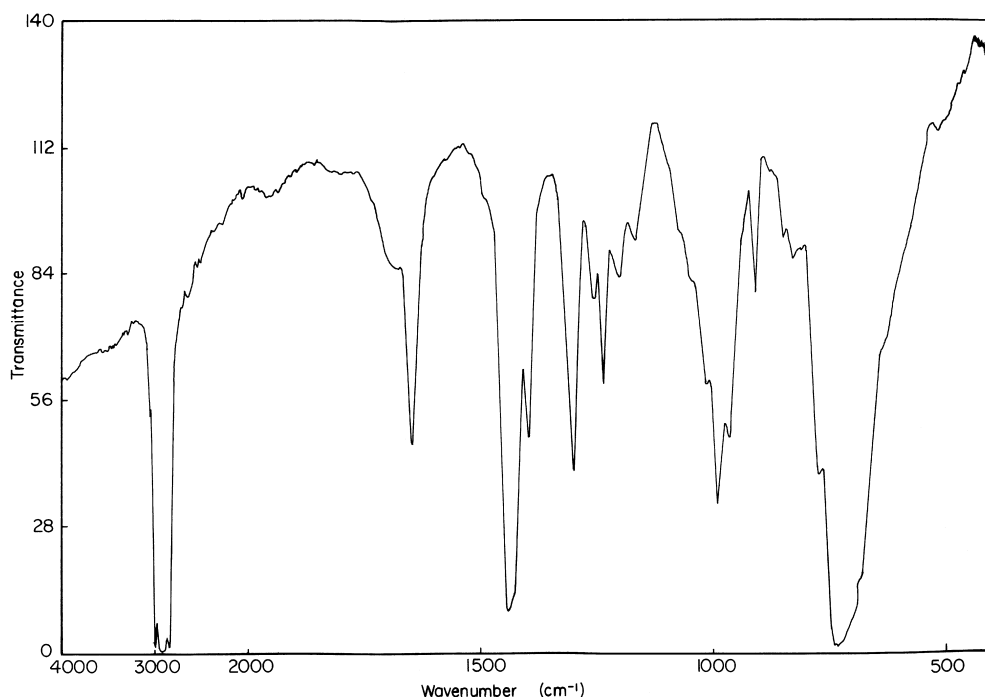
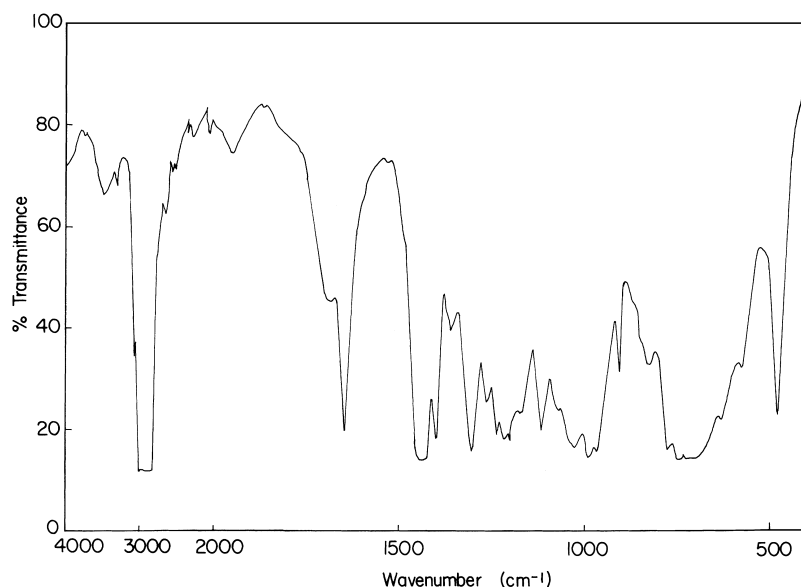
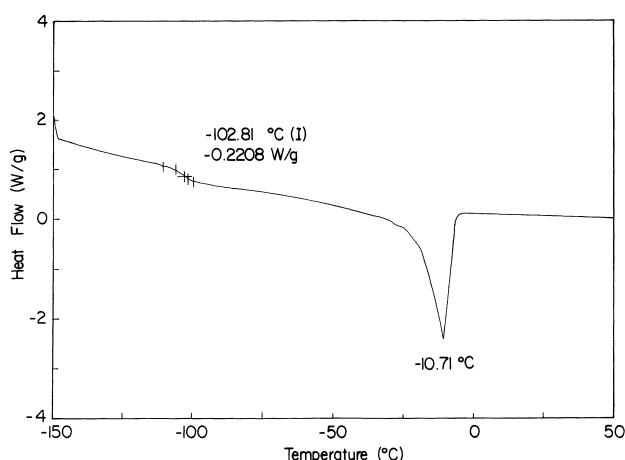
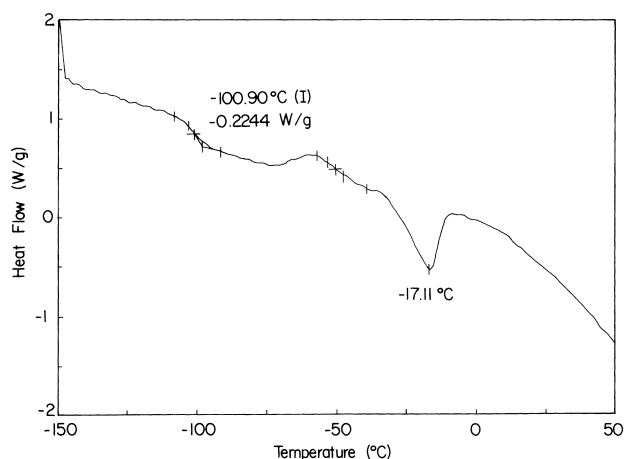


Fig. 1. FT-IR spectrum of *cis*-1,4-polybutadiene before I_2 doping.

Fig. 2. FT-IR spectrum of *cis*-1,4-polybutadiene after I₂ doping.Fig. 3. DSC curve of *cis*-1,4-polybutadiene before I₂ doping.Fig. 4. DSC curve of *cis*-1,4-polybutadiene after I₂ doping.

this condition I₂ was in excess in solution). Comparison of the data which for sample 6 and sample 7c (Table 1) shows that, for linear samples, the I₂/BD mole ratio must exceed

0.75 in order to get a conductive polymer, whereas this limit is lower (0.64) for the crosslinked sample. The linear *cis*-1,4-polybutadiene lost its conductivity when it was dried in a strong vacuum. These results show that I₂ was kept more tightly in crosslinked PBD compared to the linear PBD.

The conductivity of I₂-doped *cis*-1,4-polybutadiene as measured in this work (10^{-6} S/cm) is about five orders of magnitude smaller than that of I₂-doped *cis*-polyisoprene (10^{-2} – 10^{-1} S/cm) [8,12]. The difference in conductivities of *cis*-polyisoprene and *cis*-1,4-polybutadiene illustrates the role of the methyl group in enhancing the conductivity by increasing the electron density in the double bonds.

The *cis*-1,4-polybutadiene was reacted with I₂ at room temperature. The FT-IR spectra are shown in Fig. 1. The spectrum of *cis*-1,4-polybutadiene is the same as the spectrum in the literature [4]. The *cis* and *trans* isomers can be distinguished by their characteristic –CH₂– and CH– stretching bands in the region of 2700–3000 cm⁻¹. Following the reaction with I₂, doped polybutadiene is obtained, and a new peak is observed at 480 cm⁻¹ in the FT-IR spectra (Fig. 2), which was attributed to the C–I stretching vibration. These changes in the FT-IR spectra are consistent with the addition of I₂ to the C=C bonds along polybutadiene backbones [10]. The FT-IR spectra show that the relative intensities of the bands in the region 600–1500 cm⁻¹ significantly decrease upon doping. The origin of these changes may be the charge transfer interaction of the polymer with the I₂.

The results of the glass transition measurements are given in Figs. 3 and 4. Although the I₂-doped polymer was hard, the glass transition temperature was still observed at the same temperature as in the pristine polymer (about –100 °C). Thus, there is not a considerable change in the glass transition temperature of *cis*-1,4-polybutadiene upon I₂ doping.

The changes in mechanical properties were tested by using an Instron mechanical tester. There is a dramatic change in

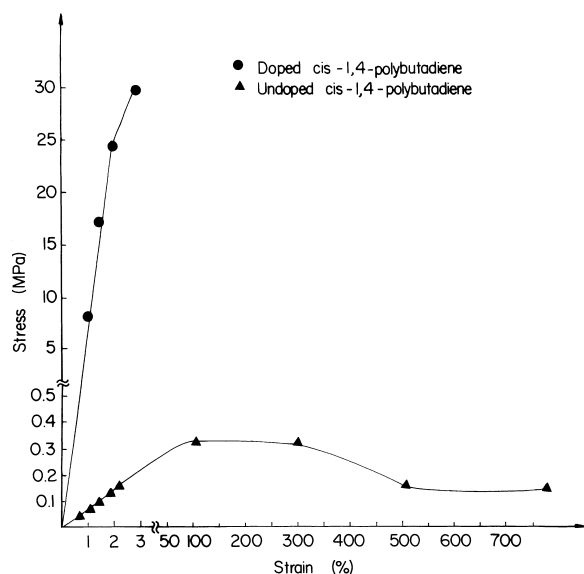


Fig. 5. Stress vs. percentage strain graph plotted for doped and undoped *cis*-1,4-polybutadiene.

Table 2
Mechanical testing results

Sample	Elongation at break (%)	Stress at break (MPa)	Elongation modulus (MPa)
PBD	2.96	0.187	1260
DPBD	760	29.6	1.7

Table 3
Elemental analysis results

Sample	%C	%H
PBD	88.32	11.43
DPBD (Sample 4c)	30.75	3.779

the mechanical properties of *cis*-1,4-polybutadiene upon doping (Fig. 5, Table 2). Its form changed from 'soft and weak' to 'hard and brittle'.

The results of elemental analysis are given in Table 3. For pristine polymer %C is less and %H is higher than the theoretical values (theoretical value of %C is 92.6, and %H is 7.4). This discrepancy cannot be explained solely by moisture absorption; it might indicate that, although the samples contain small amounts of antioxidants, some of the double bonds are saturated in atmospheric conditions. Elemental analysis results show that the doped *cis*-1,4-polybutadiene contains 64% I₂ by weight.

TGA results reveal that the first weight loss is at 192.3 °C (due to the loss of doped I₂) and the polymer decomposes at 485.5 °C (Fig. 6).

In addition to the above measurements, the temperature dependence of conductivity (σ) for I₂-doped polybutadiene was examined. One way of evaluating temperature dependence measurements is to use the Arrhenius equation:

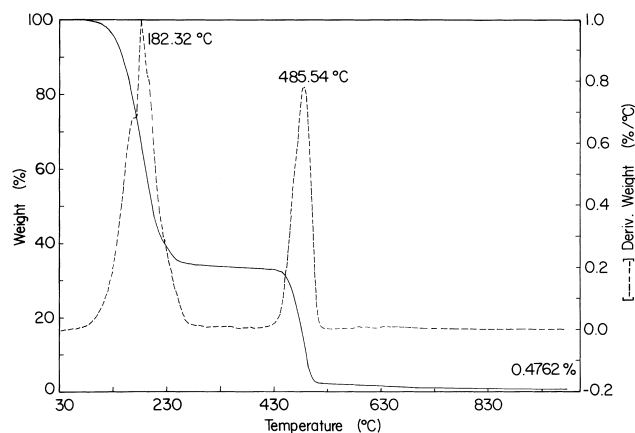


Fig. 6. TGA curve of *cis*-1,4-polybutadiene after I₂ doping.

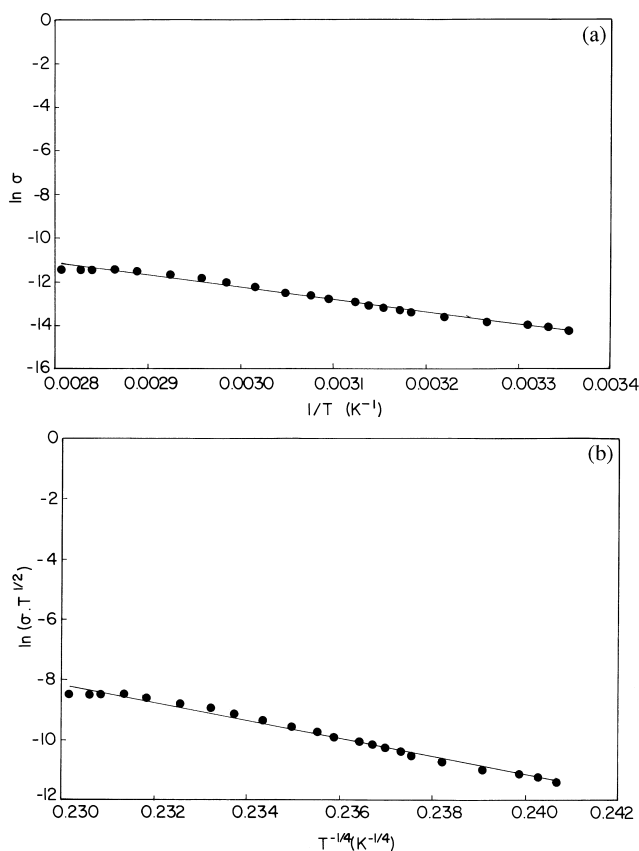


Fig. 7. Conductivity-temperature plots for doped *cis*-1,4-polybutadiene: (a) Arrhenius theory; (b) VRH theory.

$$\sigma = A \exp(-E/RT)$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant and T is the temperature. When $\ln \sigma$ is plotted versus $1/T$, it is found to fit the Arrhenius equation (Fig. 7(a)). As the temperature is increased more charge carriers overcome the activation energy barrier and participate in the electrical conduction, which is the major reason for increase in conductivity.

Another way of evaluating the results from temperature dependence measurements is to use the Mott variable range hopping (VRH) theory [13]. This theory is based on a bal-

ance between the thermodynamic constraint on a charge carrier moving to a nearby localized state of different energy and the quantum mechanical restraint on a charge carrier moving to a localized state of similar energy but spatially remote [14]. This establishes a temperature dependence on conductivity in the form $\ln \sigma$ versus $T^{-1/4}$ for three-dimensional hopping. The theory predicts the following behavior:

$$\sigma(T) = \sigma_0 T^{1/2} \exp[-(T_0/T)^{1/4}]$$

where σ_0 is the conductivity at infinite temperature and T_0 is the characteristic temperature. When $\ln(\sigma T^{1/2})$ values are plotted versus $T^{-1/4}$ a straight line is obtained (Fig. 7(b)). Results show that the data are also consistent with the VRH mechanism.

4. Conclusions

We have shown that *cis*-1,4-polybutadiene becomes conductive upon I_2 doping at room temperature. Different ratios of mole I_2 per BD unit were used for those doping reactions. The doping ratios play an important role in conductivity. The temperature dependence of electrical conductivity (σ) for I_2 -doped polybutadiene was examined and found to fit both the Arrhenius equation and VRH theory.

Acknowledgements

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