Low frequency ac conduction and dielectric relaxation in pristine poly(3-octylthiophene) films

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Abstract. The ac conductivity $\sigma(\omega)_{m}$, dielectric constant $\varepsilon'(\omega)$ and loss $\varepsilon''(\omega)$ of pristine poly(3-octylthiophene) (P3OT) films (thickness $\sim 20 \mu$m) have been measured in wide temperature (77–350 K) and frequency (100 Hz–10 MHz) ranges. At low temperatures, $\sigma(\omega)_{m}$ can be described by the relation $\sigma(\omega)_{m} = A\omega^{s}$, where $s$ is $\sim 0.61$ at 77 K and decreases with increasing temperature. A clear Debye-type loss peak is observed by subtracting the contribution of $\sigma_{dc}$ from $\sigma(\omega)_{m}$. The frequency dependence of conductivity indicates that there is a distribution of relaxation times. This is confirmed by measurement of the dielectric constant as a function of frequency and temperature. Reasonable estimates of various electrical parameters such as effective dielectric constant ($\varepsilon_{p}$), phonon frequency ($\nu_{ph}$), Debye temperature ($\theta_{D}$), polaron radius ($r_{p}$), small-polaron coupling constant ($\Upsilon$), effective polaron mass ($m_{p}$), the density of states at the Fermi level $N(E_{F})$, average hopping distance ($R$) and average hopping energy ($W$) from dc conductivity measurements suggest the applicability of Mott’s variable range hopping model in this system.

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1. Introduction

Low frequency ac conductivity and dielectric relaxation measurements have proven to be valuable in providing additional information on the mechanism of charge transport that dc conductivity measurements alone do not provide [1, 2]. For this reason, the ac conductivity technique has been extensively used to explain the charge transport mechanism in condensed matter physics [3], material science [1]–[3] and polymer science [2]. In spite of the sustained efforts to explain the mechanism of charge transport of various π-conjugated polymers (CPs) such as polyacetylene, polypyrrole, polyaniline and polythiophenes, no conclusive mechanism has emerged so far because they exhibit a great variety of transport properties [4]–[7]. The undoped or lightly doped samples of these CPs behave like amorphous semiconductors with the Peierls–Mott energy gap determined by the internal structure of the polymer repeat unit [8]. Also their behaviour can be classified as dielectric [4], [9]–[13] and their conductivity decreases with decreasing temperature in the same experimental manner [11]–[15]. It has been assumed that the mechanism of charge transport in CPs should behave in a similar way to amorphous semiconductors and dirty metals [5, 16]. According to this analogy the charge transport is represented by phonon-assisted hops over randomly distributed localized states [3, 17] and the conduction mechanism is described by Mott’s variable range hopping (VRH) model. However, to explain the high conductivity of doped polymers, an alternative view of charge transport has started to gain more attention [4, 10, 18, 19], which exploits the chain structure of the polymer. The reflectance measurements can provide information regarding the metallic state of CPs [20]. The direct measurement of the dielectric function in the far IR and at microwave frequencies probe the intra-band excitations near the Fermi level of the system [9], [21]–[23]. Dielectric loss (dielectric relaxation) studies in CPs, employing thermally stimulated depolarization current spectroscopy [24] or ac-impedance measurement techniques [11]–[15] probe the localized charge motion of the polaron within nanometre-scale regions. Recently, the VRH mechanism as possible origin of a universal relation between conductivity and mobility in a disordered organic semiconductor [25] and in low-dimensional polymer structures has been reported [26].
Among all these CPs, poly(3-alkylthiophenes) (P3ATs) have attracted immense interest from physicists, chemists and engineers because of their reasonably good environmental stability, easy processability and easy modification of the electronic and optical properties. Their structural [7], [27]–[35], morphological [7], [36]–[40], optical [7, 36], [41]–[44] and electrical [7, 39], [45]–[48] properties have been extensively investigated, however, details regarding their ac conductivity and dielectric relaxation behaviour are lacking in literature. We report here, for the first time, the measurement of ac conductivity and dielectric constant on pristine poly(3-octylthiophene) (P3OT) films as functions of frequency and temperature in wide temperature (77–350 K) and frequency (100 Hz–10 MHz) ranges. P3OT has been synthesized in our laboratory at low temperature (228 K). The improved quality and its structural behaviour have been confirmed by Fourier transform infrared (FT-IR) and x-ray diffraction (XRD) studies. The results of ac conductivity have been analysed using existing theoretical models. The dc conductivity data (77–350 K) has been used to extract various parameters such as effective dielectric constant ($\varepsilon_p$), phonon frequency ($\nu_{ph}$), Debye temperature ($\theta_D$), polaron radius ($r_p$), small-polaron coupling constant ($\Upsilon$), effective polaron mass ($m_p$), the density of states at the Fermi level $N(E_F)$, average hopping distance ($R$) and average hopping energy ($W$) which suggest the applicability of Mott's VRH model [3] in this system.

2. Synthesis and experimental techniques

2.1. Synthesis and purification of polymer

2.1.1. Synthesis of polymer P3OT. In a typical synthesis procedure [36, 45], the P3OT polymer was synthesized using a chemical oxidative polymerization technique by drop-wise addition of monomer 3-octylthiophene (3OT) (0.1 M) in oxidant ferric chloride (FeCl$_3$) (0.8 M) in chloroform (CHCl$_3$) at 228 K in an inert atmosphere (nitrogen gas) for over 6 h in a double walled glass container, with constant stirring with a glass stirrer. To maintain a desired and uniform temperature, methanol was continuously circulated through the double walled glass container with the help of a constant temperature bath (Julabo) running in the temperature range $+50^\circ$C to $-50^\circ$C with an accuracy of $\pm0.1^\circ$C. The whole process was carried out for 24 h in order to give sufficient time for complete polymerization. After mixing of the reactants, the polymerization solution turned green and was precipitated after 24 h by adding copious amounts of methanol into the polymer–oxidant mixture. Repeated purification was performed by methanol and deionized water to remove the oligomers and excess oxidant impurity with the help of a Buckner funnel and vacuum pump until the filtrate became colourless. The resultant P3OT polymer was dried at 353 K for 2 h. The polymer powder obtained was green in colour. P3OT thus obtained was insoluble and contained FeCl$_3$ as an impurity. In order to get P3OT in pristine and soluble form, FeCl$_3$ was removed by a rigorous purification process as described below.

2.1.2. Purification of as grown polymer P3OT. The removal of undesired materials from a given polymer to get the desired properties is known as polymer purification. After chemical synthesis, the resultant polymer contains unreacted monomer or oligomers and oxidant used for polymerization. Unreacted monomers, oligomers and oxidants are removed from the as grown polymer by successive washing by chemicals which show specific affinity for the molecules.
to be removed. In the present case [36], the polymerization has been carried out using 3OT and FeCl3 in CHCl3. To get pristine P3OT, the purification of polymer requires removal of any leftover 3OT monomer, oligomers and FeCl3. In order to remove these impurities, the as grown polymer was treated with aqueous ammonia (aqueous NH3) and ethylene diamine tetraacetic acid (EDTA) (liquid–liquid extraction) in separate steps. These steps are as follows.

1. As grown P3OT polymer in solid form was suspended in CHCl3.
2. Copious amounts of NH3 was poured into the P3OT–CHCl3 suspension.
3. The solution having two phases of aqueous NH3 and P3OT–CHCl3 was slowly heated to the boiling point of CHCl3. As heating progressed, the more volatile CHCl3 evaporates first, leaving P3OT solid with lower chloride content (as NH3 removes the chloride part of FeCl3 intercalated to P3OT) floating over aqueous NH3.
4. P3OT obtained in step 3 was dissolved in CHCl3 and aqueous EDTA of the desired concentration was poured into the P3OT–CHCl3 solution. The whole two phase solution was heated to the boiling point of CHCl3. As heating progressed, the more volatile CHCl3 evaporates first, leaving P3OT solid with lower iron content (as EDTA removes the iron part of FeCl3 intercalated to P3OT) floating over aqueous EDTA.
5. Steps (3) and (4) were repeated several times to minimize the FeCl3 impurity present in the polymer matrix.

As repetition of the aqueous NH3 and EDTA treatment progressed, the amount of FeCl3 was significantly reduced as evidenced by energy dispersive x-ray analysis (EDAX) studies of the obtained polymer film. When the EDAX study showed a zero content of FeCl3, we assumed that the P3OT polymer matrix was free from oxidant impurity and this is termed as ‘pristine P3OT’.

The pristine P3OT is completely soluble in CHCl3. A calculated weight (0.05 g) of pristine P3OT was dissolved in 10 ml of CHCl3 for over 12 h to ensure complete dissolution of the polymer. The resultant P3OT polymer solution was cast in a specially designed chamber having an inbuilt flat glass substrate. The solution was covered by another glass plate keeping a narrow opening to allow the evaporated solvent to escape. After completion of the solvent evaporation, the P3OT film was peeled off from the glass substrate by pouring methanol into the film growing chamber so that the polymer film leaves the glass substrate on its own, to avoid any mechanical stretching and tearing of the film during the separation from the glass substrate. The film was then dried at 353 K for 1 h to remove any solvent trapped inside the film. A good quality film of pristine P3OT (thickness ~ 20 µm) having excellent surface smoothness, free from pinholes and good mechanical strength was obtained and cut into pieces, which were subsequently used for all electronic and electrical studies [45]. The molecular weight of pristine P3OT, taken with reference to a polystyrene standard, are: \( M_w = 36,848 \) and \( M_n = 34,118 \) with a polydispersity (PD) index (\( M_w/M_n \)) of 1.08.

2.2. Experimental techniques

FT-IR spectra were recorded on a Perkin–Elmer Model 2000 Optica spectrometer in the range 600–4000 cm\(^{-1}\) in transmittance mode. The characteristic peaks of P3OT quasi-crystals were elucidated using a D-8 advanced x-ray diffractometer (Bruker) using CuK\(\alpha\) (\(\lambda = 1.5404 \text{Å}\)) radiation at low incident angle. For dc and ac conductivity measurements, gold electrodes were
vacuum (∼10^{-6} Torr) evaporated on both sides of P3OT films (∼20 µm thick), thus making an Au/P3OT/Au sandwich structure. For this, these films were masked in such a way that gold could be deposited on both sides (transverse sides) of the P3OT films sandwiching a common area of 3.14 × 0.25 cm² and the two gold strips, one from each transverse side extends beyond the common sandwiched area. The two probe method was used for dc electrical conductivity measurement. For this, the extended gold strips of both sides of the polymer film were used to make electrical contacts with the help of electrically conducting silver paste and copper wire, thus ruling out any possibility of short-circuiting [45]. The temperature dependence of dc conductivity of the pristine P3OT films (thickness ∼20 µm) was measured in a closed cycle helium cryostat (ARS, USA) with Lakeshore 331 temperature controller in the range 77–350 K by using Keithley’s 238 source meter and 480 picoammeter. For ac conductivity measurements, a specially designed three terminal cell was used by using a HP 4192 A LF impedance analyser. There was little spread (within ±2%) in the measured dc and ac conductivity values of different films of the same thickness (∼20 µm), confirming the good reproducibility of the synthesis and fabrication process.

3. Experimental results and discussion

3.1. Structural investigations

3.1.1. FT-IR investigation. Generally, synthesis and quality of the synthesized polymer was determined through study of the behaviour of the polymer in infrared radiation. To accomplish this, the polymer film was irradiated with IR radiation and its behaviour was seen in terms of several absorption bands in a typical FT-IR spectroscopy. The various absorption bands for pristine P3OT thin film are shown in figure 1. Besides the various bands observed at ∼3053, 2952, 2926, 2853, 1560, 1509, 1464, 1377, 1260, 1195, 1091, 1022, 722, 668 cm⁻¹ (corresponding to various modes of absorption of IR energies by various constituents of the P3OT polymer) [36], the characteristic band at 820 cm⁻¹ arises due to –C–H out of plane vibration which confirms the synthesis of reasonably good quality P3OT polymer, which is further confirmed by XRD and UV-VIS studies [7, 36, 46].

3.1.2. XRD investigation. Study of the position of XRD peaks and their intensity gives some idea about polymeric crystal packing. It is significant to note here that polymeric crystals are formed only in regioregular polymer, and if any crystal gets formed it gives a well defined peak in the XRD spectra of the polymer. XRD spectra of regiorandom polymer gives only a hump, not a well defined peak. Polymeric crystals are quasi in nature and strongly dependent on how polymeric chains stack/pack together. The stacking of long π-conjugated polymeric chains may be one-, two- or three-dimensional (1D, 2D or 3D) in nature. A π-conjugated chain having small side groups or side groups arranged systematically stacks three dimensionally. The dimensionality (i.e. nature of interchain coupling) of π–π stacks controls the macroscopic charge transport in this type of system. Thus if the atomic electron-wave overlaps strongly only in the same chain, the charge can hop or tunnel in 1D (intra-chain hopping or tunnelling) only. In the case where there is enough overlap between/among atoms of two or three different and closely stacked chains, then the charge can hop or tunnel in 2D or 3D, respectively. Figure 2 shows the XRD
Figure 1. FT–IR spectra of pristine P3OT film in the range 600–4000 cm\(^{-1}\) showing various absorption bands corresponding to different types of bonding having different bond energies in P3OT \(\pi\)-conjugated polymeric chain.

pattern of pristine P3OT film. The prominent peak at lower angle (\(2\theta = 4.341\)) corresponds to the interchain distance (\(D = 20.3382\) Å) of two polymeric chains repetition, which forms 2D \(\pi--\pi\) stacks (as shown in the inset of figure 2). The peak at \(2\theta = 8.643\) corresponds to an inter-layer/-stack distance of 10.2223 Å and in conjunction with the 2D stack of chains, it forms a 3D arrangement of \(\pi\)-conjugated polymeric chains [7]. Hence, in this system the process of charge transport will be 3D in nature, and has been probed further by temperature variation of dc conductivity (subsection 3.2) and temperature and frequency variation of ac conductivity (subsection 3.3) measurements.

It is significant to mention here that the room temperature dc conductivity of pristine P3OT polymer synthesized for the present study at low temperature (228 K) is \(\sim 3.16 \times 10^{-7}\) S cm\(^{-1}\) which is better than the value of conductivity (\(\sim 1.1 \times 10^{-8}\) S cm\(^{-1}\)) obtained for pristine P3OT synthesized at 253 K [45]. The improvement in conductivity has been attributed to the synthesis of P3OT at lower temperature.

Furthermore, UV-VIS absorption around 520 nm (result not shown) also indicates the regioregular chain-like conformation in P3OT synthesized in the present case [7, 36]. Although we follow the same Sugimoto route, which gives the much inferior regiorandom P3OT when polymerization is performed at 303 K with low oxidant content, in the present case the polymerization was done at significantly lower temperature (at 228 K) with high oxidant content (0.8 M) and rigorous purification steps. The P3OT polymer synthesized for the present investigation shows improved properties (physical, structural, optical, morphological, electrical, etc) [7, 36], which are comparable to those observed for its regioregular P3ATs counterpart. We believe that the improvement is due to modified synthesis parameters which gives polymers having long conjugation length and fewer defects when polymerized at low temperature as this chemical polymerization is exothermic in nature.
3.2. Temperature dependence of dc conductivity

A mechanism very often considered to explain the temperature dependence of dc conductivity is Mott’s VRH [3]. According to this model, the conductivity should vary as

\[
\sigma_{dc} = \sigma_0 \exp \left\{ - \left( \frac{T_0}{T} \right)^{1/(1+d)} \right\}
\]

where \(d = 1, 2, 3\) is the dimensionality of the conduction process; \(\sigma_0, T_0\) are constants and \(T\) is the temperature. So it seems that it is possible to determine whether the mechanism of conduction is 1D or 3D by studying the temperature variation of dc conductivity. Hence, we have measured the dc conductivity of pristine P3OT film over a wide temperature range 77 < \(T\) < 350 K. The variation of dc conductivity (\(\sigma_{dc}\)) as functions of (a) \(1000/T\), (b) \(T^{-1/2}\), (c) \(T^{-1/3}\) and (d) \(T^{-1/4}\) in the temperature range 77–350 K for pristine P3OT film is shown in figure 3. It is evident from figure 3(a) that the conduction process has temperature dependent activation energy [7, 45, 46]. The dc conductivity (\(\sigma_{dc}\)) and activation energy (\(W\)) of pristine P3OT film at 300 K are \(\sim 3.16 \times 10^{-7}\) S cm\(^{-1}\) and \(\sim 0.17\) eV and at 77 K are \(\sim 3.98 \times 10^{-11}\) S cm\(^{-1}\) and \(\sim 0.051\) eV, respectively. Conductivity was found to decrease with decreasing temperature (figure 3(a)) as has been observed in many other CPs [7, 48]. It is evident from figure 3(a) that the temperature dependence of \(\sigma_{dc}\) does not follow an Arrhenius-type of behaviour. Such a behaviour of \(\sigma_{dc}\) in CPs is generally believed to be associated with the localized nature of the hopping of the charge carriers as has been visualized by Mott [3]. The temperature dependence

\[
\frac{\sigma_{dc}}{\sigma_0} \approx \frac{T}{T_0}^{1/(1+d)}
\]
of dc conductivity (figures 3(b)–(d)) demonstrates that the log $\sigma_{dc}$ versus $T^{-1/4}$ plot (figure 3(d)), corresponding to the 3D-VRH transport, gives best linear behaviour ($\sim 0.99992$) over the whole temperature range of investigation. Therefore, it is envisaged that Mott’s 3D-VRH conduction dominates the electrical transport mechanism in pristine P3OT film and, accordingly, different Mott’s parameters have been evaluated.

In general, the dc conductivity ($\sigma_{dc}$) can be given by the following relation [3]

$$\sigma_{dc} = \sigma_0 \exp \left( -\frac{W}{k_B T} \right), \quad (2)$$

where $\sigma_0$ is a constant pre-exponential factor, $k_B$ is the Boltzmann constant and $W$ is the activation energy which includes the hopping energy $W_H$ and any energy difference $W_D$ between the localized states due to disorder. According to Austin and Mott [49], it can be shown [50] that

$$W = W_H + \frac{1}{2}W_D, \quad \text{for } T > \frac{\theta_D}{2}, \quad (3)$$

$$W = W_D, \quad \text{for } T < \frac{\theta_D}{4}. \quad (4)$$
Where $\theta_D = \hbar \omega_0 / k_B$ is the characteristic Debye temperature of the phonon frequency $\nu_{ph}$ of the material. The lowest temperature ($\sim 77$ K) activation energy (0.051 eV) can be taken as a measure of disorder energy $W_D$. An estimate of $\omega_0$ can be made by taking the limiting value of $\hbar \omega_0 \sim W_D / 2$. A value of $\sim 0.051$ eV for $W_D$ gives $\nu_{ph} \sim 6.165 \times 10^{12}$ Hz and $\theta_D \sim 296$ K.

The effective dielectric constant ($\varepsilon_p$) can be evaluated [49, 50] by using the following expression

$$\frac{1}{\varepsilon_p} = \frac{1}{\varepsilon_\infty} - \frac{1}{\varepsilon_0},$$

(5)

where $\varepsilon_0$ is the static dielectric constant and $\varepsilon_\infty$ is the low temperature and high frequency dielectric constant or infinite frequency dielectric constant. The experimentally estimated values of $\varepsilon_0$ (33.2) at 300 K and $\varepsilon_\infty$ (3.6) have been used to calculate $\varepsilon_p$ from equation (5) and $\varepsilon_p$ was found to be equal to 4.038. By taking the polaron binding energy $W_p$ as twice the activation energy ($W$) at high temperature (300 K) [49, 50] $\sim 0.17$ eV, an estimate of the polaron radius $r_p$ can be made from the following expression

$$W_p = \frac{1}{2} \left( \frac{e^2}{\varepsilon_p r_p} \right),$$

(6)

and equals about 5.224 Å. The high temperature activation energy ($\sim 0.17$ eV) leads to a value of 13 for the small-polaron coupling constant [49, 50] $\gamma = W_p / h \omega_0$, by using the estimated value of $\nu_{ph} \sim 6.165 \times 10^{12}$ Hz. The effective polaron mass ($m_p$) has been evaluated and found to be eight times the mass of the electron [51, 52]. This value of coupling constant $\gamma$ indicates that the strong-coupling requirement for the application of the small-polaron theory to P3OT is satisfied [49, 50].

For 3D-VRH conduction [3], the constants $\sigma_0$ and $T_0$ of equation (1) are given by

$$\sigma_0 = e^2 \left\{ \frac{9 N(E_F)}{8 \pi \alpha k_B T} \right\}^{1/2} \nu_{ph},$$

(7)

and

$$T_0 = \frac{\lambda \alpha^3}{k_B N(E_F)},$$

(8)

where $e$ is the electronic charge, $k_B$ is Boltzmann’s constant, $N(E_F)$ is the density of states at the Fermi energy ($E_F$), $\nu_{ph}$ is the phonon frequency ($\sim 6.165 \times 10^{12}$ Hz), $\alpha (= 1 / r_p)$ is the coefficient of exponential decay of the localized states involved in the hopping process, $\lambda$ ($\sim 18.1$) is the dimensionless constant [45, 46, 53] and $T_0$ is the characteristic temperature. The two other parameters; the average hopping distance $R$ and the average hopping energy $W$ can be defined as

$$R = \left\{ \frac{9}{8 \pi \alpha k_B T N(E_F)} \right\}^{1/4},$$

(9)

and

$$W = \frac{3}{4 \pi R^3 N(E_F)}.$$  

(10)
The value of slope $T_0$ has been estimated from the straight line of figure 3(d) and found to be $\sim 2.4 \times 10^8$ K. $\sigma_0$ is taken as the intercept of that line and is $\sim 7.7 \times 10^7$ S cm$^{-1}$. After using the evaluated value of $\alpha^{-1}(r_p \sim 5.244$ Å) and equations (7)–(10), the values of $N(E_F)$, $R$ and $W$ have been computed and found to be $\sim 6.07 \times 10^{18}$ cm$^{-3}$ eV$^{-1}$, $58.8 \times 10^{-8}$ cm and $0.193$ eV, respectively. The magnitude of $R$, $W$ and $N(E_F)$ is consistent with the values obtained earlier for other CPs [7, 11, 48, 53].

3.3. Temperature and frequency dependence of dielectric constant and ac conductivity

The ac conductivity $\sigma(\omega)_m$, dielectric constant $\varepsilon'(\omega)$ and dielectric loss $\varepsilon''(\omega)$ of pristine P3OT films (thickness $\sim 20$ µm) have been measured in the temperature range 77–350 K and in the frequency range 100 Hz–10 MHz. The dielectric parameters were evaluated by measuring equivalent parallel capacitance $C_p$ and dissipation factor $\tan \delta$ or the equivalent resistance $R_p$ of the samples. The scheme of the equivalent circuit model is shown and discussed briefly in appendix A. A frequency dependent complex conductivity can arise from interfacial polarization at contacts, grain boundaries or from other inhomogeneities present in the polymer film. These effects arising from ohmic and nonohmic contacts have been discussed earlier [54, 55]. The dielectric parameters are usually represented in terms of the dielectric constant $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$. During the last three decades, especially in the interpretation of the data of amorphous materials [56], it has been customary to represent the experimental results in terms of the dielectric constant $\varepsilon'(\omega)$ and $\sigma(\omega)$. Here, $\sigma(\omega)$ is the real part of the conductivity and is related to dielectric loss $\varepsilon''(\omega)$ by

$$\sigma(\omega) = \omega \varepsilon''(\omega) \epsilon_0,$$

(11)

where $\omega = 2\pi f$, $f$ being the frequency and $\epsilon_0$ is free space permittivity. The above parameters have been used to represent the experimental results of the present investigation on P3OT films. In an ideal insulator there are no free charges and $\sigma(\omega)$ or $\varepsilon''(\omega)$ are related to the bound charges only or the charges hopping between well defined sites, without making any contribution to the long range motion or dc conductivity. However, in real systems, there are also some free charge carriers which give rise to dc conductivity without contributing anything to dielectric polarization. Hence, the measured ac conductivity $\sigma(\omega)_m$ will have contributions from both dc and ac conduction and can be expressed as

$$\sigma(\omega)_m = \sigma(\omega) + \sigma_{dc},$$

(12)

where $\sigma(\omega)$ denotes the ac conductivity and $\sigma_{dc}$ the dc conductivity. All these parameters have been used to represent and analyse the experimental results of the present investigation.

Figure 4 shows the variation of ac conductivity $\sigma(\omega)_m$ as a function of temperature in the range 77–350 K at five fixed frequencies; 0.1, 1, 10, 100 kHz and 1 MHz for pristine P3OT film (thickness $\sim 20$ µm) as a representative result. It is evident from figure 4 that in the low temperature region the measured ac conductivity $\sigma(\omega)_m$ is considerably higher than the dc conductivity $\sigma_{dc}$ and it increases with increasing frequency. It shows a very weak dependence on temperature in the low temperature region, however, at high temperatures, $\sigma(\omega)_m$ becomes equal to $\sigma_{dc}$ and the temperature at which $\sigma(\omega)_m$ becomes equal to $\sigma_{dc}$ increases with increasing frequency.

Figure 5 shows the variation of dielectric constant $\varepsilon'(\omega)$ as a function of temperature in the range 77–350 K at five fixed frequencies; 0.1, 1, 10, 100 kHz and 1 MHz for pristine P3OT
Figure 4. Measured ac conductivity $\sigma(\omega)_m$ as a function of reciprocal temperature (77–350 K) at five fixed frequencies (0.1, 1, 10, 100 kHz and 1 MHz) for pristine P3OT film (thickness $\sim$ 20 $\mu$m). The dc conductivity data of figure 3(a) is included in this figure.

Figure 5. Dielectric constant $\varepsilon'(\omega)$ as a function of temperature (77–350 K) at five fixed frequencies (0.1, 1, 10, 100 kHz and 1 MHz) for pristine P3OT film (thickness $\sim$ 20 $\mu$m).

film (thickness $\sim$ 20 $\mu$m) as a representative result. For a good electrode (ohmic contact), $\varepsilon'(\omega)$ shows a peak when it is measured as a function of temperature (figure 5). The inset shows the $I$–$V$ characteristics of pristine P3OT films having Au–P3OT–Au structure showing ohmic contact. A decrease of static dielectric constant (figure 5) with increasing temperature clearly
indicates that the measured values of dielectric constant represent the true bulk phenomenon [55] and the electrode polarization and other spurious effects have negligible effects as has been observed earlier in the case of vinyl chloride–vinyl acetate copolymer [57]. It is also observed that the behaviour of the variation of \( \varepsilon' (\omega) \) with temperature is similar for all frequencies. At low temperatures, \( \varepsilon' (\omega) \) shows little dependence on temperature, however, in the higher temperature region at a given fixed frequency it shows strong temperature dependence and increases rapidly with increasing temperature. This rapid increase in dielectric constant is followed by a slow decrease, thus giving a peak (figure 5). The temperature at which the rapid increase in dielectric constant starts with temperature and also the temperature at which a peak in \( \varepsilon' (\omega) \) is observed increases with increasing frequency. The peak value of the dielectric constant is higher for low frequencies and lower for high frequencies. This behaviour is consistent with a Debye-type dielectric dispersion characterized by a relaxation frequency \( f_0 \), where the measuring frequency is higher than \( f_0 \) in the low temperature region and lower than \( f_0 \) at high temperatures.

Figure 6 shows the variation of derived dielectric loss \( \varepsilon'' (\omega) \) (using equations (11) and (12)) as a function of temperature in the range 77–280 K at five fixed frequencies; 0.1, 1 10, 100 kHz and 1 MHz for pristine P3OT film (thickness \( \sim 20 \mu m \)). It is evident from this figure that the loss peak has been observed only for 0.1, 1 10, 100 kHz frequencies and the magnitude of the loss peak decreases with increasing frequency as has been observed for other CPs [15]. However, the loss peak is not observed at 1 MHz frequency (figure 6), it may appear in the high temperature region and be beyond the range of measurement. The activation energy has been evaluated [57]–[59] from figure 6 by the Fuoss approach [58] in which a variable \( x \) is defined as

\[
x = \frac{1 + (1 - K^2)^{1/2}}{K},
\]
where $K = \varepsilon''/\varepsilon''_{\text{max}}$. The plot of $\log x$ as a function of $1000/T$ (figure 7) gives a straight line which can be given by an empirical relation as

$$\log x = a + \frac{b}{T},$$

(14)

where $a$ is the intercept of the straight line on the $x$-axis and $b$ is the slope which gives the value of activation energy as $U = b k_B$ (eV), where $k_B$ is Boltzmann’s constant. The values of activation energies obtained from the slopes of $\log x$ versus $1000/T$ plots (figure 7) are $\sim 0.054–0.073$ eV.

Figure 8 shows the variation of measured ac conductivity $\sigma(\omega)_m$ as a function of frequency in the range 100 Hz–1 MHz at different fixed temperatures for pristine P3OT film (thickness $\sim 20 \mu m$). It is observed that the value of slope $s$ at 77 K is $\sim 0.61$ and decreases with increasing temperature. It is also observed that at 77 K the measured ac conductivity $\sigma(\omega)_m$ shows an increase with increasing frequency. This trend is also observed at higher temperatures. Figure 9 shows the variation of dielectric constant $\varepsilon'(\omega)$ as a function of frequency in the range 100 Hz–10 MHz at different fixed temperatures for pristine P3OT film (thickness $\sim 20 \mu m$). The dielectric constant at 77 K shows little dependence on frequency. However, at higher temperatures a rapid increase in dielectric constant is observed with decreasing frequency. It is evident from this figure that a frequency independent region for $\varepsilon'(\omega)$ is observed in the low frequency region at higher temperatures. However, this region could not be observed at all the temperatures because of experimental limitations.

### 3.3.1 Low temperature region where $\sigma(\omega)_m \gg \sigma_{dc}$.

At low temperatures a frequency dependent conductivity described by [3]

$$\sigma(\omega) = A\omega^s,$$

(15)
Figure 8. Variation of measured ac conductivity $\sigma(\omega)_m$ with frequency (100 Hz–1 MHz) at different fixed temperatures for pristine P3OT film (thickness $\sim 20 \mu m$).

Figure 9. Variation of dielectric constant $\varepsilon' (\omega)$ with frequency (100 Hz–10 MHz) at different fixed temperatures for pristine P3OT film (thickness $\sim 20 \mu m$).

is observed where the exponent $s$ is observed to be less than unity. The values of measured ac conductivity at 0.1, 1, 10, 100 kHz and 1 MHz at 77 K are reported in table 1. In the low temperature region, i.e., at 77 K where $\sigma(\omega)_m \gg \sigma_{dc}$, the variation of $\sigma(\omega)_m$ as a function of frequency can be expressed in terms of equation (15). The value of parameter $s$ is $\sim 0.61$, which decreases with increasing temperature. The activation energy ($U$) for the charge carriers calculated at 77 K is $\sim 0.014 \text{eV}$, which provides evidence of electronic hopping conduction [15, 60] in pristine P3OT film at low temperatures. An estimate of the density of states
Table 1. The ac conductivity \(\sigma(\omega)\), slope at 77 K and the density of states at the Fermi level; \(N(E_F)\), computed by using equations (16) and (17) assuming \(U_{ph} = 10^{13}\) Hz and \(\alpha = 1.0, 2.0\) and \(4.0\) Å\(^{-1}\) for pristine P3OT film.

| Frequency (kHz) | \(\sigma(\omega)\) at 77 K \((10^{-10} \text{ S cm}^{-1})\) | Slope at 77 K | \(N(E_F)^a\) \((10^{18} \text{ cm}^{-3} \text{ eV}^{-1})\) | \(N(E_F)^b\) \((10^{19} \text{ cm}^{-3} \text{ eV}^{-1})\) | \(N(E_F)^c\) \((10^{20} \text{ cm}^{-3} \text{ eV}^{-1})\) |
|----------------|---------------------------------|---------------|-------------------------------|-----------------|-------------------|
| 0.1            | 0.38                            | 0.61          | 5.47                          | 3.09            | 1.75              |
| 1              | 0.85                            | 0.61          | 3.19                          | 1.81            | 1.02              |
| 10             | 2.68                            | 0.61          | 2.26                          | 1.28            | 0.72              |
| 100            | 9.25                            | 0.61          | 1.72                          | 0.97            | 0.55              |
| 1000           | 50.2                            | 0.61          | 1.71                          | 0.96            | 0.54              |

\(^a\) Taking \(\alpha = 1.0\) Å\(^{-1}\).

\(^b\) Taking \(\alpha = 2.0\) Å\(^{-1}\).

\(^c\) Taking \(\alpha = 4.0\) Å\(^{-1}\).

near the Fermi level \(N(F_F)\) could be made from the ac conductivity \(\sigma(\omega)\) at low temperatures by using Austin and Mott’s relation [49] given as

\[
\sigma(\omega) = \left( \frac{1}{3} \right) \pi e^2 k_B T (N(E_F))^2 \left( \frac{\omega}{\alpha^5} \right) \left\{ \ln \left( \frac{\upsilon_{ph}}{\omega} \right) \right\}^4,
\]

where the hopping near the Fermi level is expected to dominate. In equation (16), \(k_B\) is Boltzmann’s constant, \(e\) is the electronic charge, \(\omega = 2\pi f\) is a frequency factor and \(\alpha\) is the radius of the carrier wavefunction. Assuming \(U_{ph} = 10^{13}\) Hz and taking the value of ac conductivity at 77 K and at 0.1, 1, 10, 100 kHz and 1 MHz, and taking the numerical value of \(\alpha\) in the range 1–4 Å\(^{-1}\), the values of \(N(E_F)\) have been computed by using equations (16) and (17) and are given in table 1. The above equation is valid for uncorrelated hops between pairs of sites and the condition which is given [49] as

\[
\left\{ \left( \frac{4\pi}{3} \right) (N(E_F)k_B T)^{1/3} \right\} \alpha^{-1} \ln \left( \frac{\upsilon_{ph}}{\omega} \right).
\]

This condition is valid for the values of \(\alpha\) reported in table 1. The reasonable estimate of \(N(E_F)\) from equations (16) and (17) suggests that the charge carrier hopping near the Fermi level is in between nearest neighbour sites. In spite of the fact that equation (16) gives a reasonable estimate of \(N(E_F)\), it fails to explain the temperature dependence of \(\sigma(\omega)\). Equation (16) predicts a linear temperature dependence of \(\sigma(\omega)\), however, the measured values of ac conductivity show weak temperature dependence in the low temperature region. Pollak [61] has argued that the temperature dependence of ac conductivity is due to multiple hops. However, it has been shown in transition metal oxides glasses [62] that multiple hops cannot give strong temperature dependence of \(\sigma(\omega)\). Pike [63] has tried to explain the temperature dependence of \(\sigma(\omega)\) and the exponent \(s\) and suggested the following expression

\[
1 - s = \frac{6k_B T}{W_m},
\]

where \(W_m\) is the activation energy and \(k_B\) is Boltzmann’s constant. Similar temperature dependence of \(s\) has also been suggested earlier [64, 65]. The activation energy \((W_m)\) calculated...
using equation (18) is $\sim 0.102\,\text{eV}$ at 77 K which is higher than the activation energy ($U$) $\sim 0.014\,\text{eV}$ obtained at 77 K from ac measurements (figure 4) for pristine P3OT film. This shows that both Mott and Pike’s model give a qualitative picture and fail to give quantitative agreement with the experimental results.

### 3.3.2. High temperature region where $\sigma(\omega)_m$ approaches $\sigma_{dc}$.

The dielectric relaxation in the high temperature region can be due to (i) electrode barrier or surface effects or macroscopic inhomogeneities [54, 55, 66, 67] and (ii) bulk effects: (a) micro-inhomogeneities [67, 68] and (b) true bulk behaviour (conventional Debye-type relaxation) [55, 57, 68]. At 77 K there is evidence of dielectric dispersion in the low frequency region while at higher temperatures the dielectric constant shows a large dispersion (figure 9). The measured values of dielectric constant are independent of film thickness (results not shown) and the scatter in the measured values is within the accuracy of the measurements. This suggests that the dielectric dispersion in this system is not due to the electrode polarization or surface barrier at the electrodes. It is evident from figure 8 that the decrease of slope $s$ with increasing temperature is an outcome of the larger increase of conductivity with temperature at lower frequencies as compared to that at higher frequencies.

In the low temperature region the measured ac conductivity $\sigma(\omega)_m$ is almost independent of temperature and the strong temperature dependence occurs at higher temperatures for higher frequencies (figure 4). The nature of the temperature dependence of the measured ac conductivity $\sigma(\omega)_m$ in the low temperature region makes it difficult to define a characteristic relaxation frequency $f_0$. However, in the high temperature region where $\sigma(\omega)_m$ approaches dc conductivity $\sigma_{dc}$, the ac component of conductivity may show clearer evidence for $f_0$. In particular the dielectric loss $\varepsilon''(\omega)$ derived from figures 4 and 8 by using equations (11) and (12) may show a Debye-type loss peak at $f = f_0$. The dielectric loss $\varepsilon''(\omega)$ calculated at 200 K using equations (11) and (12) is shown in figure 10 as a representative result. A clear and broad peak in $\varepsilon''(\omega)$ is observed. However, the values of $\varepsilon''(\omega)$ are derived from the measured ac conductivity $\sigma(\omega)_m$ in the temperature region where $\sigma(\omega)_m$ becomes close to $\sigma_{dc}$. This introduces a large error in the evaluation of $\varepsilon''(\omega)$. The error bar is shown in figure 10. The half width of the plot of $\varepsilon''(\omega)$ against log of frequency should be of the order of 1.40 decade for Debye-type dispersion. However, the width appears to be of the order of 2–3 decades of frequency suggesting a wide distribution of relaxation times in pristine P3OT film. A difficulty in this approach is that the magnitudes of $\sigma(\omega)_m$ and $\sigma_{dc}$ are comparable at some temperatures (figures 4 and 8) and the uncertainty in the evaluation of $\varepsilon''(\omega)$ (figures 6 and 10) is large. Hence, it has been preferred to present the results in terms of $\varepsilon'(\omega)$ and $\sigma(\omega)_m$ and more emphasis has been given to $\varepsilon'(\omega)$ in the interpretation of the results.

The dielectric constant for a Debye-type process is given [69] by

$$\varepsilon'(\omega) - \varepsilon_\infty = \frac{(\varepsilon_0 - \varepsilon_\infty)}{1 + \left(\frac{f}{f_0}\right)^2},$$  \hspace{1cm} (19)

where $f$ is the measuring frequency and $f_0$ is the relaxation frequency at which a peak in dielectric loss $\varepsilon''(\omega)$ is observed. $\varepsilon_0$ and $\varepsilon_\infty$ are the static and infinite frequency dielectric constants. In the low temperature region $f/f_0 \gg 1$ then $\varepsilon'(\omega) \rightarrow \varepsilon_\infty$ and at high temperature $f/f_0 \ll 1$, then $\varepsilon'(\omega) \rightarrow \varepsilon_0$. In the low temperature region the change in $\varepsilon'(\omega)$ with temperature is negligible and then it has a sharp rise at the temperature at which $f = f_0$. It can be observed that strong temperature dependence starts at higher temperatures for higher frequencies or at
Figure 10. Variation of derived dielectric loss $\varepsilon''(\omega)$ as a function of frequency (100 Hz–1 MHz) at 200 K. Error bars have been shown in the figure.

lower temperature for lower frequencies indicating thereby that $f_0$ increases with an increase in temperature. It can be seen here that the region where there is a strong temperature dependence of $\varepsilon'(\omega)$ at a given frequency (figure 5) is the same at which $\sigma(\omega)_m$ approaches $\sigma_{dc}$ (figure 4). Thus the variation of $\varepsilon'(\omega)$ with temperature confirms the existence of loss peaks indicated in figure 6. The measured values of $\varepsilon'(\omega)$ at frequencies 0.1, 1, 10, 100 kHz and 1 MHz show a saturation region at the high temperature end of the spectrum (figure 5) and this may be taken as an estimate of the static dielectric constant. The static dielectric constant has been estimated from the plots of dielectric constant versus temperature (figure 5) and the values have been plotted as a function of reciprocal temperature in figure 11(a). These values are in good agreement with the values of $\varepsilon_0$ achieved at higher temperatures in the dielectric constant versus frequency spectrum (figure 4). It is evident from figure 11(a) that $\varepsilon_0$ decreases with increasing temperature. Figures 5 and 9 are consistent with Debye-type dispersion and suggest that the loss peaks depicted in figures 6 and 10 are real. The existence of well defined loss peaks has also been observed in vinyl chloride–vinyl acetate copolymer [57], and polypyrrole, poly(N-methyl pyrrole) and their copolymers [15].

The evaluation of relaxation frequency $f_0$ from ac conductivity measurements becomes difficult especially when the measurements have been made as a function of temperature. The alternative method for the determination of $f_0$ from the measured dielectric constant $\varepsilon'(\omega)$ versus temperature (figure 5) seems to be unrealistic. However, it does not have an ambiguity caused by the closeness of measured ac conductivity $\sigma(\omega)_m$ and dc conductivity $\sigma_{dc}$ in the high temperature region (figure 4). It can be seen from equation (19) that at the temperature at which $\varepsilon'(\omega) - \varepsilon_\infty$ becomes equal to $(\varepsilon_0 - \varepsilon_\infty)/2 + \varepsilon_\infty$ at a given frequency, then the measuring frequency $f$ becomes equal to the relaxation frequency $f_0$. The above discussion indicates that the well defined dielectric loss peaks (figure 6) have been observed in the temperature region where the measured ac conductivity $\sigma(\omega)_m$ approaches the dc conductivity $\sigma_{dc}$ (figure 4). The relaxation frequency $f_0$ can be estimated from the measured dielectric constant $\varepsilon'(\omega)$ as a function of temperature or frequency (figures 5 and 9) and has been plotted in figure 11(b).
static dielectric constant $\varepsilon_0$ can also be determined from the measured frequency variation of dielectric constant $\varepsilon'(\omega)$ or temperature variation of dielectric constant $\varepsilon' (\omega)$ at fixed frequency. The estimated value of static dielectric constant $\varepsilon_0$ (figure 11(a)) could at best be accurate within $\pm 5\%$.

4. Conclusions

In conclusion, we have synthesized P3OT polymer with significant improvement in polymer quality following a low-cost chemical polymerization route at low-temperature. The improvement in polymer quality has been confirmed by FT-IR, UV-VIS, XRD and conductivity studies. The material used for the present study has shown the structural characteristics in which
\(\pi\)-conjugated chains are arranged in 3D and open a path for 3D movement of charge carriers in this system. Temperature dependent dc conductivity behaviour shows the applicability of the 3D-VRH mechanism in this system. Further, through the ac conductivity measurement, the ac conductivity \(\sigma(\omega)_m\), dielectric constant \(\varepsilon'(\omega)\) and loss \(\varepsilon''(\omega)\) of pristine P3OT films as functions of frequency and temperature have been reported for the first time in a wide temperature range 77–350 K and frequency range 100 Hz–10 MHz. The measured ac conductivity \(\sigma(\omega)_m\) can be described by the relation \(\sigma(\omega) = A\omega^s\), where the value of parameter \(s\) at 77 K is \(\sim 0.61\) which decreases with increasing temperature. Well defined dielectric loss peaks have been observed in the temperature region where \(\sigma(\omega)_m\) approaches the dc conductivity \(\sigma_{dc}\). These observed loss peaks are associated with the hopping of the charge carriers and shows a decrease in maximum magnitude with increasing frequencies having a wide distribution of relaxation times. The activation energy \((U)\) estimated at 77 K gives an indication of electronic hopping conduction at low-temperatures. Various electrical parameters extracted from measured dc conductivity data suggest the application of Mott’s 3D-VRH model in this system.

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**Appendix A**

In the presence of surface barriers at the electrodes (due to non-ohmic contacts) the electrical equivalent of the sample can be represented as shown in scheme A1 [66].

For a simple barrier model, the barrier capacitances and resistances at both the electrodes have been assumed to be equal and are represented by the single capacitance \(C_S\) and the resistance \(R_S\). The corresponding bulk capacitance and resistance are represented by \(C_B\) and \(R_B\). If \(C_p\) and \(R_p\) represent the equivalent parallel capacitance and resistance of the sample from which the values of dielectric constant and ac conductivity are evaluated and assuming \(C_S, R_S\) and \(C_B, R_B\) to be independent of frequency, then \(C_p\) and \(R_p\) can be given by [66]

\[
C_p = \frac{C_S R_S^2 (1 + \omega^2 C_B^2 R_B^2) + C_B R_B^2 (1 + \omega^2 C_S^2 R_S^2)}{R_S (1 + \omega^2 C_B^2 R_B^2) + R_B (1 + \omega^2 C_S^2 R_S^2) + 2 R_S R_B (1 + \omega^2 C_S C_B R_S R_B)}, \tag{A.1}
\]
and

\[ R_p = \frac{R_S^2 (1 + \omega^2 C_B^2 R_B^2) + R_B^2 (1 + \omega^2 C_S^2 R_S^2) + 2 R_S R_B (1 + \omega^2 C_S C_B R_S R_B)}{R_S (1 + \omega^2 C_B^2 R_B^2) + R_B (1 + \omega^2 C_S^2 R_S^2)}. \]  

(A.2)

If we assume that \( C_S \gg C_B \) and \( R_S \gg R_B \), then it can be shown that if \( \omega C_S R_B \ll 1 \), then \( C_p = C_S \) and \( R_p = R_S \); if \( \omega C_S R_B \gg 1 \), then \( C_p = C_B \) and \( R_p = R_B \). Thus the surface capacitance and bulk resistance are two important parameters (at least for samples having low resistance), which control the frequency dispersion. Therefore, \( \varepsilon'(\omega) \) can exhibit frequency dispersion even if it is assumed to be independent of frequency. A more complex dependence of \( \varepsilon'(\omega) \) on frequency is expected if we consider the contribution of relaxation times of the surface states [70]. To know whether the dispersion is due to the electrode barrier or due to bulk phenomena [71], measurements can be made on different thicknesses of the samples with the same electrode area. If the measured values of \( \varepsilon'(\omega) \) and \( \varepsilon''(\omega) \) are independent of the sample thickness then the measured values correspond to the bulk phenomenon and if they depend upon the thickness then the electrode barrier effects may dominate [66].

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