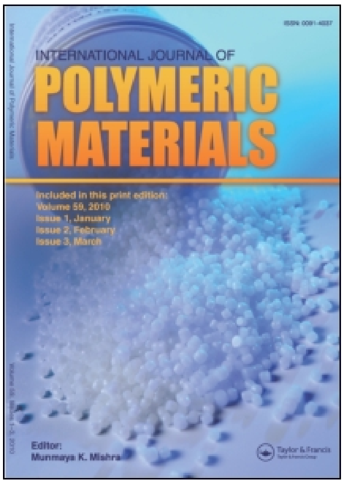

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STUDY OF HOPPING CONDUCTION IN POLYISOXAZOLINE

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Temperature and frequency-dependent ac-conductivity of polyisoxazoline have been measured. The ac conductivity is found to be proportional to ω^s. *The values of the exponent s decrease with the increase in the temperature, in the high temperature region. The hopping over the barrier model appears to be not valid. Long's polaron model is the suitable one to interpret the obtained data.*

Keywords: polyisoxazoline, electrical conduction, hopping mechanism

INTRODUCTION

Conduction can occur by the thermally activated movement of electrons from one localized state to another, a process called hopping and first described by Miller and Abrahams [1]. This is a process in which an electron in an occupied state with energy below the Fermi level receives energy from a phonon, which enables it to move to a nearly state above the Fermi level. Thus, the electron was supposed always to move to the nearest *empty state*.

For dc conduction the electrons have to cross the entire sample in many successive hops. If the hopping sites are distributed at random, the current path will inevitably include some long-distance hops, which have a very small hopping probability. At high frequencies the field is reversed before such an unlikely hop become necessary, so that hopping occurs mainly between close neighbors (pair approximation) [2]. The sample can be simulated by an array of resistors and capacitors, in series and parallel (random network) [3]. Therefore, one expects constant conductivity up to a certain threshold and then an

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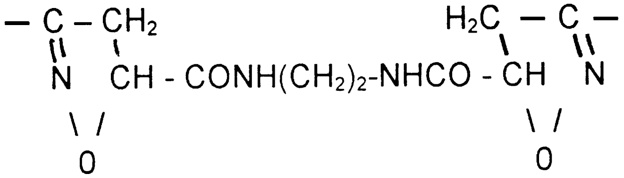
increase more or less linearly with frequency. The threshold frequency increases with the dc conductivity because high dc conductivity implies that there are only very few long-distance hops [4].

A semiconducting polymer, which contains heterocyclic rings in its main chains, attracts recently worldwide attention due to its industrial applications as conducting materials [5–8]. In this investigation I try to continue the work on the electrical properties of polyisoxazoline [9] by studying the mechanisms of hopping conduction and the suitable models.

EXPERIMENTAL WORK

Polyisoxazoline was synthesized by the reaction of terephthalohydroxamoyl chloride with corresponding dipolarophiles in refluxing toluene and was purified by extracting in hot methanol. Polyisoxazoline has the chemical structure was compressed to form discs of 1 mm



thickness and 5 mm diameter. The discs were kept for 30 min under a given temperature and electric voltage. The ac dielectric measurements were done by using an RLC bridge to measure the capacitance and the dielectric losses of the prepared samples in the frequency range 10^3–10^6 Hz at different temperatures from 300 to 400 K with heating rate 2 K/min. The real (ε') and imaginary (ε'') parts of the dielectric constant were calculated using the relation [10]

$$\varepsilon' = Cd/\varepsilon_o A \tag{1}$$

$$\varepsilon'' = \varepsilon' \tan \delta \tag{2}$$

where C the capacitance, d the sample thickness (0.1 mm), εo the vacuum permitivity (8.85×10^{12} F/m), A the electrode area (1 cm^2), and δ the loss angle.

RESULTS

The dielectric constant of polyisoxazoline is shown in Figure 1 as a function of temperature for different frequencies. As observed from these curves, a peak in the dielectric constant appears at each

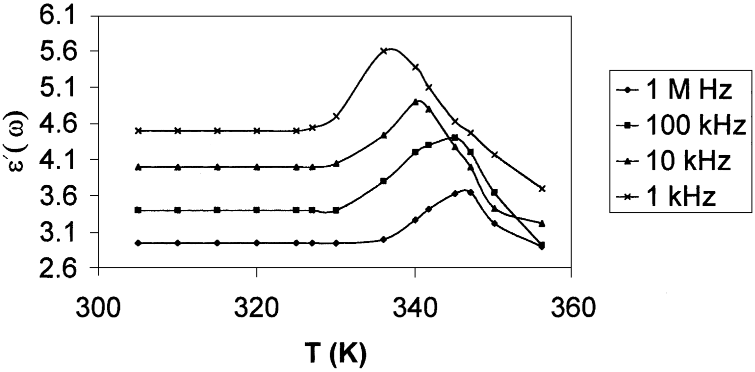


FIGURE 1 Real part of the dielectric constant *vs.* temperature at different frequencies for polyisoxazoline.

frequency. This peak moves to higher temperatures with increasing frequency. This behavior indicates a Debye-type dielectric dispersion [11] characterized by a relaxation frequency in the polymer. The magnitude of this dispersion depends on the temperature. This is because the dielectric dispersion is related to $\sigma ac(\omega)$ which in turn depends on the temperature through the real, $\sigma'(\omega)$, and imaginary, $\sigma''(\omega)$, parts of the ac conductivity. $\sigma'(\omega)$ and $\sigma''(\omega)$ are calculated using

$$\sigma'(\omega) = \omega\varepsilon_0\varepsilon'' \tag{3}$$

$$\sigma''(\omega) = \omega\varepsilon'(\varepsilon_o - \varepsilon_\infty) \tag{4}$$

where ε_o and ε_∞ are, respectively, the static and high frequency dielectric constants.

The variation of ε' with frequency, Figure 2, shows a linear behavior, which indicates that the charge stored in the sample decreases with increased applied frequency. Figure 2 exhibits also that the increase of temperature increases the value of ε'. This behavior can be explained according to the fact that both the heating and the field cause an increase in the random motion of the main chains and consequently increases the free volume, *i.e.*, separates the chains from each others which frees the polymer polar groups due to the separation between the chains which leads to increasing of ε' values.

The variation of ε'' with temperature is shown in Figure 3. One advantage of this plot is that it can show directly the Debye-type relaxation character in the polymer and find the characteristic resonance frequency $f_0(=1/2\pi\tau$ where τ is the relaxation time) for the relaxation process. It is interesting to mention here that, similar to ε'

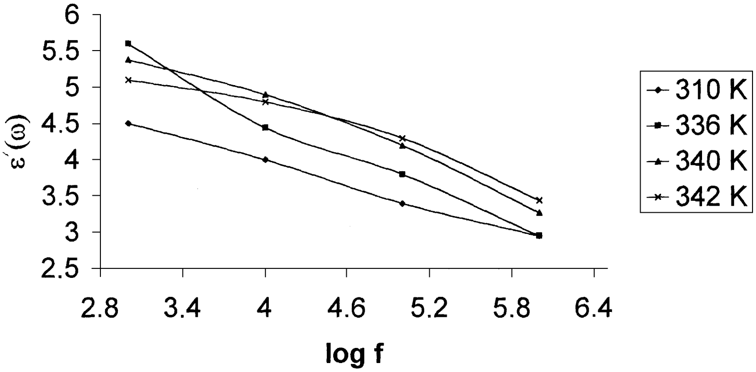


FIGURE 2 Real part of the dielectric constant *vs.* frequency at different temperatures for polyisoxazoline.

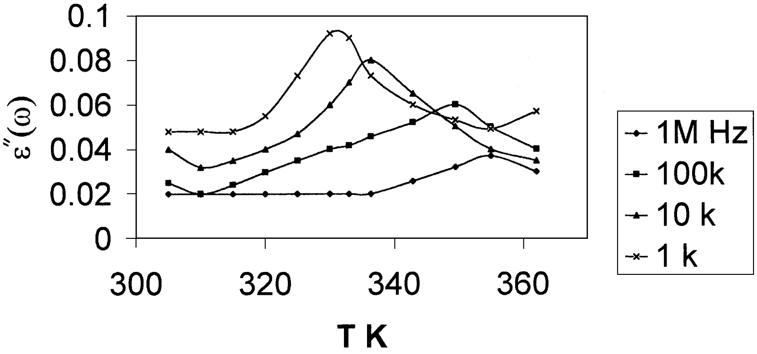


FIGURE 3 Imaginary part of the dielectric constant *vs.* temperature at different frequencies for polyisoxazoline.

curves, a peak in ε'' curves was also observed. This also supports the characteristic feature of a Debye-type relaxation.

Figure 4 shows the temperature variation of the relaxation frequency calculated from Figure 3 for polyisoxazoline. It can be observed that the relaxation frequency is similar for the polymer with the lower values of the conductivity. The thermal variation of the ac conductivity with temperature for polisoxazoline at different frequencies was shown in Figure 5. Both Figures 4 and 5 show similar trends indicating that a relaxation process is involved. The frequency dependence of the σ_{ac} at temperatures 300, 320 and 340 K is shown in Figure 6. The values of σ_{ac} for all temperatures are found to increase with increasing frequency.

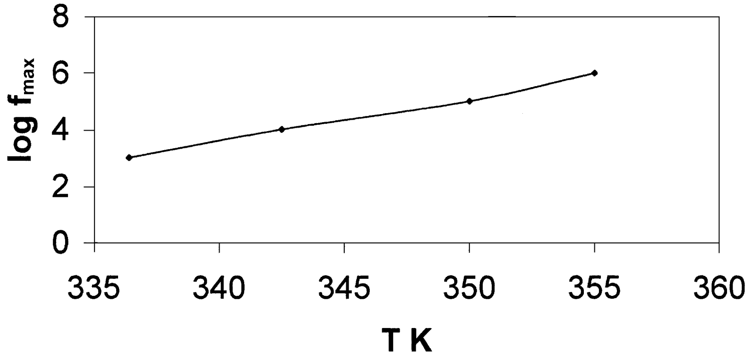


FIGURE 4 Log f_{max} against 1,000/T for polyisoxazoline.

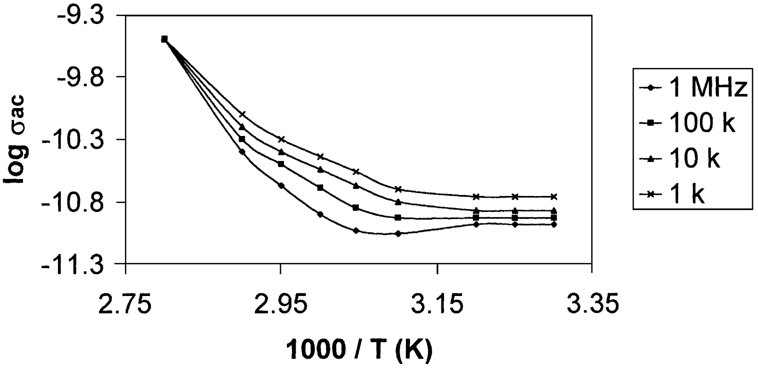


FIGURE 5 Log σ_{ac} *vs.* 1,000/T for polyisoxazoline at different frequencies.

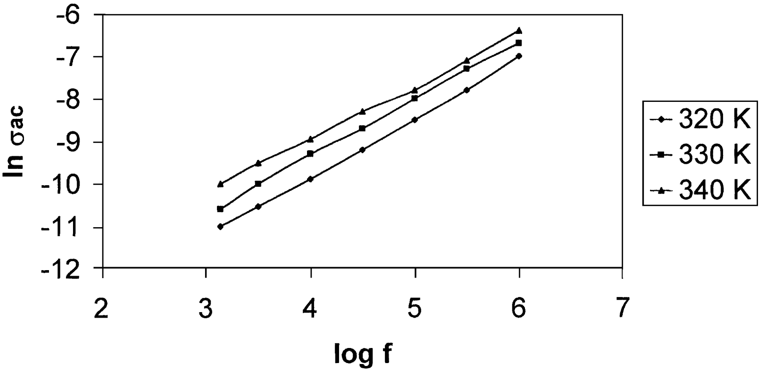


FIGURE 6 Ln σ_{ac} *vs.* log f at different temperatures for polyisoxazoline.

DISCUSSION

The charge propagation is assumed to occur by hopping of electrons through localized states with energetic and positional disorder. The distributions of hopping site energies and distances are Gaussian, and the jump rates can be described by an expression due to Miller and Abrahams [1], originally proposed to describe low temperature impurity hopping in semiconductors. The electron−phonon coupling is sufficiently weak that polaronic effects can be neglected, and the process is incoherent, characterized by a loss of phase memory after each jump. The Miller-Abrahams-expression is based on a single phonon approximation and assumes that downward jumps in energy are not impeded by an energy-matching condition for dissipation of the difference in electronic energy. It is also assumed that downward jumps are not accelerated by the electric field. The validity of using the Miller-Abrahams expression for computing jump rates in disordered solids has been discussed by Emin, but due to the asymmetry of the jump rates, any analytic treatment of the hopping problem becomes difficult, in particular if the distribution of hopping site energies is Gaussian.

It is assumed that [12] for Fermi glasses electronic jumps of energy $\sim$kT are the only contributors to the conductivity. This indicated that the number of states allowed for electronic jumps is $N(E_F)kT$. In the present case we are not dealing with Fermi glasses, but with a polymer at which the conductivity affected by the charge carriers fluctuates at the percolation level E_c. Thus one can say that the conductivity is determined only by carriers from a narrow energy integral $\sim$kT near the percolation level. If the percolation level lies in the region of a density-of-states tail, the number of states

$$E_c - kT \leqslant E \leqslant E_c + kT \tag{5}$$

is given by the integral [13]

$$\int_{E_c-kT}^{E_c+kT} N(E)dE \tag{6}$$

where N(E) is described by [14]:

$$N(E) = N_v \exp\left(\frac{-E}{kT_o}\right) \tag{7}$$

which indicates that the density of states in the region of the tail falls exponentially with depth in the band gap (N_v is the number of states in the valency band).

While the conductivity of polyisoxazoline is governed entirely by charge carriers with energies in a narrow energy interval $\sim$kT near the percolation level E_c. At lower energies (in the case of regions with the narrowest band gap) the bands of high conductivity (and high mobility) do not form an infinite cluster. At energies exceeding E_c (*i.e.*, in regions with a wider band gap) such infinite clusters are shunted by the electrical cluster because its resistance is lowest among infinite clusters. This is due to the fact that regions with a wider band gap (lying higher in the density-of-states tail) correspond to lower mobility. Therefore, the lower limit in the integral (6) is governed by the decay of the density of states, and the upper one by the rapid fall-off of the mobility corresponding to those local regions of a disordered solid where the regions is wider and contribute to the upper part of the density-of-states tail [15].

In order to account for the temperature dependence of the ac conductivity, various models have appeared in the literature [16–18]. Pike [19] proposed the hopping of the carriers over the barrier (HOB) model. This model considers the hopping of the carriers between two sites over a barrier separating them, rather than quantum mechanical tunneling through the barrier. The distribution of relaxation times for this process arises from the exponential dependence of the relaxation times on the barrier height.

According to Mott's argument [20, 21], at low temperatures an electron, instead of hopping to a near neighbor, can hop to a distant but energetically more favorable state. Bloch, Weisman and Varma [22] proposed a temperature dependence of the conductivity in the form:

$$\ln(\sigma(T)/\sigma_o) = -(T_1/T)^{1/2} \tag{8}$$

where

$$\sigma_o = (e^2N(E)f/L)(mt/h)(\beta^{-1})^{-2} \tag{9}$$

and

$$T_1 = 16\alpha/nkN(E) \tag{10}$$

(here e is the electronic charge, N(E) is the density of states, f the attempting frequency, L the polymer chain cross-sectional area, h plank's constant, α the localized length, β^{-1} the transverse localization length, t the mean free time, m the interaction transfer integral, n the nearest neighbor chains, and k is the Boltzmann's constant). On the other hand, Kurkijarvi's [23] showed that for a single infinite chain the hopping conductivity should have the temperature dependence of the form:

$$\ln(\sigma(T)/\sigma_o) = -(T_o/T) \tag{11}$$

rather than that of Eq. (8). Brenig *et al.* [24] have shown that the conductivity of an infinite long chain is of the form (11), but that of a collection of parallel non-interacting chain of finite length is of the form (8). The resulting conductivity, however, depends on the length of the chains and therefore violates Ohm's law. Shante [25] found that within the standard percolation models the hopping conductivity has a temperature dependence of the form

$$\ln[\sigma(T)/\sigma_o] = -[T_o(m)/T]^{1/m}(\beta^{-1})^{-2} \tag{12}$$

where m is a weakly temperature dependent constant.

The values of $\sigma_{ac}(\omega)$ are found to obey the general relation

$$\sigma_{ac}(\omega) = A\omega^s \tag{13}$$

where A and s are parameters to be obtained from the experimental $\sigma_{ac}(\omega) - \mathrm{T}$ curves. Equation (13) is valid for several amorphous and crystalline materials. The exponent s as estimated from the slopes of Figure 6 and its value lies between 0.82 and 0.94. The maximum value of s lies within the limit of the tunneling models readily obtained. In addition, s is predicted to have temperature dependence and the magnitude of s at any temperature is determined by the binding energy E_b of the carrier in its localized sites. The temperature dependence of s in the HOB model should follow an equation of the form [26]

$$1 - s = 6kT/E_b \tag{14}$$

where E_b is the polaron binding energy. The variation of s with temperature is shown in Figure 7. It is observed that the predicted values obtained from HOB model are not in good agreement with the experimental values.

Long's polaron tunneling model [27], however accounts for the decrease of s with increasing temperature, in contrast to the tunneling

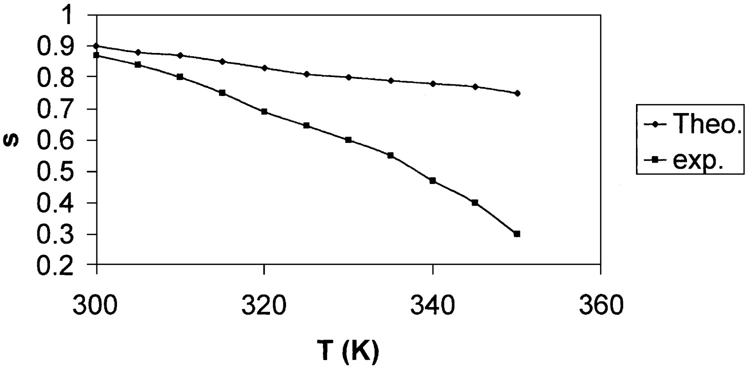


FIGURE 7 Variation of the exponent s with temperature for polyisoxazoline.

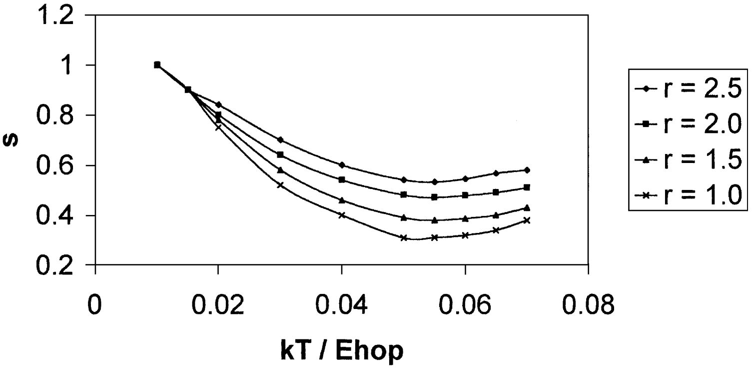


FIGURE 8 Variation of the exponent s against kT/E_{hop} for polyisoxazoline.

model of Austin and Mott [24], Pollak [25] and others [14, 20] indicating an almost constant value of s at different temperatures. To test Long's model for polyisoxazoline, the values of s were plotted against kT/E_{hop} as shown in Figure 8. Here the relations relate E_{hop} to the polaron hopping energy E_h are [17]

$$E_h = E_{hop}(1 - r_p/R) \tag{15}$$

where

$$E_{hop} = e^2/4\pi\varepsilon_p\varepsilon_r \tag{16}$$

here r_p is the polaron radius, R the hopping length. The exponent s has been calculated theoretically from the relation [20]

$$s = 1 - (4 + 6\beta E_{hop} r'_p / R'^2_\omega) / R'^2_\omega (1 + \beta E_{hop} r' / R^2_\omega)^2 \tag{17}$$

where R'_w and r'_p are related by the dimensionless quadratic equation [5]

$$R'_w + (\beta E_{hop} \ln \omega\tau_o) R'_\omega - \beta E_{hop} r'_p = 0 \tag{18}$$

here

$$R'_w = 2\alpha R_w$$

where α is the wave function decay constant, R_w is called the optimum hopping length and τ_o the characteristic relaxation time.

The theoretical curves as shown in Figure 8 are drown from Eq. (18) taking $\ln(\omega\tau_o) = -20$ and $r'_p = 1$, 1.5, 2, and 2.5. The best fit to the experimental points was obtained for the E_{hop} value equals 1.72 eV. At low temperatures all the experimental points lie between the theoretical curves for $r_p = 1$ up to 2.5. The value of r_p is found to be responsible (being within the limits suggested by Austin and Garbett [14]) and is in good agreement with those obtained from the analysis of the dc conductivity [9]. However, at high temperatures, the observed decrease of the exponent with increasing temperature is higher than that predicted.

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