Thermal Conductivity of Polythiophene Doped With Iodine

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Abstract

Polythiophene (PT) was chemically synthesized, undoped and then re-doped using iodine. FTIR analysis confirmed that synthesized sample was polythiophene and was doped by iodine as desired. XRD analysis was used to calculate crystallinity. There was decrease in crystallinity due to doping. D.C.electrical conductivity increased by order of eight. Log σ versus 1/T graphs showed semiconducring nature of all samples. Thermal conductivity (κ) measurements of undoped and doped samples were carried out, using indigenously designed instrument similar to Lee's method. Thermal conductivity of undoped polythiophene at room temperature (303 K) is 7.367 X 10^{-5} Cal/cm/sec/k. Thermal conductivity increases with increase in temperature.

Keywords: FTIR, XRD, DC electrical conductivity, Thermal conductivity, Polythiophene.

Introduction

One of the several properties of polymers, thermal conductivity (κ), is of considerable interest to technologist and scientist. Thermal conductivity is important in material science, research, electronics, insulation and related fields, especially where high operating temperatures are achieved.

Also, for thermoelectric applications, material must posses high electrical conductivity and low thermal conductivity. Now a day's major research has been focused in material science and in condensed matter physics to develop highly efficient thermoelectric materials. Conducting polymers like polyacetylene[1], polyaniline[2], polythiophene[3] and their derivatives can be looked upon as a future generation thermoelectric material due to their high electrical conductivity and inherent low thermal conductivity at room temperature[4].

The literature survey says that, electrical conductivity of conducting polymer can be increased by several orders of magnitude due to doping by iodine. Hence in the present work iodine was used as a dopant for chemically synthesized polythiophene. Thermal conductivity of undoped and iodine doped samples were measured using indigenously designed and built instrument similar to Lee's method. Thermal conductivity measurements were carried out at 30^{0}C, 50^{0}C, 100^{0}C and 150^{0}C and are reported. Attempts were made to test whether iodine doped polythiophene is useful as thermoelectric material or not.

Methodology

Chemical synthesis: The polythiophene was chemically synthesized as reported by T. Yamamoto al[5]. The synthesis was carried out in dry tetrahydrofuran (THF) by treating magnesium with 2,5 dibromothiophene in the presence of nickel chloride. Reaction of magnesium with bromine of 2,5 dibromothiophene takes place and either 2 – bromo – 5 - magnesiobromothiophene or 2 – magnesiobromo – 5 – bromothiophene as an intermediate product is formed. This intermediate product further reacts with magnesium and MgBr$_2$ is liberated by joining two intermediate products with each other in presence of nickel chloride. Latter step is repeated again and again and finally polythiophene is formed.

The synthesized polymer was undoped using liquid ammonia. It is then redoped by exposing it to vapors of iodine for two hours duration. Weight of polymer after exposing it to vapors of iodine was increased.

Characterization: Undoped and doped samples were characterized by FTIR and XRD techniques. An FTIR spectrum was recorded using Shimadzu FTIR-8400S spectrophotometer in the range of 400 cm^{-1} to 4000 cm^{-1}. XRD of both samples were recorded using Philips Analytical X-ray model P W 1710 unit (Netherland) over a range of 2θ = 5^{0} to 40^{0}.

Electrical Conductivity Measurement: Two probe technique for conductivity measurements of both samples was used. Voltage was varied from 0 V to 20 V (in steps of 1 V) and corresponding current was measured on Keithley electrometer (model no. 6514) (USA). These measurements were repeated in the temperature range from 313 K to 373 K. Figure-1 shows the experimental set up used for measurements. All the measurements were carried out on pellets with electrical probes of 1cm^2 size.
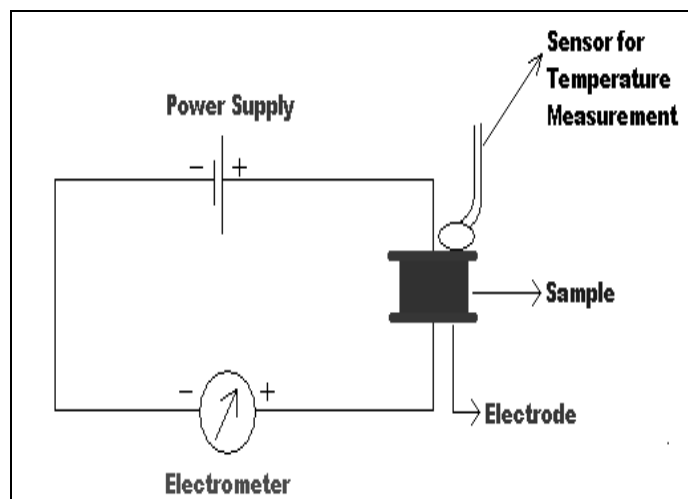
Figure-1
I-V Measurement Experimental Set up

Design and construction of thermal conductivity measuring instrument: Thermal conductivity measuring instrument has been constructed similar to Lee's apparatus. However in Lee's method measurement is carried out by passing steam through hollow brass cylinder and hence measurement is possible only at one temperature: at boiling point of water. In the newly designed instrument electrical heater is used (instead of steam chamber) whose temperature can be set and varied from room temperature to 250^0C. The temperature set can be held constant for long duration till the steady state of lower disc is reached. Hence thermal conductivity measurements using newly designed instrument can be carried out at various temperatures from room temperature to 250^0C. Furthermore, generally in Lee's method experimental is carried out by exposing instrument to natural atmosphere. In the newly designed instrument facility is made available to carry out the experiment in vacuum chamber. By carrying out experiment in vacuum avoids oxidations, if any, of polymeric material due to heat. Also losses of heat due to atmosphere get reduced. The sensors used for measuring temperature of upper and lower disc are PT100 and the measured temperatures are indicated on digital display having accuracy of 0.1^0C.

Results and Discussion

Structural Properties: Undoped polymer sample when exposed to vapors of iodine, the weight of the sample was found to increase. The rise in weight of the sample was used to calculate atom equivalent of iodine per thiophene unit. In the present work atom equivalent of iodine per thiophene unit was found to be 0.498 which corresponds to 75 wt % of iodine per polythiophene.

As reported by G. Tourillon a sharp band at 788.91 cm⁻¹ in the present work was observed. This band is characteristic of the α, α'-coupling of poly-2,5-thiophene[6]. This proves that the synthesized sample is polythiophene. Also a band at 965 cm⁻¹

associated to C – Br band does not appear in FTIR spectrum of synthesized polymer confirming that the synthesized sample is polythiophene and the absence of monomer in the synthesized sample[7]. Other bands observed in FTIR spectra of synthesized sample matches well with the reported values by G. Tourillon[6]. This also confirm that the sample synthesized is polythiophene.

After doping by iodine in addition to above mentioned bands, a new band at 584.39 cm⁻¹ was observed. Author D. L. Pavia et al[8] reported that all the bands below 667 cm⁻¹ are associated to C–I band. Thus it appears that after doping by iodine, C–I bond must have formed. It is also observed that due to doping and due to formation of new C-I bonding, bands appeared in undoped polythiophene showed some amount of shift. Bands associated with C=C stretching in undoped sample and appearing at 1543.1 and 1633.76 cm⁻¹ shifts to 1488.94 and 1635.59 cm⁻¹ respectively. Even a characteristic bands of polythiophene appearing at 788.91 cm⁻¹ in undoped polythiophene slightly shifts to 784.97 cm⁻¹ after doping by iodine. Slight shift from 671.25 cm⁻¹ to 675.04 cm⁻¹ in band associated to C_γ–H is also observed. While a band appearing at 692.47 cm⁻¹ associated to C_γ–H in undoped sample disappears after doping. This confirms that iodine forms a complex with polythiophene chain probably at C=C of polythiophene. Appearance of new C-I band and shifting of some of the bandsafter doping by iodine leads to the conclusion that the dopant molecule forms a complex with polythiophene.

For comparison the various absorption bands observed have been tabulated in Table-1.

Table-1
Values of IR absorption peaks of chemically synthesized and iodine doped polythiophene

For undoped PT in the present work cm-1	For 120 min. Iodine doped PT cm-1	Association
1543.1 and 1633.76	1488.94 and 1635.59	C= C stretch
1425.44	1334.65	υ cycle
1220.98	1195.78	υ cycle
1020.38	1029.92	C–H in plane bend
788.91	784.97	=C–H out of– plane bend
692.47 and 671.25	675.04	Cγ–H
-----	584.39 and 620	C–I

XRD scans of undoped and iodine doped polythiophene samples are shown in Figure-2. In the undoped polythiophene three predominant peaks are observed at $2\theta = 19.66^0$, 23^0 and 28^0. Fourth small peak is observed at $2\theta = 26.33^0$. However all four

peaks have been taken in consideration for calculating crystallinity of undoped sample. After doping sample by iodine peaks have been shifted to larger values of angle at 20.09^0 and 32.90^0 which indicates that the crystal structure has been modified after doping.

Figure-2
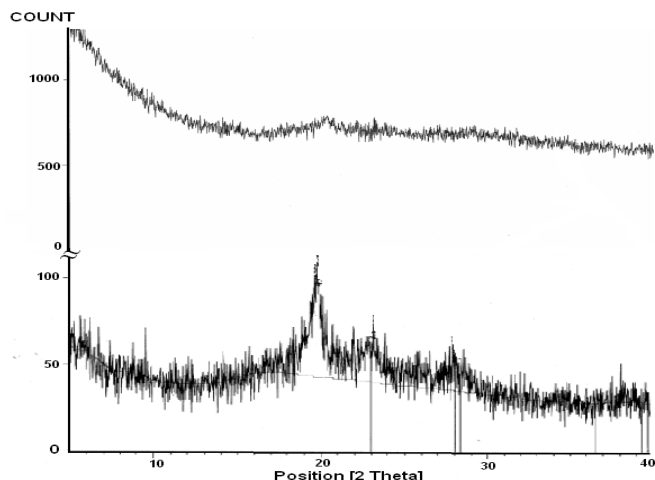**XRD scan of Undoped (Bottom) and Iodine doped (Top) polythiophene**

Manjunath et al[9] in 1973 reported a formula to calculate the crystallinity of sample using XRD scans. The said formula is used to calculate the crystallinity of both samples with 8 to 10 % error and is also tabulated in Table-2. It is observed that there is decrease in crystallinity due to doping. The decrease in crystallinity after doping of polythiophene by iodine was also reported by Yamamoto et al[10]. Since crystallinity values calculated are greater than 50 %; it can be concluded that samples are semi-crystalline in nature. Iodine atoms in iodine doped samples are getting inserted in polythiophene matrix; poses in the hindrance to the packing of polymer chain, thereby disturbing and reducing the crystallinity of the sample.

Table-2
Values of peak positions (2θ), crystallinity from XRD pattern of undoped and iodine doped polythiophene samples

Sample	Peak position at $2\theta^0$	Crystalinity (%)
Undoped PT	a) 19.7 b) 23 c) 26.3 d) 28	66
120 min. I_2_PT	a) 20.1 b) 32.9	58

Electrical Conductivity Measurements: Two probe technique was used to find out electrical conductivity of both the samples. Conductivity values at 318 K at an applied field of 50 V/cm are reported in Table-3.

Table-3
Conductivity values of samples at 318 K at an applied field of 50 V/cm

Sr. No.	Sample	Conductivity (S/cm)
1	Undoped PT	1.48×10^{-12}
2	120 min. I_2_PT	1.90×10^{-4}

The conductivity value after doping by iodine increases from 10^{-12} S/cm to 10^{-4} S/cm. Thus a dramatic increase by eight orders of magnitude due to doping by iodine is observed.

In order to understand conduction mechanism in undoped sample, conductivity measurements at various temperatures were carried out. Graph of log σ against 1/T at 50 V/cm field is shown in figure-3. From the graph it is observed that in case of undoped sample, initially i.e. from 312 K to 323 K conductivity decreases and from 323 K to 368 K conductivity increases.
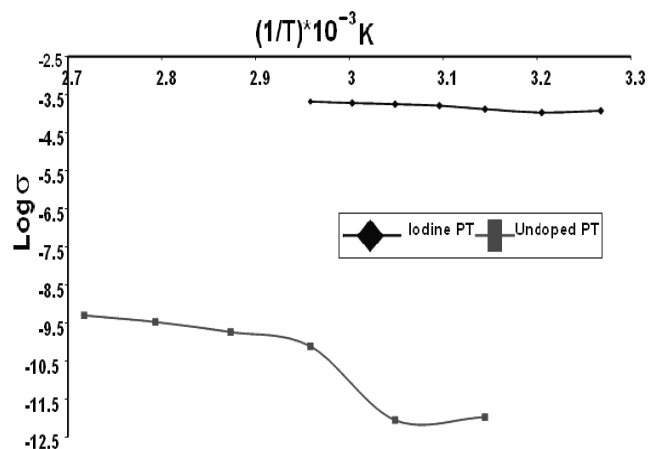

Figure-3
Log σ versus 1/T for undoped and iodine doped samples at 50 V/cm field

This decrease in conductivity with rise in temperature indicates metallic nature while increase in conductivity with increase in temperature shows semiconducting behavior of the undoped polythiophene sample. Temperature 323 K is a transition temperature at which behavior of sample changes. In case of iodine doped samples conductivity slowly increases with rise in temperature in the entire range of temperature under consideration i.e. from 306 K to 353 K. This behavior shows semiconducting nature of the iodine doped polythiophene.

Thermal Conductivity: Thermal conductivity measurements, at various (30^0C, 50^0C, 100^0C and 150^0C) temperatures, of doped polythiophene using indigenously designed and built instrument are summarized in table 4 and is calculated using the formula
$K = \{M S (d\theta/dt)\}/ \{\pi r^2 (\theta_1 - \theta_2)/d\}$

where M is mass of lower plate, S – specific heat of steel = 502 J/kg . k, r – radius of sample, θ_1 – temperature of upper plate (hot surface) ^{0}C, θ_2 – temperature of lower plate (cold surface) ^{0}C, d – thikness of sample, (dθ/dt) – slope of cooling curve at θ_2.

From the table 4 it is observed that, thermal conductivity increases as temperature increases. Thermal conductivity of undoped polythiophene samples at room (30^{0}C) temperature is 7.367 X 10^{-5} cal/cm/sec/K whereas reported value of 'κ' for polythiophene at room temperature is 4.08 X 10^{-4} cal/cm/sec/K[11].

Thermal conductivity depends in general on number of free electrons and phonons. In undoped PT sample motion of phonons must have been responsible for carrying heat from one point to another point at room temperature. The number of phonons and/or their orientation/alignment must have been changed in such a way that as the temperature of undoped PT sample increases thermal conductivity of it also increases.

Table-4
Thermal conductivity values at various temperatures in Cal/cm/sec/k

Sample	At 30^0 C	At 50^0 C	At 100^0 C	At 150^0 C
Undoped-PT	7.37 X 10^{-5}	1.14 X 10^{-4}	4.68 X 10^{-4}	7.18 X 10^{-4}
120 min I$_2$-PT	5.04 X 10^{-5}	7.73 X 10^{-5}	3.19 X 10^{-4}	4.91 X 10^{-4}

From the Table-3 it is observed that after doping undoped sample by iodine electrical conductivity (σ) increases by six to eight orders of magnitude. Electrical conductivity increases if i Number of charge carrier increases. ii Mobility of free charge carriers increases. iii Both number as well as mobility of free charge carriers increases.

In the present case electrical conductivity increases from 10^{-12} S/cm to 10^{-4} S/cm after doping indicating that there is an increase in number of free electrons. However this increase in number of electrons does not play any role in affecting thermal conductivity. On the other hand motion of phonons must be getting disturbed by increase in number of electrons. These increased electrons may not be providing path to phonons to carry heat from one point to other point. Hence thermal conductivity of iodine doped samples is less than undoped sample even though after doping number of electrons and hence conductivity increases.

Furthermore due to increase in temperature mobility of phonons must have been increased which caused increase in thermal conductivity due to increase in temperature.

Thermal conductivity of polymers also depends on temperature, crystalinity and orientation of atoms. The reason for decrease in thermal conductivity within iodine doped sample lies in the fact that crystalinity decreases after doping. This decrease in crystallinity is responsible for decrease in thermal conductivity of iodine doped sample.

Conclusion

Polythiophene can be doped with iodine and it form complexes with polythiophene. Crystal structure gets modified after doping polythiophene by iodine. After doping polythiophene with iodine, dc conductivity increases dramatically. Thermal conductivity of undoped polythiophene is very low which gets further reduced by doping it by iodine while electrical conductivity increase minimum by order of eight after doping polythiophene by iodine. High electrical and low thermal conductivity of iodine doped sample make it more suitable material for thermoelectric applications.

Acknowledgements

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