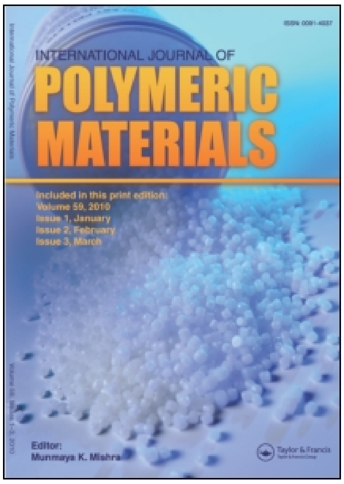

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# On the Splitting of d.c. Contribution to the Dielectric Loss. Case of Poly(monocyclohexylitaconate)

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# On the Splitting of d.c. Contribution to the Dielectric Loss. Case of Poly(monocyclohexylitaconate)

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The splitting of the d.c. conductivity on the low frequency side of the dielectric loss has been performed by using the complex dielectric polarizability $\alpha$, instead of the permittivity. Data dealing with the dielectric loss for poly(monocyclohexylitaconate) have been used to compare both methods. The dielectric relaxation peaks in $M''$ and $\alpha''$, are in general in good qualitative agreement. There is a small shift which is attributed to the fact that $M$ is a modulus and $\alpha$ a compliance.

KEY WORDS Poly(monocyclohexylitaconate), dielectric loss, dipolar dielectric relaxation, conductivity, interfacial contribution.

## INTRODUCTION

One of the problems in the study of the $\alpha$ dipolar dielectric relaxation in polymers and different materials is the presence of d.c. conductivity, on the low frequency side of the dielectric loss. In fact, dielectric loss $\varepsilon''$ could be considered as:

$$\varepsilon'' = \varepsilon''_d + \varepsilon''_c + \varepsilon''_i \tag{1}$$

where subscripts $d$, $c$ and $i$ refers respectively to the dipolar, free charges and interfacial contribution to the total loss $\varepsilon''$. By using a log $\varepsilon''$ versus log $f$ plot is possible to obtain separately each component, taking into account that the conductive contribution has a $f^{-1}$ dependence.

This method is suitable in cases where a strong dipolar relaxation process is present, that is to say, in cases where a prominent maximum in $\varepsilon''$ appears. In these cases the low frequency part is appreciably affected by d.c. conductivity.[1] However, there are other cases in which the presence of dipolar relaxation is hidden due to the d.c. conductivity. In these cases the splitting between the dipolar part

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from the d.c. conductivity is more difficult because the values of the d.c. conductivity are clearly dominant over the dipolar contribution. Therefore, this last contribution only affects in a marginal way in the whole dielectric loss. For this reason, the results are subjected to many source of errors. In order to solve this problem it has been proposed[2] to use the electric modulus $M^*$ instead of dielectric permittivity $\varepsilon^*$. The electric modulus is defined by the following equation:

$$M^* = \varepsilon^{*-1} \tag{2}$$

In this case the real and imaginary parts of the electric modulus can be calculated from the permittivity by means of

$$M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2}; \qquad M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{3}$$

where $\varepsilon'$ and $\varepsilon''$ represent the two components (real and imaginary) of the complex dielectric permittivity.

Another way to split the dipolar contribution from d.c. conductivity is to use the complex dielectric polarizability $\alpha^*$ instead of the complex permittivity by means of:

$$\alpha^* = \frac{\varepsilon^* - 1}{\varepsilon^* + 2} \tag{4}$$

From this equation it is easily obtained:

$$\begin{aligned} \alpha' &= \frac{(\varepsilon' - 1)(\varepsilon' + 2) + \varepsilon''^2}{(\varepsilon' + 2)^2 + \varepsilon''^2} \\ \alpha' &= \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2} \end{aligned} \tag{5}$$

The use of Equation (4) is justified under the basic theoretical background furnished by Scaife[3] and Havriliak *et al.*[4] $\alpha^*$ having a macroscopic meaning. Equation (4) can be considered as a normalization procedure for dielectric data. Strictly speaking the transformation defined by Equation (4) was only proposed by Scaife[3] in terms of $\varepsilon_\alpha^*$, that is, only refers to the dipolar contribution, however, according to our experience when is used for $\varepsilon^*$, i.e. for the full spectrum, the conductivity and interfacial contribution also decreases.

It is well known[5] that poly(monoitaconates) show a dielectric behaviour in the $\alpha$ zone where a continuous increasing of the loss permittivity and loss tangent is observed, mainly at low frequencies with increasing temperature. This behaviour is similar to that observed in charge transfer complexes.[6]

The purpose of the present note is the comparison of the results obtained by both procedures (given by Equations (2) and (4)) by using experimental data obtained for poly(monocyclohexylitaconate) (PMCHI).

## EXPERIMENTAL

Monomer was prepared by esterification of itaconic acid (1 mol) with cyclohexyl alcohol (3–4 mol) using acetyl chloride as catalyst.[7,8] Polymerization was carried out in bulk, at 67°C under $N_2$ in the presence of AIBN (0.3% mol) as initiator.[8] Purification of the polymer was achieved by repeated dissolution in THF and reprecipitation with diethyl ether before vacuum dried.[8]

Dielectric measurements were carried out with a GENRAD bridge 1620 with a three terminal cell in the frequency range between 0.2 and 100 kHz at temperatures between r.t. and 100°C.

## RESULTS AND DISCUSSION

In Figure 1 are represented the dielectric loss as well the real and imaginary part of the complex electric modulus and the real and imaginary part of the complex

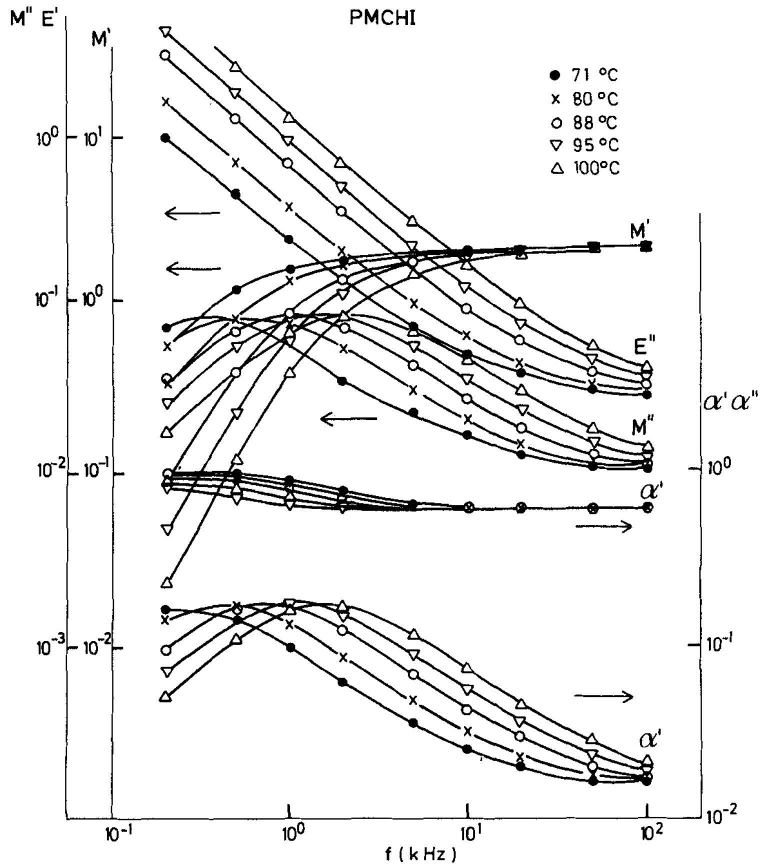

FIGURE 1 Dielectric loss, the real and imaginary parts of the electric modulus and the real and imaginary parts of complex polarizability against frequency at five temperatures: (●) 71°C; (×) 80°C; (○) 88°C; (▽) 95°C; (△) 100°C.

polarizability at five temperatures, i.e. 71, 80, 88, 95 and 100°C, calculated from Equations (3) and (5) for poly(monocyclohexylitaconate) samples.

We can observe the continuous increasing of the dielectric loss when the frequencies diminish. On the contrary, we can observe the dielectric relaxation peaks in $M''$ and $\alpha''$. In general, we can observe a good qualitative agreement between the imaginary part of both functions. The shift observed in the maxima of $M''$ and $\alpha''$ is due also to the fact that $M^*$ is a modulus and $\alpha$ a compliance. The specific values of that shift depend on the shape of the loss curve. In other work[9] these shifts have been calculated for some specific empirical models representing the loss curve. All these results show that polarizability can be used alternatively to the electric modulus, to represent relaxations related to the glass transiton Tg hidden in the dielectric spectrum due to the big contribution of d.c. conductivity.

It is interesting to note that the activation energy corresponding to the peaks observed in $M''$ and $\alpha''$, according to an Arrhenius type equation is about 18 Kcal mol$^{-1}$. This value is too low for a glass transition but is in good agreement with a relaxation due to conductivity.

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