Electrical transport in ethyl cellulose–chloranil system

P K KHARE*, R K PANDEY[†] and P L JAIN[‡]

Department of Postgraduate Studies and Research in Physics and Electronics, Rani Durgavati University, Jabalpur 482 001, India
[†]Department of Physics, Dr H S Gour University, Sagar 470 002, India
[‡]Government Postgraduate College, Damoh 470 661, India

Abstract. The charge-transport behaviour in pure and chloranil (Chl) doped ethyl cellulose (EC) system has been studied by measuring the dependence of current on field, temperature, electrode material and dopant concentration. The role of doping molecular concentration in the polymer matrix and modification in the conduction characteristics are studied. Lowering of the activation energy due to doping was observed. The current was found to increase with an increase in the chloranil concentration. An explanation for this has been attempted on the basis of formation of molecular aggregates between chloranil molecules and ethoxy groups of ethyl cellulose. It is suggested that chloranil occupies interstitial positions between the polymer chains and assists in carrier transportation by reducing the hopping barriers. The current–voltage characteristics of different samples are analyzed using space charge limited current theory and quantitative information about the transport parameters is derived. The values of effective drift mobility and trapped charge carrier concentration which result in the build up of space charge have been calculated.

Keywords. Electrical transport; ethyl cellulose; chloranil; charge transfer complex; molecular aggregates; Richardson–Schottky; Poole–Frenkel; space charge limited current.

1. Introduction

The transport of electric charge across the surfaces of insulators is a topic of considerable technical interest, but one in which the mechanisms involved are poorly understood in general. The elucidation of the charge injection and carrier migration processes will become essential for the future use of these materials (Shrivastava *et al* 1979; Khare and Srivastava 1992). The study of electrical conduction is of considerable significance from two major points of view—firstly, for its own sake, because charge transfer characteristics are of fundamental interest and secondly for the information studies can provide on the nature of electrical contacts, which may have a great influence on the measured electrical properties. The charge storage property of polymers can be considerably modified with the help of suitable dopants (Khare *et al* 1998a). The broadest method that can be applied to enhance the conductivity of polymeric material is the formation of molecular aggregates or charge-transfer (CT) complexes. The electrical conduction behaviour of a number of polymer CT complexes and molecular aggregates has been investigated recently (Khare and Singh 1994; Laxmi-Narayana *et al* 1994; Khare and Chandok 1995a; Khare and Jain 1997; Upadhyay *et al* 1998), yet the mechanism

of conduction and the role of impurity in these systems is not known to any degrees of certainty. The carrier mobility can be greatly influenced by impregnating the polymers with suitable dopants (Khare and Singh 1994; Khare *et al* 1997a, 1998b).

The present paper describes the electrical transport in the ethyl cellulose (EC)–chloranil (Chl) system observing the variation of current under different conditions of poling temperatures, electrode materials, thicknesses and Chl concentrations.

2. Experimental

Ethyl cellulose (EC) and an electron acceptor chromatographically purified chloranil (Chl) doped EC films were deposited onto cleaned vacuum aluminium coated glass plates by isothermal immersion of the substrates into a fresh solution of well-stirred mixtures of 3·0 g of EC in 30 ml of chloroform at room temperature for 10 min. Using the same technique, we also prepared Chl doped EC films under identical conditions from solutions of well-stirred mixtures of 3·0 g of EC and Chl in chloroform. The doping concentration was changed by varying the amount of Chl added to the solvent such that the total volume of the solvent and the Chl was always 30 ml. Although samples with different dopant concentrations were investigated, only the results for two types of

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*Author for correspondence

samples are reported here. The samples doped to the lower concentration of Chl (1%) and higher concentration of Chl (4%) were designated as P_1 and P_2, respectively. The further increase in the dopant concentration does not result in increase of the current. The films were dried and determined to be $\approx 20 \, \mu$m thick, by measurement of their capacitance. After the film deposition the glass slide was wrapped in an aluminium mask. When exposed to aluminium/silver/copper in vacuum, the metal was deposited on the film. Thus, a sample in the sandwich structure was obtained. The activation energies for the undoped samples (≈ 0.63 eV in the lower temperature region and 0.52 eV in the higher temperature region) were found to be decreased as a result of Chl doping (to 0.58 eV; 0.43 eV and 0.55 eV; 0.40 eV for lower and higher Chl concentrations, respectively). A d.c. power supply EC-4800 and a Keithley 600B electrometer were used to apply the desired electric field and record the current. Measurements were made at thermostatically controlled temperatures in the range 313–363 K.

3. Results and discussion

Figure 1 shows the current–voltage (*I–V*) characteristics of undoped and chloranil (Chl) doped ethyl cellulose (EC) samples. At the lower concentration, the current was found to be lower. As the dopant concentration was increased, the current was found to increase. The effect of electrode materials on *I–V* characteristics of undoped and Chl doped EC matrix (all taken at 323 K) has also been placed in the same figure. The magnitude of the current was found to be higher in dissimilar electrode combinations than similar electrode system. The *I–V* curves show two regions of conduction, i.e. ohmic conduction at lower fields (< 20 kV/cm) and a non-ohmic conduction at higher fields (> 20 kV/cm) for the undoped and doped samples. Figure 2 shows the *I–V* characteristics for undoped and doped films of different thicknesses. Curves 1 to 5 correspond to thicknesses 30, 25, 20, 15 and 10 μm, respectively. It is seen from these curves that there are distinctly two regions. Further, the transition voltage (V_{tr}) at which the non-ohmic behaviour starts appearing is seen to depend on the thickness of the film.

The above results indicate that with the increase of temperature, the probability of thermal ionization of the trapping centres increases thus causing a shift in the quasi-Fermi level, which gives rise to a lowering of the barrier across which electrons have to be transported and the conduction becomes more or less ohmic. At lower fields, the injection of carriers from contact is less and the initial current is governed by the intrinsic free carriers in the materials. The current will be ohmic until the injected free carrier density becomes comparable with the thermally created carrier density. However, at sufficiently higher fields, the carriers are mainly due to injected space charges (Khare and Chandok 1995b; Khare *et al* 1998a).

The high-field electronic conduction mechanism commonly discussed for various films are space-charge limited conduction (SCLC), Richardson–Schottky (R–S), Poole–Frenkel (P–F) emission and tunneling of carriers into or via traps (Lamb 1967; Simmons 1970). In order to establish the dominant mode of conduction in a particular material, one has to look into the detailed analysis of *I–V* data of the material in terms of the theoretical considerations available for different types of processes.

The *I–V* characteristics follow the relationship of the form $\log I$ vs (field)$^{1/2}$ and thus predict either the Richardson–Schottky (R–S) limited mechanism from the electrodes or the bulk-limited Poole–Frenkel (P–F) effect. The latter effect is caused by thermal ionization of trapped electrons from donor-like centres in the presence of an external field. If one considers the RS or PF emission as the dominant mode of conduction then the current density *I* follows the relation (Lamb 1967; Simmons 1970)
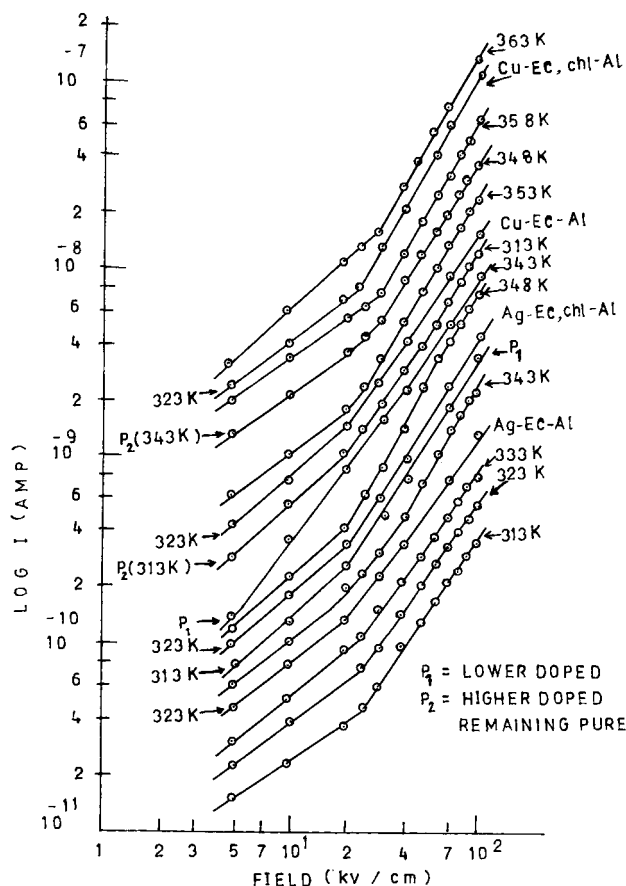
$$I = I_0 \exp(\beta \, E^{1/2}/kT), \tag{1}$$

Figure 1. Current–voltage characteristics of pure and Chl doped ethyl cellulose films with similar and dissimilar electrode systems.

where

$$I_0 = AT^2 \exp(-\phi/kT) \quad \text{for RS,}$$

and

$$I_0 = \sigma_0 \, V/d \quad \text{for PF,}$$

and the constants

$$\beta_{RS} = (e^3/4\pi\varepsilon\varepsilon_0)^{1/2} = 1/2 \, \beta_{PF}, \tag{2}$$

where ε_0 is the permittivity of vacuum, A the Richardson's constant, σ_0 the low field conductivity and E the applied field, i.e. $E = V/d$. Equation (1) suggests that the plot of $\log I$ vs $E^{1/2}$ should be a linear one having a slope of β/kT. The value of β was estimated from such graphs. Table 1 gives the theoretical values of R–S coefficients (β_{RS}) and P–F coefficients (β_{PF}) along with the experimental values of β for different pair of electrode combinations. Evidently the experimental values lie between the two theoretical values. The β_{exp} values complicate the interpretation of results in terms of either of these mechanisms. Jonscher and Ansari (1971) suggest that the basic difference between the two processes (one is electrode limited while the other is not) may be successfully utilized for selecting

Figure 2. Current–voltage characteristics for undoped and Chl doped ethyl cellulose films of different thicknesses.

the mechanism. Consequently, graphs are plotted between $\log I$ vs (field)$^{1/2}$ (figure 3) using three different pairs of electrodes (i.e. Al–Al, Al–Cu and Al–Ag). The plots trace a separate straight line. Further, by interchanging the + ve and – ve electrodes the current was found to be unchanged. The value of high frequency dielectric constant was calculated by using (2). It was found that on substituting the value of β_{RS}, $\varepsilon > 10$ and on substituting the value of β_{PF}, $\varepsilon > 17$. However, as the reported value for EC is $\approx 3\cdot00$ (Mark *et al* 1965); such a large discrepancy in the obtained and reported values of ε ruled out the possibility of RS or PF mechanisms governing the high field currents.

In the present case, in the high field conduction region, the *I*–*V* characteristics have a slope of > 2 and we suggest that the region is governed by space-charge-limited currents (SCLC). This is because, when the *I*–*V* data are analyzed with the mathematical details available for SCL currents, a correspondence between theory and experimental values is observed.

In a trap-free solid, the space charge limited current (SCLC) I_0 is given by (Lampert and Mark 1970)

$$I_0 = (10^{-13} \mu_e \varepsilon A V^2)/d^3, \tag{3}$$

where μ_e is the effective drift mobility of the carriers, ε the relative dielectric constant of the solid, A the area of the sample, d the thickness of the sample and V the applied voltage. In presence of shallow traps only a fraction of the carriers injected from the contact will be free, the remainder will be immobile within the traps. The ratio of free carriers n to trapped ones n_t is constant and independent of the applied voltage. In this range, the current I_t is given by (Lampert and Mark 1970)

$$I_t = \theta \, I_0, \tag{4}$$

$$\theta = \frac{n}{n_t} = \left(\frac{N_c}{N_t}\right)\exp\left(\frac{-E_t}{kT}\right), \tag{5}$$

where N_c is the effective density of states in conduction band and N_t represents the concentration of shallow trapping levels which are all assumed to have equal energy so that they are situated E_t eV below the bottom of conduction band.

Conduction in polymers is explained not on the basis of band theory but in terms of the existence of mobility edge. Charge carriers are free to move only when they possess a certain value of mobility. If the charge carrier is near the bottom of conduction band, it is in the delocalized state and requires no thermal activation. However, if it is in the localized trapped state, it requires thermal activation and mobility increases with the increase in temperature (Ranjeet Singh *et al* 1997). The mobility values obtained in the present polymer are well within the limits of measured
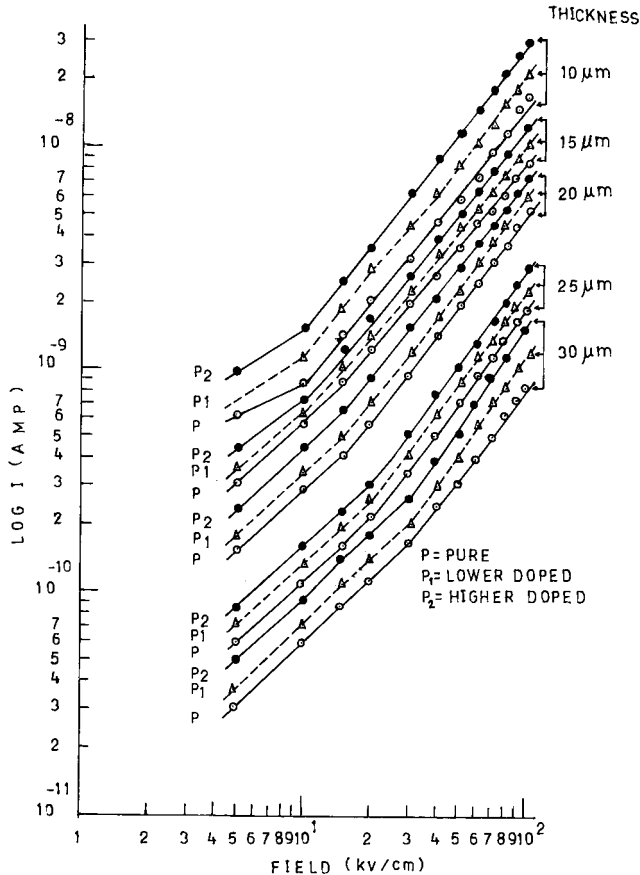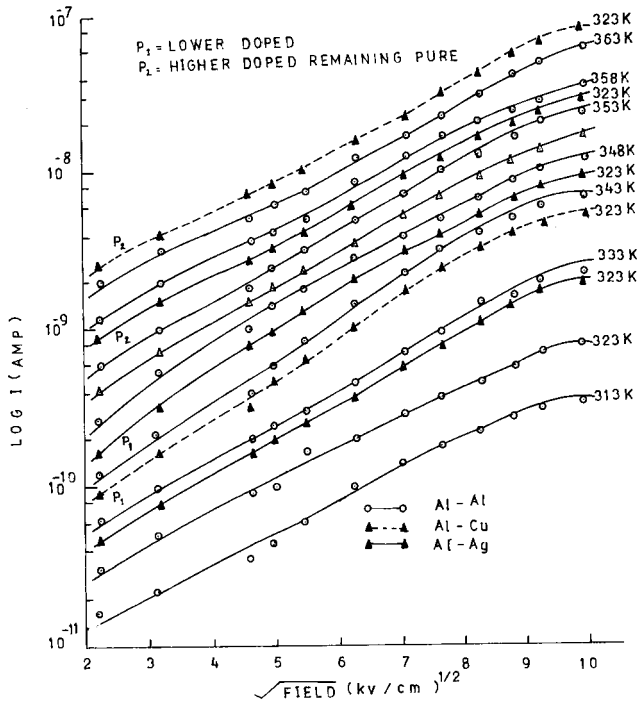
Table 1. Theoretical values of Richardson–Schottky coefficient (β_{RS}) and Poole–Frenkel (P–F) coefficient alongwith the experimental values of β.

Electrode systems	Temp. (K)	Theoretical		Experimental β-values 10^{-21} JM$^{1/2}$ V$^{-1/2}$
		β_{RS} 10^{-21} JM$^{1/2}$ V$^{-1/2}$	β_{PF} 10^{-21} JM$^{1/2}$ V$^{-1/2}$	
Al–Al	313	4·768	9·536	6·829
	323	6·523	13·046	9·857
	333	7·125	14·250	10·543
	343	8·066	16·132	12·667
	353	8·997	17·994	13·689
	363	9·117	18·234	14·114
		10^{-20} JM$^{1/2}$ V$^{-1/2}$	10^{-20} JM$^{1/2}$ V$^{-1/2}$	10^{-20} JM$^{1/2}$ V$^{-1/2}$
Al–Cu	313	6·442	12·884	9·857
	323	7·179	14·358	10·014
	333	7·892	15·784	11·312
	343	8·023	16·046	12·444
	353	8·563	17·126	12·999
	363	9·222	18·444	13·764
Al–Ag	313	7·234	14·468	10·854
	323	7·997	15·994	11·111
	333	8·256	16·512	12·447
	343	9·345	18·690	14·875
	353	9·957	19·914	15·789
	363	10·634	21·268	17·412

Figure 3. Log I vs $\sqrt{\text{field}}$ plots.

mobilities in polymers (Wintle 1971; Davies and Lock 1973).

At higher fields (figure 1) the change of slope can be taken as an indication of deviation from Ohm's law into the space-charge limited current (SCLC) mechanism. This departure from Ohm's law in high field occurs as a result of active barrier perturbation even in the absence of thermal and chemical effects (Khare *et al* 1994). Space charge limited currents set in at that voltage V_t at which the intrinsic current equals the SCL current. Thus,

$$n_0 e \mu_e \left(\frac{V_t}{d} \right) = 10^{-13} \mu_e \varepsilon \theta \left(\frac{V_t^2}{d^3} \right)$$

$$V_t = 10^{13} n_0 e d^2 (\varepsilon \theta)^{-1}, \tag{6}$$

where n_0 is the concentration of free carriers before injection. Thus, the voltage at which deviation from ohmic behaviour takes place is a measure of the density of the normal volume-generated carriers.

The trap concentration N_t is defined by

$$N_t = \frac{2 \varepsilon \varepsilon_0}{e d^2} V_{TFL}, \tag{7}$$

where e is the electronic charge and V_{TFL} (trap-filled limit) is the upper limit of the voltage at which sufficient charge has been injected into the insulator to fill the traps. Using the experimental value of V_{TFL}, N_t was calculated to be $8·765 \times 10^{14}$ cm^{-3}. The values of μ_e and n_t have been calculated for different thicknesses and are listed in table 3. It is seen from table 3 that the charge carriers which result in formation of the space charge and hence limiting the high field conduction possess the average values of

Table 2. Values of θ, μ_e, N_t and n_0 for pure and chloranil doped ethyl cellulose.

Temperature (K)	θ ($\ldots \times 10^{-2}$) Sample			Effective mobility (μ_e) ($\ldots \times 10^{-9}$) $m^2 v^{-1} s^{-1}$ Sample			N_t ($\ldots \times 10^{14}$) cm^{-3} Sample			n_0 ($\ldots \times 10^{10}$) cm^{-3} Sample		
	Pure	P_1	P_2	Pure	P_1	P_2	Pure	P_1	P_2	Pure	P_1	P_2
313	2·637	6·425	8·875	4·987	6·678	9·875	9·935	11·864	14·743	6·567	9·87	12·654
323	3·876	–	–	5·102	–	–	9·102	–	–	7·623	–	–
333	4·678	–	–	5·654	–	–	8·654	–	–	8·118	–	–
343	6·878	9·743	12·604	7·017	10·815	11·432	8·017	10·356	13·478	9·102	11·456	13·578
348	8·957	–	–	7·654	–	–	7·764	–	–	10·111	–	–
353	9·015	–	–	8·884	–	–	6·885	–	–	11·052	–	–
358	11·143	–	–	9·667	–	–	5·888	–	–	11·999	–	–
363	12·225	–	–	10·789	–	–	4·985	–	–	12·012	–	–

Table 3. Values of μ_e and N_t with thickness (Al–Al electrode).

Thickness (μm)	μ_e ($\ldots \times 10^{-9}$) $cm^2 v^{-1} s^{-1}$	N_t ($\ldots \times 10^{14}$) cm^{-3}
10	3·967	12·478
15	4·563	10·032
20	4·987	9·987
25	5·114	8·876
30	5·635	8·012

$\mu_e \approx 4.854 \times 10^{-9}$ cm^2 V^{-1} s^{-1} and $n_t \approx 9.88 \times 10^{14}$ cm^{-3}, respectively.

The equilibrium concentration of charge carriers in the conduction band can be obtained from the equation

$$n_0 = \frac{\varepsilon\varepsilon_0\theta}{qd^2}V_{tr}, \qquad (8)$$

where V_{tr} is the voltage at which the transition from ohmic to square-law behaviour takes place. Again θ is the ratio of the free carrier density to the trapped carrier density and can be found from the ratio between the current at the start of the rise to that at the end of the rise in the square-law region. Using the value of θ, n_0 was calculated from (8) and listed in table 2. It is to be noted that (i) log–log plot of I vs d in the square-law region should be a straight line with slope – 3 and log–log plot of V_{tr} vs d should be a straight line with slope 2. Such plots were made (not shown) and the slopes of – 2·92 and 1·93, respectively were obtained which supports the possibility of space charge limited currents.

The space charge limited currents may also determine the transient behaviour such as a large burst of current immediately after the application of voltage followed by a steady decline in current on standing. In the present case the large currents obtained just after the application of

voltage subsided to much smaller steady values after a certain length of time. The possible explanation is that the sudden application of voltage causes a cloud of carriers, i.e. a space charge, to be injected from the contact into the sample. This free charge gives rise to a large burst of current. If the space charge remained untrapped, the value of the transient current would continue as a steady current. However, one must take into account the effects of trap densities in the sample. The free charge forced into the sample settles the rate being determined by the capture cross section of traps for free carriers (Singh and Srivastava 1972).

In the present case, the slope of I–V curves exceed the value 2. Usually a slope of 2 indicates shallow trapping but this does not seem to exclude the possibility of deep traps in the present case. The attribution of the currents in high field region to SCL conduction is further supported by the following observation (i) EC being an amorphous material, would provide a large number of trapping centres and trapping of charge carriers in these trapping sites would result in the build-up of a space charge, (ii) the build-up of a space charge is also confirmed by our earlier thermally stimulated discharge current study (Khare *et al* 1996, 1997b).

The electrical conductivity for samples doped at lower concentration remains low even beyond glass transition temperature T_g. It seems that chain motion is not effective in mobilizing the traps formed by dopant molecules and charge carriers released from mobilized traps, are again trapped in traps provided by dopant molecular sites. Thin polymer films are known to be a mixture of amorphous and crystalline regions (Chopra *et al* 1971). The conductivity behaviour of such films may be dominated by the properties of the amorphous regions (Kosaki *et al* 1971). The presence of amorphous regions give rise to localized states. Since there are many localized states, the release or excitation of the carriers in these states dominates the conduction process. Consequently, doping should not affect the conductivity too much (Marikhin *et al* 1965),

unless the dopant is present in sufficient quantity to markedly affect the position of the Fermi level. Dopant molecules enter either the amorphous regions of the polymer or the defect regions like chain folds. If they are present in low concentration, they will give rise to additional molecular sites for trapping of charge carriers (Jonscher 1967). Such localized sites can be defined in molecular terms using the difference in ionization potential as an indication of trap depth. As the dopant concentration is increased, the molecules start bridging the gap separating the two localized states and lowering the potential barrier between them thereby facilitating the transfer of charge carriers (Kulshrestha and Srivastava 1980; Sinha *et al* 1981). A comparison of currents of pure and Chl doped EC reveals that an increase in current is observed with doping. Enhancement of current with an increase in Chl concentration may be explained on the basis of charge transfer complex (CTC) formation. Chloranil when doped in polymer, may reside at various sites. It may be substituted into the polymer chains or reside at the amorphous/crystalline boundaries and diffuse preferentially through the amorphous regions forming CTC, or it may exist in the form of molecular aggregates between the polymer chains. The CTC are supposed to create localized states of various depths which will lead to trapping sites distributed over a considerably wide energy range. The formation of CTC is considered to reduce the barrier between the trapping sites providing a conducting path through the polymer matrix and would result in the enhancement of its conductivity. Such a phenomena is supposed to decrease the activation energy of the carrier and increase its mobility towards the electrode during polarization. The increase in current with doping is supposed to lead to the accumulation of more and more positive charge in front of the cathode resulting in an increased strength at the polymer–electrode interface. In the process of polarization, the negative charge migrating under the influence of the charging field is supposed to accumulate in the vicinity of the anode due to presumably blocking polymer–metal contact and is immobilized during the cooling phase of the charging process (Khare and Singh 1994). In such cases, a considerable amount of charge is supposed to pass through the bulk of the sample and the observed current for doped samples should be sufficiently less than that in undoped samples by one or two orders in magnitude. Such observation goes against the possibility of CTC formation. The possibility of a new crystallite embedded in the amorphous mass cannot be precluded. Hence, it is reasonable to assume that Chl molecules occupy the interstitial positions between the polymer chains of amorphous phase and link these chains to some kind of bonds by a charge-exchange process between the Chl molecule and ethoxy group of EC. This process reduces the interstitial barriers and increase the transition probability of electrons hopping across these barriers. The interfacial barriers probably also decrease because of the presence of Chl at the interfaces. Thus, the whole structure of EC will be more open for charge transportation follow up impregnation with Chl.

References

Chopra K L, Rastogi A C and Malhotra G L 1971 *Thin Solid Films* **24** 125

Davies W K and Lock P J 1973 *J. Electrochem. Soc.* **120** 266

Jonscher A K 1967 *Thin Solid Films* **1** 213

Jonscher A K and Ansari A A 1971 *Philos. Mag.* **23** 205

Khare P K and Srivastava A P 1992 *Thin Solid Films* **208** 233

Khare P K and Singh Ranjeet 1994 *Polym. Int.* **34** 407

Khare P K and Chandok R S 1995a *Polym. Int.* **36** 35

Khare P K and Chandok R S 1995b *J. Polym. Mater.* **12** 23

Khare P K and Jain S K 1997 *Indian J. Pure & Appl. Phys.* **35** 408

Khare P K, Sandeep Shrivastava and Srivastava A P 1994 *Indian J. Phys.* **A68** 129

Khare P K, Keller J M, Gaur M S, Singh Ranjeet and Datt S C 1996 *Polym. Int.* **36** 303

Khare P K, Jain S K and Paliwal S K 1997a *Bull. Mater. Sci.* **20** 699

Khare P K, Kuraria R K and Jain S K 1997b *Bull. Mater. Sci.* **14** 133

Khare P K, Paliwal S K, Kuraria R K, Vishwakarma H L, Ashish Verma and Jain S K 1998a *Bull. Mater. Sci.* **21** 139

Khare P K, Ashish Verma and Paliwal S K 1998b *Bull. Mater. Sci.* **21** 207

Kosaki M, Yoda M and Ieda M 1971 *J. Phys. Soc. Jap.* **31** 1598

Kulshrestha Y K and Srivastava A P 1980 *Thin Solid Films* **69** 269

Lamb D R 1967 *Electronic conduction mechanism in thin insulating films* (London: Methuen & Co.)

Lampert M A and Mark P 1970 *Current injection in solids* (NY: Academic Press) p. 21

LaxmiNarayana K, Dasardhudu and Rao N 1994 *Polym. Int.* **35** 315

Marikhin V A, Shitsker A I and Yastrebinskii A A 1965 *Sov. Phys. Solid State* **7** 352

Mark H F, Gaylord N G and Bikalas N M (eds) 1965 *Encyclopedia of polymer science and technology* (NY: Interscience)

Ranjeet Singh, Khare P K and Reeta Singh 1997 *Indian J. Phys.* **A71** 39

Shrivastava S K, Ranade J D and Srivastava A P 1979 *Jpn J. Appl. Phys.* **18** 2303

Simmons J G 1970 *Handbook of thin film technology* (NY: McGraw Hill)

Sinha H C, Talwar I M and Srivastava A P 1981 *Thin Solid Films* **82** 229

Singh Ranjeet and Srivastava A P 1972 *Indian J. Pure & Appl. Phys.* **10** 811

Upadhyay J K, Khare P K, Ashish Verma and Paliwal S K 1998 *J. Polym. Mater.* **15** 289

Wintle H J 1971 *Jpn J. Appl. Phys.* **10** 659