Electrical Behavior of Polycarbonate Doped with Nickel Chloride

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SYNOPSIS

The dc electrical conductivity (σ) and permittivity (ϵ') of polycarbonate (PC) discs doped with different concentrations of $NiCl_2$ are studied. Both (σ) and (ϵ') increase with increasing the concentration of $NiCl_2$, with a maximum value at 30 wt %. The activation energies for pure and doped PC are 0.49 and 0.53 eV, respectively. The increase in the electrical conductivity with increasing $NiCl_2$ concentration is attributed to the formation of charge-transfer complexes (CTC); the increase in ϵ' may be due to the rise in the interfacial polarization which results from the increase in boundaries between PC and $NiCl_2$ phases. The currents in PC discs, both pure and doped with $NiCl_2$, in the high-field region are attributed to space charge limited conduction. The time dependence of conduction current before and after reversal of applied voltage is also investigated. Some parameters such as the density of mobile ions and their drift mobilities are estimated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Polycarbonate (PC) has numerous industrial applications due to its high impact strength, low dielectric loss, good dimensional stability, and relatively long time scale for aging below the glass–rubber transition temperature T_g.

Mehendru et al.[1] studied the dielectric absorption in PC films at frequencies of 0.5–100 kHz and in the temperature range 290–450 K. The magnitude of absorption in PC doped with iodine increases and the absorption peaks were found to shift toward lower temperatures with increasing iodine concentration.

Graeme and Michael[2] studied the dielectric response of commercial PC. They found for basic and UV-resistant grades that several dispersion regions common to both materials may be identified, together with an additional region at high temperatures in the ultraviolet-resistant material.

Amin et al.[3] studied the effect of γ-irradiation on the electrical properties of PCs. Recently, the authors studied the effect of UV irradiation and ther-

mal annealing on the electrical conductivity of PC films.[4] The I–V characteristics of PC films were studied by Chand et al.[5] as a function of the iodine concentration, in order to locate the effect of iodine on the carrier mobility and other parameters.

When voltage is applied to an insulator, charging current, absorption current, and conduction current may flow through it for few minutes or even hours.[6] In polar dielectrics, absorption current is caused by the orientation of dipolar molecules, which rotate under the action of an external electric field.[7]

By reversing the polarity, a maximum in the current–time (I–t) curve appears, and after a certain period, it will have elapsed. Similar phenomena were reported in the I–t curves of some highly plasticized PVC,[8] PVF,[9] and NBR[10] films. This current peak corresponds to the usual thermostimulated current[11] and relaxation current.[12]

EXPERIMENTAL

Bisphenol-A-derived PC in the form of white granules was obtained from the Organic Chemical Laboratory, State University of Ghent, Belgium. The granules of PC were dissolved in benzene and then
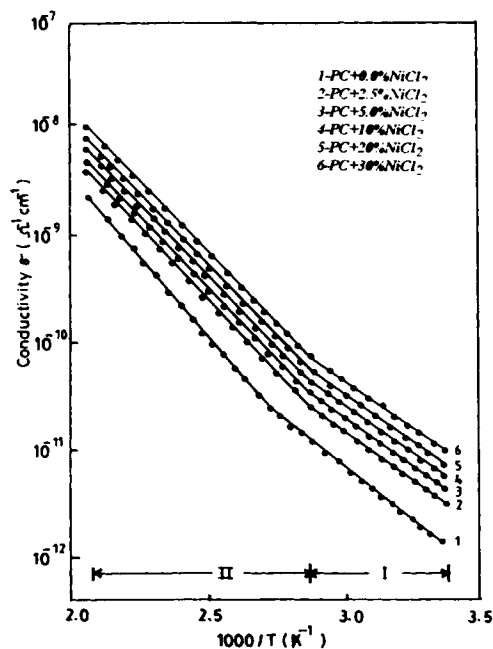
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Figure 1 Conductivity (σ) of pure and $NiCl_2$-doped PC as a function of temperature.

kept in an oven for 3 days at 40°C. The solution was then spread on a clean flat glass slide. Afterward, the polymer was dried at 40°C for 4 days to remove the residual solvent. Then, the dry polymer was ground to powder. By taking 2 mgs of PC and 2.5–30 wt % of $NiCl_2$, mixing thoroughly, and pressing this powder under 10 tons/cm^2, we obtained a disc of doped PC (diameter 0.6 cm and thickness 0.049 cm). The samples were coated with a thin film of gold using a gold ion sputter (JOEL JFC-1100 E), then fixed between two gold electrodes.

The conduction current was measured using a dc nanometer Continu EVA- made in France. The permittivity was measured using a precision capacitance bridge (Tesla, BM 400 G) working at 800 Hz and with a least count of 10^{-4} pF.

RESULTS AND DISCUSSION

Figure 1 shows the electrical conductivity of PC discs doped with different concentrations of $NiCl_2$ (0, 2.5, 5, 10, 20 and 30 wt %, respectively) at a fixed applied voltage of 600 V. By comparing with pure PC, it is seen that the electrical conductivity increases with increasing $NiCl_2$ concentrations. The linearity is observed over the two ranges of temperatures. The activation energy ΔE(eV) for undoped PC and PC doped with $NiCl_2$ over the two regions are given in Table I. The decrease in the activation energies of

Table I Activation Energies ΔE (in Regions I and II)

Sample	I	II
Undoped PC	0.47	0.57
PC + $NiCl_2$	0.44	0.53

the charge carriers for doped PC discs with $NiCl_2$ is presumably due to the decrease of the conducting channels of $NiCl_2$ grains caused by the greater expansion of the polymer matrix.[13]

The dependence of the electrical conductivity (σ) on the concentration of $NiCl_2$ in PC discs at 304 K is shown in Figure 2. It is clear that the electrical conductivity is linearly enhanced with $NiCl_2$ content. This may be explained on the basis of formation of a charge-transfer complex involving the PC molecules and $NiCl_2$.[14] The PC disc consists of crystalline regions that are embedded in an amorphous matrix[15] and the motion of the charge carriers is embedded at the crystalline–amorphous interfaces.[1,16] The $NiCl_2$ molecules diffuse preferably into the amorphous regions of the polymer and this influences the carrier transport in these regions. Furthermore, the electron-donor nature of the polymer and the electron-acceptor nature of the $NiCl_2$ may even result in the formation of charge-transfer complexes (CTC).[1,17]

The complexes thus formed may effectively reduce the crystalline–amorphous interfacial barrier by providing conductive paths through the amorphous regions and, thus, interconnecting the crystallites. Such a reduction in the barrier would facilitate the movement of the charge carriers during conduction.[14]

The current–voltage characteristics of PC discs doped with different concentrations (2.5, 5, 10, 20,
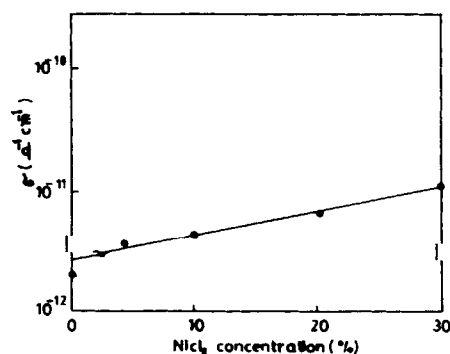

Figure 2 The conductivity (σ) of PC as a function of the $NiCl_2$ concentration at 304 K.

and 30 wt %) of $NiCl_2$ were investigated at different temperatures. The measurements were carried out below T_g (at 373 K, not included) and above T_g (at 453 K), respectively (Fig. 3). For all samples, we notice that the current is enhanced with increasing concentration of $NiCl_2$. There are two distinct stages, namely, the ohmic and the space charge limited stages, respectively. A square law region ($I \propto V^2$) dominates in the voltage region ($\sim$ 400–1000 V). The expressions derived by Mott and Gurney[18-20] for the space charge limited current (SCLC) in an insulator is given by

$$J = 10^{-13}\mu_0\epsilon'(v^2/d^3) \qquad (1)$$

and

$$J = \mu_0 n_0 eE \qquad (2)$$

where J is the current density between two parallel electrodes with volts (V) across the thickness (d); μ_0, the mobility of free-charge carriers; n_0, the free carriers concentration; ϵ', the dielectric permittivity of the material; e, the electronic charge; and E, the electric-field intensity.

From the above equations, one can determine μ_0 and n_0 for PC discs doped with $NiCl_2$ and the values are listed in Table II.

From the experimental data of the I–V curves (Fig. 3), the attribution of the currents in the PC disc and PC doped with $NiCl_2$ in the high-field region
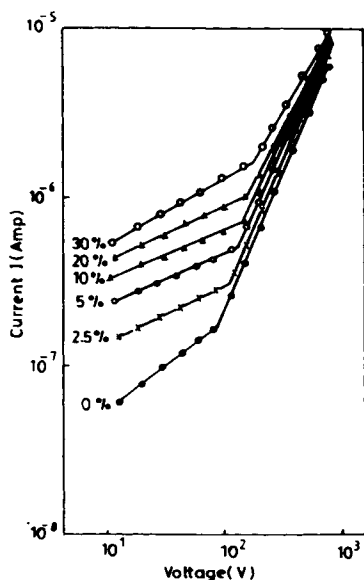

Figure 3   I–V characteristics for PC discs (at 453 K), doped with different concentrations of $NiCl_2$.

Table II   Conduction Parameters for PC Discs Doped with $NiCl_2$ at 373 K and 453 K

T (K)	PC + $NiCl_2$ Wt %	μ_0 $(cm^2\ V^{-1}\ s^{-1})$	n_0 (cm^{-3})
373	0.0	1.13×10^{-5}	7.05×10^{11}
	2.5	1.84	7.11
	5.0	2.97	7.32
	10.0	4.95	7.56
	20.0	7.78	7.73
	30.0	8.49	7.92
453	0.0	3.35×10^{-3}	4.27×10^{10}
	2.5	3.66	9.69
	5.0	3.71	12.41
	10.0	3.90	16.33
	20.0	4.72	19.54
	30.0	5.66	23.57

to space charge limited conduction is further supported by the following observations:

(i) SCLCs are usually observed when the contacts are ohmic[21,22] and the possibility of ohmic contacts to PC discs is quite high since the work function of the polymer matches quite well[23] with that of the used electrode, i.e., the gold electrode.

(ii) PC, being an amorphous material, would provide a large number of trapping centers and trapping of charge carriers in these trap sites would result in the build-up of a space charge.

(iii) Thermally stimulated discharge current studies[24,25] showed clearly a distinct relaxation peak, which has been attributed to the detrapping of charge carriers on a macroscopic level, i.e., to a space charge.

The dielectric permittivity (ϵ') as a function of temperature is shown in Figure 4. For pure PC, it is nearly constant over the temperature range from 303 to 393 K and increases at temperature 393 K. However, for $NiCl_2$-doped discs (2.5–30 wt %), the dielectric permittivity increases continuously with temperature. This increase in ϵ' is due to the rise in the interfacial polarization, which is evidently due to the increase in boundaries between the PC and $NiCl_2$ phases.

The nature of the temperature dependence of dielectric permittivity ϵ' may be different in polar dielectrics. In most cases, an ionic mechanism of polarization increases ϵ' when the temperature increases.[26] Sometimes, the dependence of dielectric
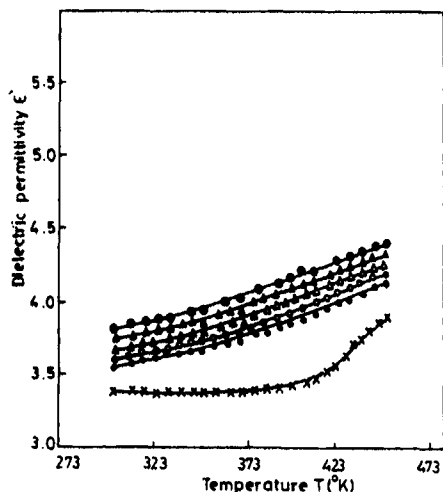
Figure 4 The permittivity (ϵ') for pure and NiCl$_2$-doped PC as a function of temperature: (x) 0%; (•) 2.5%; (O) 5%; ($\triangle$) 10%; ($\blacktriangle$) 20%; (●) 30%.

permittivity ϵ' of polymers on temperature is estimated by means of the temperature coefficient of permittivity ($TC_{\epsilon'}$):

$$TC_{\epsilon'} = (1/\epsilon') \times (d\epsilon'/dT) \qquad (3)$$

This formula may likewise be written in the form

$$TC_{\epsilon'} = d(\ln \epsilon')/dT = (2.3026) \times [d(\log \epsilon')/dT]$$

In the case of polymers, the value of $TC_{\epsilon'}$, can be calculated by differentiating the following equation with respect to the temperature[26]:

$$(\epsilon' - 1)/(\epsilon' + 2) = (N\alpha)/(3\epsilon_0) \qquad (4)$$

in which case both ϵ' and N depend on temperature T, but not on α and where N is the number of molecules per unit volume of the matter; ϵ_0, the permittivity of the free space; and α, the polarizability of matter and could be given by

$$\alpha = \alpha_0 + (D^2/3KT),$$

where D is the dipole moment, and α_0, the electronic and ionic polarizability. Differentiation gives

$$[3/(\epsilon' + 2)^2] [d\epsilon'/dT] = [\alpha/3\epsilon_0] [dN/dT]$$

We finally have in conformity with eq. (4)

$$TC_{\epsilon'} = -[(\epsilon' - 1) (\epsilon' + 2)/\epsilon'] [\alpha_L] \qquad (5)$$

where α_L is the linear expansion coefficient of matter.

It is quite clear that this result is trustworthy only for the descending portion of the dependence of ϵ' on temperature for a given polar matter. This includes, obviously, at room temperature (298 K), the values of $TC_{\epsilon'}$ calculated from eq. (5) for PC (using $\alpha_L = 7 \times 10^{-5}$ K^{-1} for PC).[27] The $TC_{\epsilon'}$ value is -2.64×10^{-4} K^{-1} at room temperature.

To obtain comprehensive data for analysis, it is necessary to discuss the effect of doping with NiCl$_2$ on the time dependence of current for PC discs. The temporal variation of the conduction current at fixed temperatures for pure PC as in Figures 5 and 6 and doped PC with different concentrations of NiCl$_2$ (5, 10, 20, and 30 wt %) were carried out. Figure 7 shows only the relaxation time of PC + 5 wt % NiCl$_2$ (figures for other concentrations are not included). The solid lines refer to I-t plots with an applied voltage of 1 kV, while the dotted lines refer to the reversal of polarity which shows a current peak.

For pure PC, the time corresponding to the peak of the hump (t_{max}) decreases with temperature, while
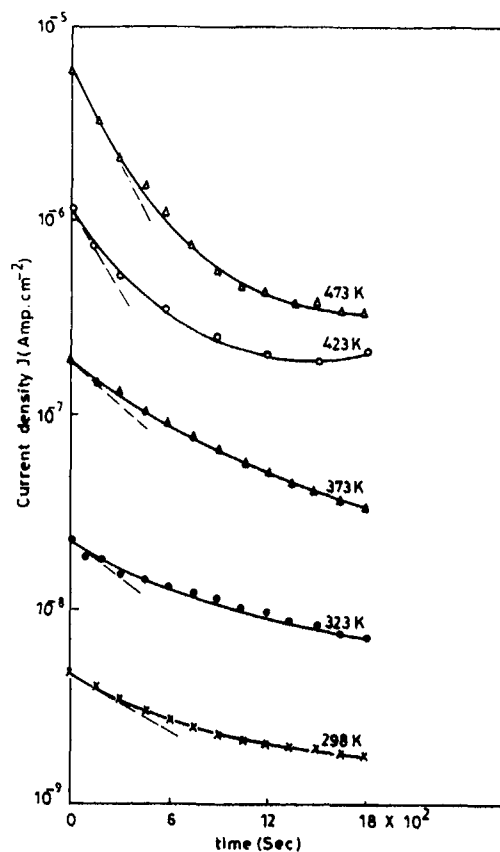

Figure 5 Time dependence of current density for PC discs at different temperatures for the first application of voltage (1 kV).
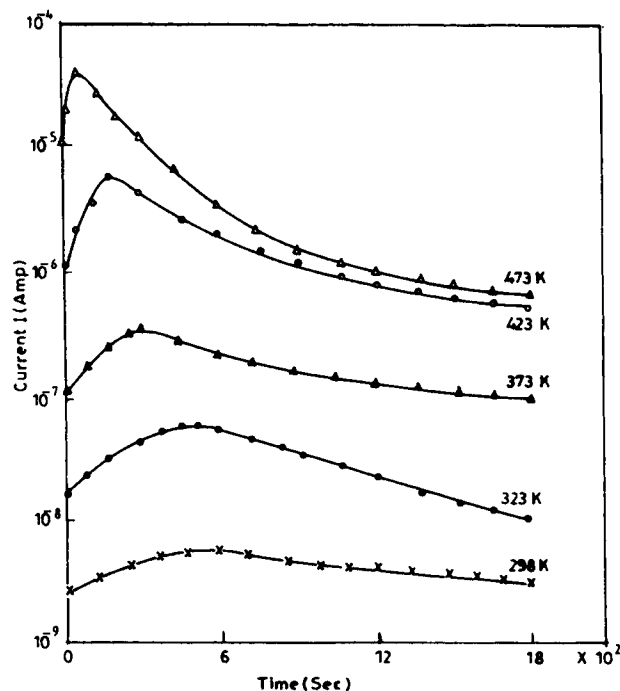
Figure 6   Time dependence of current for PC discs at different temperatures, after reversal of polarity [1 kV].

for a fixed temperature, the peak shifts to longer times as the concentration of $NiCl_2$ increases in the PC discs.

Now, to study the situation of ions that drift to the neighbourhood of the electrode, a mechanism of the hump in I-t curves may be visualized as follows: the fraction of total ions arriving at one electrode may be accumulated there as immobilized ions without discharging at the electrode.[9] These ions can be rendered mobile again after the reversal of the applied voltage polarity. Therefore, the current may show a maximum when the effective mobile ion density in the bulk attains its highest value.

To indicate this mechanism, suppose a unit area of an electrode and one species of ions. After applying the voltage (V), N_0 ions are supposed to be accumulated in a thin layer of PC near the electrode. It is also assumed that the number of ions released per unit time from the layer and subsequently contributing to the current as mobile ions after polarity reversal is proportional to the number of ions (N) remaining in the layer.

Thus, the change of N is given by[9]

$$N = N_0 \exp(-Kt) \qquad (6)$$

where t is the time after the reversal of voltage polarity, and N_0, N at $t = 0$. Also, the change in the current density J with respect to t is given by

$$J = q n \mu_j E \qquad (7)$$

where μ_j is the drift mobility of ions calculated from the initial slope of the I-t curves. It may be ascribed to the mobile ion density (n) if the electric field (E) is assumed to be constant, which, nevertheless, is not always expected because the space charge of the ionic layer in question may distort the electric field. Thus, the time of flight of ions between electrodes (t_f) can be correlated to t_{max} in the I-t curves Figure 6. Then,

$$t_{max} \simeq t_f = d^2/(V\mu_t) \qquad (8)$$

where μ_t is the drift mobility of ions calculated using t_{max}, and d, the distance between electrodes.

Hence, the drift ion mobility μ_t is estimated using eq. (8) in which t_{max} is determined from the curve of the reversed voltage polarity in the I-t plots. The apparent activation energy (E_{μ_t}) may be calculated from the equation[28]

$$\mu = \mu_0 \exp(-E_{\mu_t}/KT) \qquad (9)$$

Figure 8 indicates the drift mobility of ions against $1/T$ for pure PC discs, and the value of E_{μ_t} is found to be 0.095 eV. The drift mobilities for doped PC
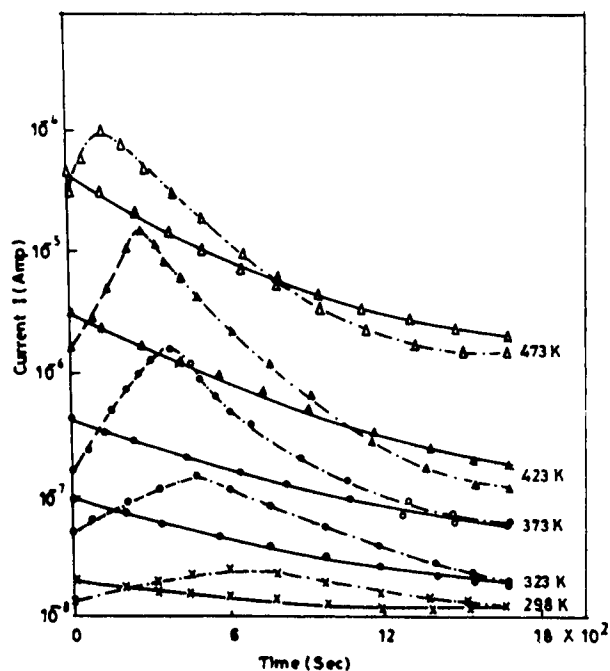

Figure 7   Time dependence of current for PC discs doped with 5 wt % $NiCl_2$ at different temperatures (applied voltage = 1 kV). (Solid lines) For the first application of voltage; (dotted lines) after reversal of polarity.
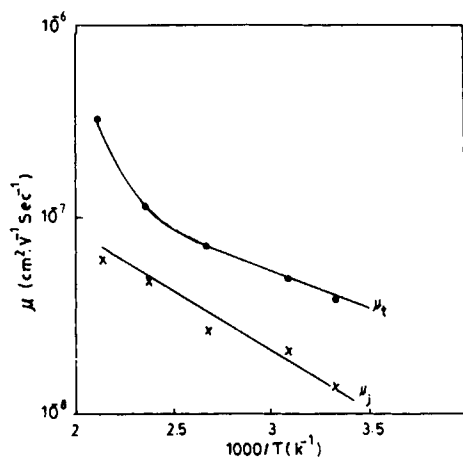
Figure 8 Temperature dependence of ion mobility μ for PC discs; μ_t derived from t_{max}, Figure 6, and μ_j derived from Figure 5.

Figure 9 Temperature dependence of ion mobility μ_t derived from t_{max} for PC discs doped with different concentrations of $NiCl_2$: ($\triangle$) 5%; ($\bigcirc$) 10%; ($\bullet$) 20%; ($\mathbf{x}$) 30%.

with different concentrations of $NiCl_2$ are shown in Figure 9 and the values of E_{μ_t} are listed in Table III.

The number of ions accumulated near the electrode $m(t)$ on applying the dc voltage in one direction during time interval between ($t = 0$) and ($t = t$) per unit area is obtained from Faraday's law:

$$m(t) = \int_0^t (J/q) \, dt \tag{10}$$

and the current density (J) at time (t) is given by

$$J = J_0 \exp[-\mu \, E \, t/d] \tag{11}$$

If we plot the relation $\ln(J)$ against time (t), when a dc voltage is initially applied on the PC disc, as in Figure 5, the slopes at the initial values are equal to ($\mu E/d$). In plotting relation (9), E_{μ_j} is taken instead of E_{μ_t}, where E_{μ_j} is the activation energy derived from the initial slope of current–time curves by eq. (11).[8] Figure 8 shows this relation, and the value of E_{μ_j} is found to be 0.12 eV.

On the other hand, since μ_j is known, the density of mobile ions (n) in the sample due to the release from the ionic layer can be obtained using eq. (7). The values of n for PC are listed in Table IV.

From the above results, the apparent activation energies for pure PC discs, concerning the transport phenomenon E_{μ_t} and E_{μ_j}, are 0.095 and 0.12 eV, respectively, while the activation energies for electrical conduction are found to be $\Delta E_c = 0.47$ and 0.57 eV at low and high temperatures, respectively, for undoped PC.

The difference in the values of activation energies may give information about the origin of the mobile
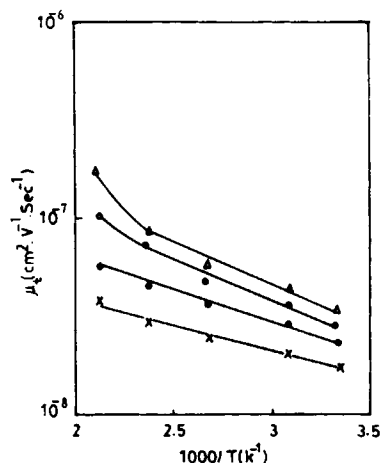
ions in PCs. The energy for ion pair creation ψ is estimated from[9,29]

$$\psi = 2(\Delta E_c - E_u) \tag{12}$$

For PC, $\Delta E_c = 0.57$ eV and $E\mu = 0.095$ eV, which gives the maximum value of the energy for ion pair creation, i.e., ψ is equal to 0.95 eV. This value is rather small compared with the chemical bond energy of $C = O$ (11.6 eV), which implied that impurities are responsible for the mobile ions.

The above conclusion seems to be contradictory to the postulate used in the derivation of μ_j that thermal creation of ions is negligibly small. Then, if the difference is insignificant, ΔE_c can be regarded as the activation energy of ion transport and the weakly trapped ions may be the main ion source at least at the early stage of a dc voltage application.

Now, in the temperature dependence (I-t) curves which were explained by the behavior of charge carriers, two mechanisms can explain this phenomenon[25]: The first is "a clean-up" effect which is associated with the effective decrease in the density

Table III   Dependence of the Apparent Activation Energy $E\mu_t$ on the Concentration of $NiCl_2$

Sample	$E\mu_t$ (eV)
PC + 5% $NiCl_2$	0.078
PC + 10% $NiCl_2$	0.074
PC + 20% $NiCl_2$	0.055
PC + 30% $NiCl_2$	0.046

Table IV   The Density of Mobile Ions for PC at Different Temperatures

T (K)	298	323	373	423	473
n (cm^{-3})	6.96×10^{13}	4.19×10^{14}	6.83×10^{15}	4.62×10^{16}	3.51×10^{17}

of mobile ions within the sample as they arrive at the electrode. The second mechanism is the effective drop of the electric field in the bulk of the sample due to the space–charge effect of ions drifting to the electrodes.

The effect of these two mechanisms on the conduction current may be intensified by the enhancement of mobility with increasing temperature. This is because the two mechanisms are directly affected by the ion drift mobility.

CONCLUSION

The electrical conductivity of PC increases with increase of the NiCl$_2$ content, which may be due to the formation of charge-transfer complexes (CTC). The currents in PC discs both pure and doped with NiCl$_2$ in the high-field region are attributed to space charge limited conduction. The permittivity also increases, probably due to the rise in the interfacial polarization which results from the increase in boundaries between PC and NiCl$_2$ phases. Both the free carrier mobility (μ) and the charge carrier density (n) increase with increasing temperature.

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