Electrical conductivity and optical properties of a new synthesized poly(tetramethylene ethylene diamine) polymer organic semiconductor

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Electrical conductivity and optical properties of poly(tetramethylene ethylene diamine) polymer have been investigated. The electrical conductivity of the polymer increases with increase of temperature. The Arrhenius conductivity curve of the polymer shows the linear and non-linear regions. The non-linear behavior of the polymer confirms the ionic conductivity behavior analyzed by the Vogel–Tamman–Fulcher (VTF) theory. The room temperature conductivity of the poly(tetramethylene ethylene diamine) polymer was found to be 2.56×10^{-8} S/cm. The optical band gap of the polymer was analyzed by optical absorption spectra and was found to be 4.15 eV with direct optical transition. The refractive index of the polymer was analyzed by the Single oscillator model. The oscillator energy E_o, dispersion energy E_d, and long wavelength refractive index n_∞ values of the polymer were found to be 9.69 eV, 31.36 eV and 2.05, respectively. The obtained electrical and optical results indicate that the poly(tetramethylene ethylene diamine) polymer is a organic semiconductor with calculated electrical and optical parameters.

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1. Introduction

Polymer materials have been used in various electronic applications such as light emitting diodes, field effect devices, light emitting diodes, and photovoltaic cells [1-6]. These materials are the most promising organic semiconductors due to their electrical and optical properties and currently there is great interest in the electrical and optical properties of polymers. Furthermore, understanding the electrical conductivity mechanism of polymers is interesting both from fundamental and technological point of view. The charge transport properties of these materials are strongly dependent on their chemical and electronic structures. The electrical and optical properties of polymers can be changed by dopants or controlling synthesis. The semiconductor polymers can be formed by connecting a kind of organic group, dopants and cationic anions.

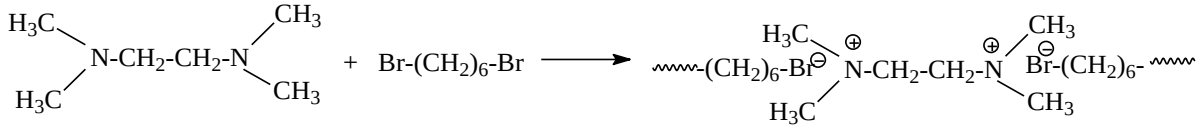
We have evaluated that a new semiconductor polymer can synthesized by designing new chemical structures. Thus, we can offer the semiconductor polymer with good electrical, and optical through the synthesis of chemical.

In the present study, a new poly(tetramethylene ethylene diamine) polymer were synthesized to obtain new semiconductor polymer. The semiconducting properties of the polymer have been investigated by direct current conductivity and optical characterization methods.

2. Experimental

2.1. Synthesis of the poly(tetramethylene ethylene diamine) polymer

5 ml of tetramethylene ethylene diamine (TEMED) was added to 20 ml of diethylether and 5,2 ml of dibromohexane was added to this solution. The reaction was proceeded at room temperature for 48 h. Precipitated white solid product was filtered and was washed excess of diethyl ether to remove soluble fractions. The white polymeric product was dried under vacuum at room temperature for 24 h. The yield was 10,33 g (86 %). The synthesis procedure of the polymer is given in Scheme 1.



Scheme 1

The poly(tetramethylene ethylene diamine) polymer (PTEMED) was characterized by using FT-IR spectroscopy. The FT-IR spectrum of cationic polymer (Fig. 1) was as expected, with bands for the alkyl group at 2900–2800 cm^{-1}. If FT-IR spectrum of the polymer was compared with TEMED (Spectral Database for Organic Compounds, SDBS No: 2373) new bands were observed at 1133 cm^{-1} and 3010 cm^{-1} because of quaternization.

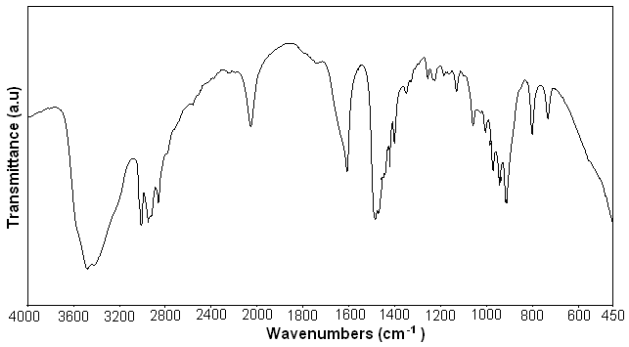


Fig. 1. The FT-IR spectrum of the poly(tetramethylene ethylene diamine) polymer.

2.2. Measurements

For studying the electrical conductivity measurements, the poly(tetramethylene ethylene diamine) polymer was pressed at 10 ton/cm^2 pressure forming a circular disc. Electrical conductivity was measured as a function of temperature by alternating polarity method to eliminate electrical polarization, triboelectric and piezoelectric effects using KEITHLEY 6517A electrometer [7-8].

For the optical measurements, the polymer was dissolved in water and then the polymer was prepared in the form of the film of 16 μm thickness by drop casting method. The reflectance spectrum of the polymer was recorded at ambient temperature using Shimadzu 3600 UV-Vis-NIR spectrophotometer with integrating sphere attachment.

3. Results and discussion

3.1 Direct current conductivity properties of poly(tetramethylene ethylene diamine) polymer

Fig. 2 shows the Arrhenius plot of direct current conductivity of poly(tetramethylene ethylene diamine) (TMED) polymer. The electrical conductivity of the polymer increases with increase of temperature. This increase is due to stronger segmental motion of polymer. The Arrhenius plot of the polymer shows the different regions, which are linear and non-linear regions (I and II). In the first region, the electrical conductivity is exhibits a non-linear behavior. This confirms the ionic conductivity behavior of the polymer. Thus, the ionic conductivity of the polymer can be analyzed by the Vogel–Tamman–Fulcher (VTF) [9–11] equation

$$\sigma = DT^{-1/2}\, exp\left(\frac{-B}{T-T_o}\right) \qquad (1)$$

where D and B are constants, T is the temperature and T_o is the ideal glass transition temperature. The VTF plot for the polymer is shown in Fig. 3. The plot gave good straight line, suggesting that the conductivity mechanism is affected by the segmental motion of the polymer chains. The T_o was obtained from the Fig. 3 and was found to be 280 K. The VTF parameters, A and D for the first and second regions were found to be 9.41×10^{-3} S/cm $K^{1/2}$, 42.2 and 5.41×10^{-6} S/cm $K^{1/2}$ and 475.4, respectively. The B values are pseudo activation energy for ionic transport. The activation energy values for I. and II. regions were found to be 3.62 meV and 40.88 meV, respectively. The room temperature conductivity of the poly(tetramethylene ethylene diamine) polymer was found to be 2.56×10^{-8} S/cm. This conductivity value is a typical value for the organic semiconductors. The transport of ions in this polymer is believed to be supported by segmental movements of the polymer chain.

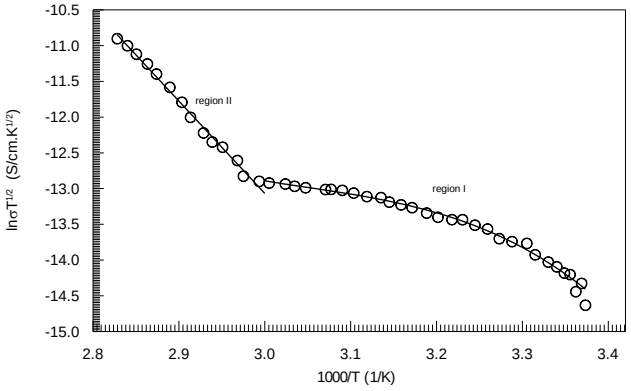


Fig. 2. Arrhenius curve of electrical conductivity of the TMED polymer.

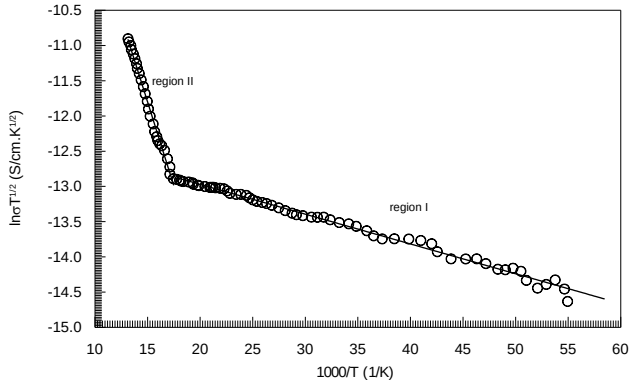


Fig. 3. Vogel–Tamman–Fulcher (VTF) for the TMED polymer.

3.2. Optical properties of the poly(tetramethylene ethylene diamine) polymer

The absorption (A), transmittance (T) and reflectance (R) spectra of the poly(tetramethylene ethylene diamine) polymer are shown in Fig. 4(a-c). The transmittance spectra show an absorption edge for the polymer. The transparency of the polymer is about 70%. At longer wavelengths, the transmittance indicates two electronic bands. As seen in Fig. 4, the absorption increases with decreasing wavelength up to about 400 nm due to the optical band transition from the valence band to conduction band. In order to determine the absorption edge of the polymer, we plotted the curve of dA/dE vs. E, as shown in Fig. 5. This plot indicates a peak, corresponding to absorption edge. The maximum peak position corresponds to the 4.27 eV. The optical band gap energy of the polymer film can be determined by the following relation [12]

$$\alpha = \left(\frac{C}{h\nu}\right)(h\nu - E_g)^{1/m} \qquad (2)$$

where C is an energy-independent constant and E_g is the optical band gap. For the determination of the optical band gap, we potted curve of $(\alpha h\nu)^2$ vs. hν and is given in Fig. 6. The optical band gap was determined by extrapolating the linear portion of the plot to $(\alpha h\nu)^2 = 0$. The optical band gap of the polymer was found to be 4.15 eV.

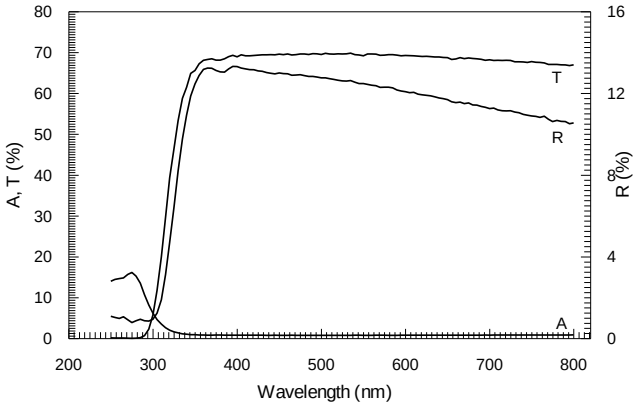


Fig. 4. Absorption, transmittance and reflectance spectra of the TMED polymer.

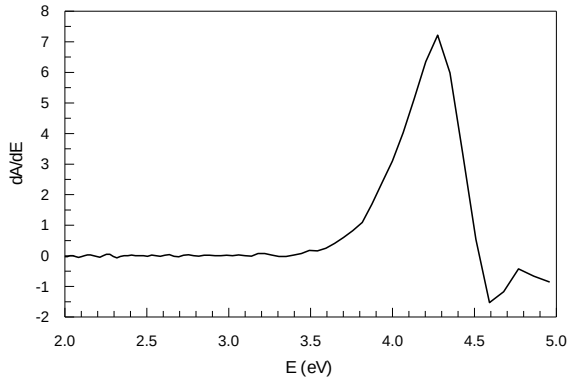


Fig. 5. The curve of dA/dE vs. E for the TMED polymer.

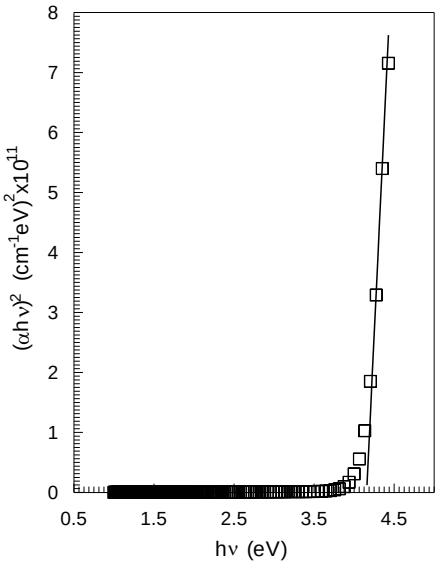


Fig. 6. Plot of $(\alpha h\nu)^2$ vs. $h\nu$ of the TMED polymer.

Fig. 7 shows the refractive index dispersion curve of the film. The refractive index of the film was calculated according to methods in Refs [6-7]. As seen in Figure, the refractive index decreases with increase in wavelength and indicates the normal dispersion. For the determination of the oscillator energy and strength of the optical band gap, we use the following relation [13],

$$n^2 - 1 = \frac{E_d E_o}{E_o^2 - (h\nu)^2} \qquad (3)$$

where E_o is the average excitation energy for electronic transitions, E_d is the dispersion energy, n is the refractive index, hν is the photon energy The E_d and E_o values was determined from Fig. 8 and were found to be 31.36 eV and 9.69 eV, respectively.

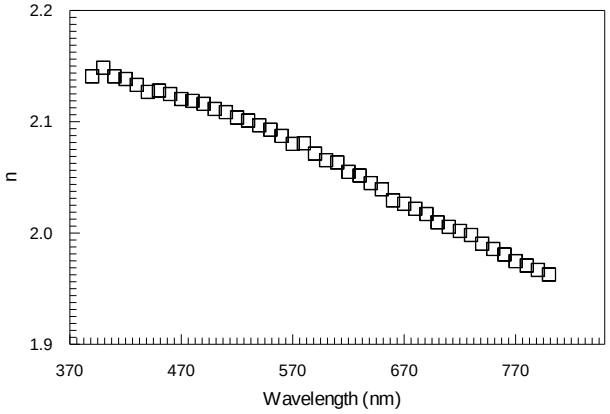


Fig. 7. Plot of refractive index of the TMED polymer.

The long wavelength refractive index for the film can be determined by the following relation,

$$\frac{n_\infty^2 - 1}{n^2 - 1} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2 \qquad (4)$$

where, λ_o is an average oscillator wavelength and n_∞ is the long wavelength refractive index. The λ_o and n_∞ values for the film was determined from Fig. 8 and were found to be 128.1 nm and 2.05, respectively. The average oscillator parameter, S_o which is the strength of the individual dipole oscillator was found to be 1.97×10^{14} m^{-2}. The refractive index dispersion parameter E_o/S_o for the polymer film was determined to be 4.98×10^{-14} eV m^2. This value of E_o/S_o is of the same order as that obtained by Didomenico and Wemple [14]. The E_o/S_o value is associated with the type of the optical transitions. M_{-1} and M_{-3} moments of the optical spectrum of the polymer can be calculated by the following relation [15-16],

$$E_o^2 = \frac{M_{-1}}{M_{-3}}$$

$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad (5)$$

The M_{-1} and M_{-3} values were calculated using these relations and were determined to be 3.23 and 0.034 (eV^{-2}), respectively.

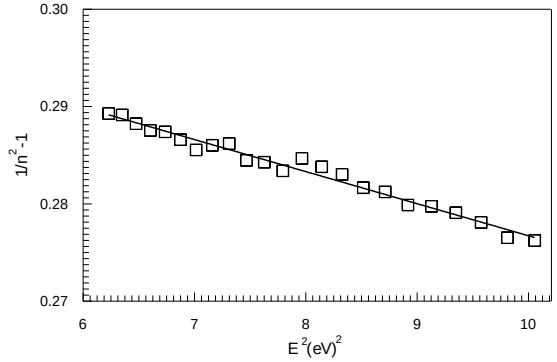


Fig. 8. Plot of $1/n^2$-1 vs. E^2 of the TMED polymer

The real and imaginary parts of the dielectric constant dependence of photon energy are shown in Fig. 9. The real part of the dielectric constant increases with photon energy and decreases and reaches to be constant. After about 4 eV, the dielectric constant of the polymer is non-dispersive. Furthermore, the imaginary part of the dielectric constant increases with photon energy and shows a peak, which is identified by the mean transition energy from the valence band to the conduction-band state.

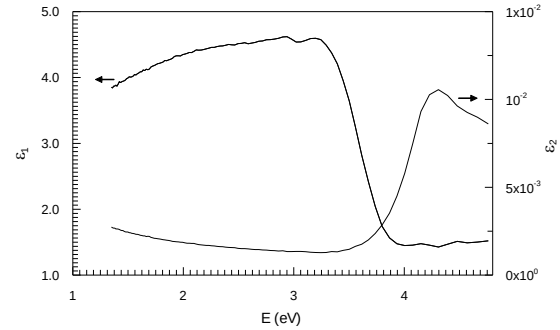


Fig. 9. Plots of the real and imaginary parts of the dielectric constant of the TMED polymer.

4. Conclusions

Electrical conductivity and optical properties of poly(tetramethylene ethylene diamine) polymer have been investigated. The polymer shows the ionic conductivity. The refractive index of the polymer obeys the Single oscillator model with oscillator energy E_o =9.69 eV), dispersion energy (E_d=*31.36 eV)*, and long wavelength refractive index (n_∞ =2.05). The obtained electrical and optical results indicate that the poly(tetramethylene ethylene diamine) polymer is an organic semiconductor with room temperature electrical of 2.56×10^{-8} S/cm and optical band gap of 4.15 eV.

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