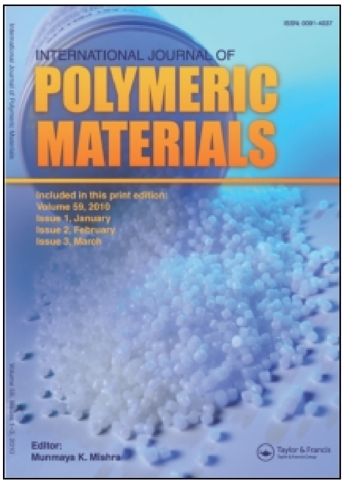

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DC CONDUCTIVITY IN POLY-N-VINYLCARBAZOLE: A STUDY OF DIELECTRIC MEASUREMENTS

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Dynamical dielectric measurements have been carried out on thin films of poly-N-vinylcarbazole. The dielectric response data were graphically represented in the conductivity complex plane, from which the values of the contribution of the DC conductivity were estimated. These values were in good agreement with the values obtained from DC current measurements, already reported in the literature. These results allow to conclude that the graphical representation of the complex conductivity in the complex plane represents a simple way for estimating the DC conductivity from dielectric data, without the experimental limitation to measure at very low frequencies, and without the difficulties appearing during DC current measurements.

Keywords: DC conductivity, dielectric function, capacitance, dielectric loss, frequency

1. INTRODUCTION

The dielectric response of solid materials provides information about the different mechanisms of conduction at different frequencies [1, 2, 3]. Indeed, by characterizing the dielectric response, the complex dielectric function $\varepsilon^*(\varepsilon) = \varepsilon'(\omega) - \varepsilon''(\omega)$ is defined, where $\varepsilon'(\omega)$ represents the dielectric constant and $\varepsilon''(\omega)$ the dielectric loss, with ω being the radian frequency. This dielectric function allows to define a complex conductivity given by:

$$\sigma^*(\omega) = \mathrm{i}\ \omega\varepsilon_0\varepsilon^*(\omega) \tag{1}$$

The real and imaginary parts of Eq. (1) are available through experimental measurements of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ respectively, *i.e.*,

$$\begin{aligned} \sigma'(\omega) &= \omega\varepsilon_o\varepsilon''(\omega) \\ \sigma''(\omega) &= \omega\varepsilon_o\varepsilon'(\omega) \end{aligned} \tag{2}$$

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if the material contains some mobile charge carriers, then these carriers would give rise to a finite DC conductivity, σ_o, making a contribution to the dielectric function, which is written as [4]:

$$\varepsilon^*(\omega) = F^*(\varepsilon_\infty, \varepsilon_s, \omega\tau) - i\frac{\sigma_o}{\omega\varepsilon_o} \quad (3)$$

where F^* is a complex polarization function which depend on the low frequency limited dielectric constant, ε_s; on the high frequency limited dielectric constant, ε_∞; and on the product of the radian frequency and relaxation time, $\omega\tau$. According to Eq. (3) and Eq. (1), the real part of the conductivity given by Eq. (2) generally is written as:

$$\sigma'(\omega) = \sigma_o + \sigma_{ac}(\omega) \quad (4)$$

σ_o represents the contribution to the instantaneous response to the external electric field, and $\sigma_{ac}(\omega)$ is the AC conductivity and represents the delayed response to the external electric field. The dependence of the AC conductivity on frequency has been observed to follow a power law given by:

$$\sigma_{ac}(\omega) \propto \omega^n \quad (5)$$

then Eq. (4) can now be written in the form:

$$\sigma'(\omega) = \sigma_o + A(T)\omega^n \quad (6)$$

A is a constant which depends on temperature, n is close to unity at the region of high frequencies and decrease by decreasing frequency in a continuous process [5]. The behaviour with frequency given by Eq. (5) some time it is attributed to a dielectric response due to the migration of carriers by a hopping mechanism between localized states, but also to a dielectric response due to the orientation of dipoles with a distribution of relaxation time. In this context, Eq. (6) is applicable only if σ_o and σ_{ac} can be experimentally separables, it means that they must stem from different origins. One way to establish this argument, is by comparison the values of σ_o obtained from DC measurements, with those obtained from dielectric data. A typical procedure to obtain σ_o from the dielectric response, is by estimating the real part of conductivity, given by Eq. (2), at several frequencies and then to extrapolate the data to zero frequency according to:

$$\sigma_o = \lim_{\omega \to 0} \sigma'(\omega) \quad (7)$$

however, the correct estimation of the value of σ_o using Eq. (7) can be difficult due to insufficient range of frequency available for given an unanbiguous extrapolation. In the case of high insulating polymers, the

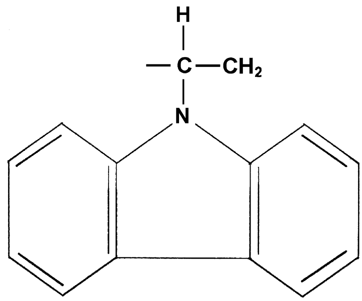

FIGURE 1 Chemical structure of poly-N-vinylcarbazole.

experimental difficulties becomes serious since frequencies extremelly low are required and it is necesary very specialized equipment where measurements are very time consuming [5]. An alternative is to represents the dielectric data in the complex conductivity plane as reported by Wei and Sridhar [6], who represented in the complex plane the orientational dipolar contribution to the complex conductivity, $\sigma_x^*(\omega)$, defined by:

$$\sigma_x^*(\omega) = \sigma^*(\omega) - i\ \omega\varepsilon_o\varepsilon_\infty \tag{8}$$

consequently, Eq. (2) would be modified in the form:

$$\begin{aligned}\sigma_x'(\omega) &= \omega\varepsilon_o\varepsilon''(\omega)\\ \sigma_x''(\omega) &= \omega\varepsilon_o[\varepsilon'(\omega) - \varepsilon_\infty]\end{aligned} \tag{9}$$

The representation is carried out by plotting $\sigma_x''(\omega)$ *vs.* $\sigma_x'(\omega)$. This graphical method has been used by Wei [6] for analizing dielectric data of glycerol and LiCl/ propanol solution, and recently in polycarbonate of bisphenol A [7]. In this communication we are using the method in poly_N-vinylcarbazole (PVK). This material, whose quimical structure is shown in Figure 1, is a photoconductor polymer which has been subjected to a wide study in the last past decades [8, 9] but all of them from DC measurements, in this opportunity we are reporting DC dark conductivity deduced from the dielectric measurements.

2. EXPERIMENTAL DETAILS

Poly-N-vinylcarbazole(PVK) was commercially obtained in the form of pallets from Aldrich Chemical Co. Weighted amount of PVK was purified by dissolving it in analar chloroform and reprecipitating in isopropyl alcohol, repeating the processe several times. Purified PVK was then dissolved in tetrahidrofluoran and thin films 10 μm thick, were prepared by spreading the solution under a blade. Once the films had been prepared, they were placed into a dissecator under vacumm to evaporate any residual solvent. Finally, gold electrodes were thermally evaporated on both side of the films, to have samples in the form of parallel plate capacitors.

The dielectric response was obtained with a digital RLC bridge General Radio model 1689, by measurements of the sample capacitance [C(ω)] and loss tangent (tan δ) in the range of frequency between 10 Hz and 10^5 Hz. Using these values we can calculate the complex dielectric function $\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega)$, with the help of the relations:

$$\begin{aligned} \varepsilon'(\omega) &= C(\omega)/C_o \\ \varepsilon''(\omega) &= \varepsilon'(\omega)\ tan\ \delta \end{aligned} \tag{10}$$

where C_o is the capacitance without dielectric. The geometry of the samples was invariant over the whole range of temperature used for measurements, actualy from 285 K to 487 K, which was monitored by a cromel-alumel thermocoupla placed near to the sample and connected to digital thermometer Fluke model 3010.

3. EXPERIMENTAL RESULTS

Figure 2 shows, in a linear-log representation, the frequency dependence of the real (ε') and imaginary part (ε'') of the complex dielectric function at

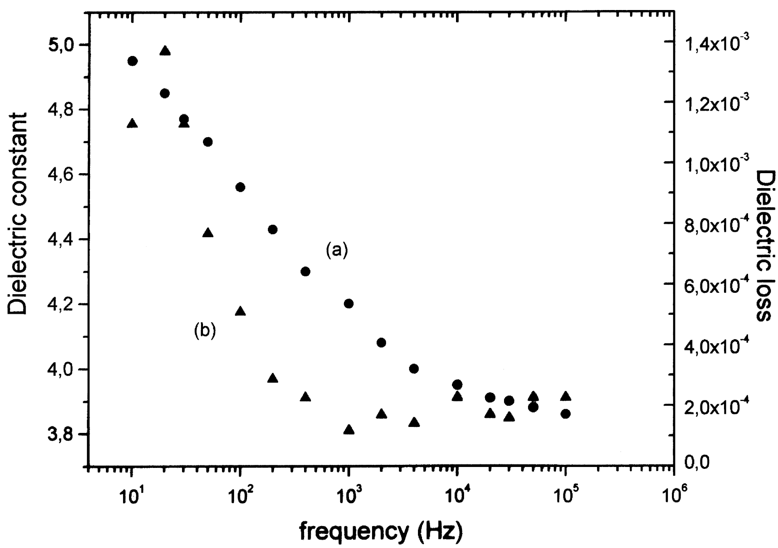

FIGURE 2 Linear-log plot of the complex dielectric function for a typical sample 1×10^{-5} m thick, at room temperature.

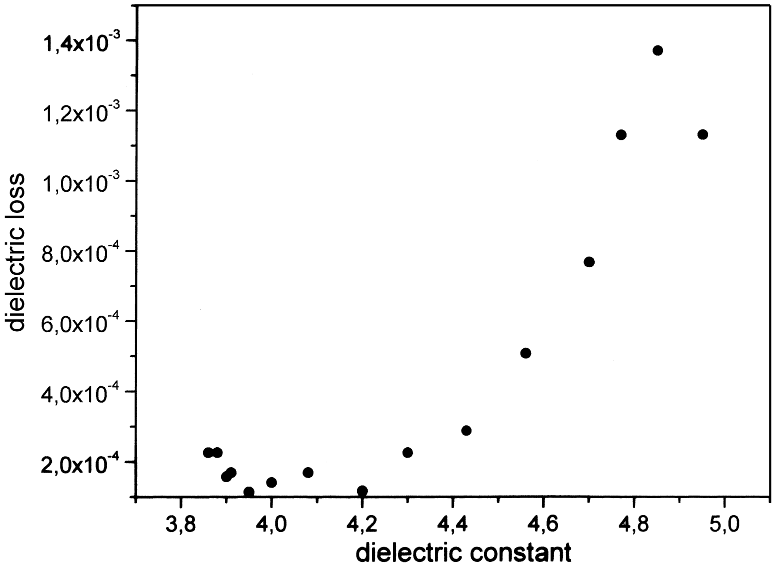

FIGURE 3 Arch diagram of the complex dielectric function for the same sample as Figure 2.

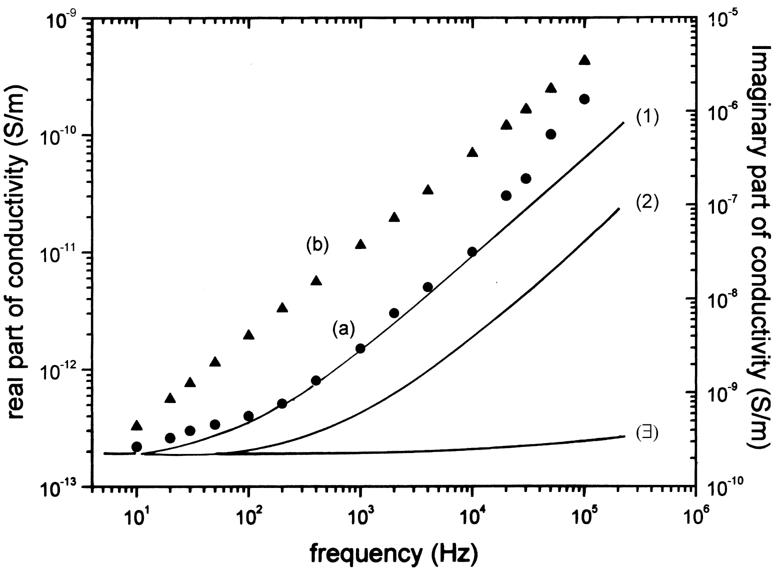

FIGURE 4 Spectrum of the complex conductivity for the same sample as Figure 2. The filled lines in curve (a) corresponds to the theoretical fitting using the formulas of (1) Cole-Cole, (2) Cole-Davidson, (3) Havriliak-Negami.

room temperature. Figure 3 illustrates the Cole-Cole diagram of the dielectric function, it is noted a deviation from the expected closed arc, probably due to the presence of a DC conductivity. Figure 4 depicts the spectra of the complex conductivity obtained from Eq. (2) in a log-log representation. It can be observed a linear fitting of the real part of the conductivity (curve a) at frequencies above 5×10^3 Hz. According to Eq. (5), the slope of this branch was estimated in 0.79. An extrapolation of the data to zero frequency, in order to have a possible DC conductivity according to Eq. (6), is not feasible since our short experimental limit of frequency.

4. DISCUSSION OF RESULTS

We have been pointed out that Figure 3 shows evidence of the presence of a DC conductivity. In this case, the complex dielectric function is given by Eq. (3). The behaviour of the real part of conductivity shown in Figure 4 through the high frequency region, very often is attributed to the migration of charge carriers by a hopping mechanism between localizad states; but a similar profile can be also reproduced due to a polarization processes with a distribution of relaxation time. The solid line shown in Figure 4(a) illustrates theoretical calculations using, as a function F^* in Eq. (3), the empirical relations of Cole-Cole [10], Cole Davidson [11] and Havriliak-Negami [12]. Better fit to the experimental points seem to get out with the formulae of Havriliak-Negami. In this case, we can write Eq. (3) as:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{[1 - (i\omega\tau)^{1-\alpha}]^\beta} - i\frac{\sigma_o}{\omega\varepsilon_o} \tag{11}$$

where αyβ are parameters associated to the distribution. From Eq. (11) it is obtained the real and imaginary part of the dielectric function and then, by using Eq. (9), the components of the orientational contribution of conductivity are:

$$\begin{aligned} \sigma'_{\rm x}(\omega) &= \omega\varepsilon_{\rm o}\left(\frac{\varepsilon_s - \varepsilon_\infty}{K}\sin\beta\varphi\right) + \sigma_{\rm o} \\ \sigma''_{\rm x}(\omega) &= \omega\varepsilon_{\rm o}\left(\frac{\varepsilon_s - \varepsilon_\infty}{K}\right)\cos\beta\varphi \end{aligned} \tag{12}$$

where

$$\begin{aligned} \mathrm{K} &= [1 + 2(\omega\tau)^{1-\alpha}\,\sin\frac{\pi\alpha}{2} + (\omega\tau)^{2(1-\alpha)}]\beta^{1/2} \\ \varphi &= \tan^{-1}\left[\frac{(\omega\tau)^{1-\alpha}\cos(\pi\alpha/2)}{1 + (\omega\tau)^{1-\alpha}\sin(\pi\alpha/2)}\right] \end{aligned}$$

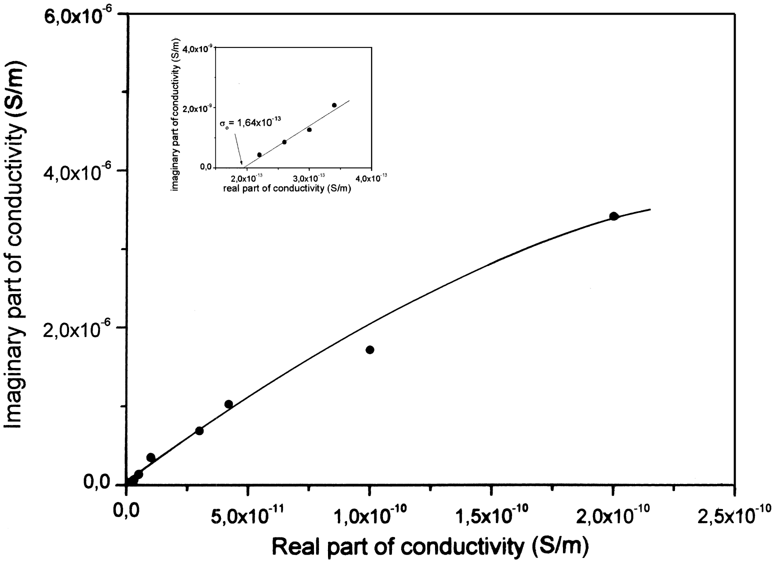

FIGURE 5 Conductivity plot in the complex plane. The filled line corresponds to the theoretical formulae of Havriliak-Negami.

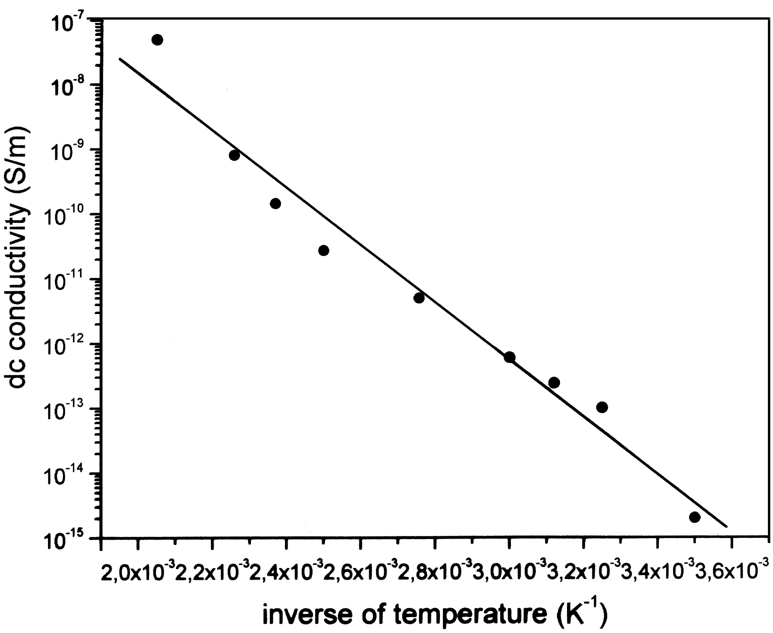

FIGURE 6 Arrhenius plots of DC conductivity.

we can see that $\sigma'_x(0) = \sigma_o$ and $\sigma''_x(0) = 0$; consequently, in a plot $\sigma''_x(\omega)$ *versus* $\sigma'_x(\omega)$, the curve must cut the $\sigma'_x(\omega)$ - axis at σ_o when $\omega \to 0$. Figure 5 shows such a plot for the data of Figure 3 and using Eq. (9). It is observed a tendency to intercept the $\sigma'_x(\omega)$ - axis at the low frequency range. The inset illustrates an extrapolation to $\sigma''_x(0)$, from which σ_o is estimated, using linear regresion, in the order of 1.64×10^{-13} S/m. The filled line correspons to the theoretical curves obtained using Eq. (12) for $\alpha = 0{,}5$; $\beta = 0{,}9$; $\tau = 1{,}0 \times 10^{-4}$ and $\varepsilon_\infty = 3{,}8$ in the same experimental range of frequency. The same behaviour was observed at differents temperatures, from which one can study the dependence of σ_o with temperature. Figure 6 depicts an Arhenius plot of DC conductivity from whose slope it is obtained an activation energy in the order of 0.37 eV. The values of all of these parameters are in just agreement with those determined from DC current-voltage characteristic, which have been reported elsewhere [13, 14].

5. CONCLUSIONS

The discussions of the experimetal results being presented in the preceding sections, give enough argument that the graphical representation of the complex conductivity in the complex plane, represents a simple way for estimating the DC conductivity from dielectric data, without the experimental limitation to measure at very low frequencies. By comparing the values of σ_o estimated from dielectric measurements with the values obtained from the I-V characteristic, we can establish if the conductivity of the material under test can be visualized as the sum of the DC and AC contributions. In our experiments, the values of DC conductivity estimated from the dielectric response were in just agreement with the values obtained from DC measurements. We then can conclude, that in our samples of poly-N-vinylcarbazole σ_o and σ_{AC} stem from conduction mechanisms of different origins, and consequently the DC contribution can be experimentally separated from the AC one.

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