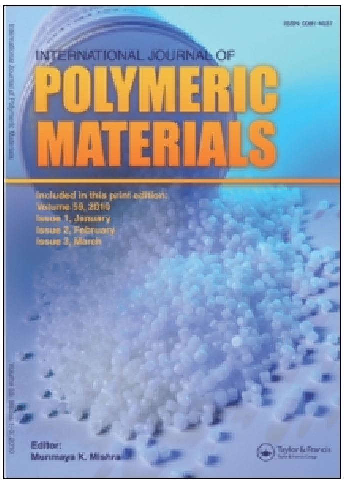

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Dielectric Anisotropy in Die-drawn Isotactic Polypropylene Copolymer

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The electrical behavior of die drawn isotactic polypropylene was investigated at room temperature in the frequency range 10 Hz to 10^6 Hz. The electric permittivity and electric modulus were determined from ac impedance measurements. In the low frequency range a dramatic increase in the imaginary and real components of dielectric permittivity was observed both parallel and normal to the chains alignment. This change is associated with a well defined relaxation peak in the plot of the imaginary component of electric modulus *versus* frequency. A high degree of anisotropy was observed in dielectric permittivity and electric modulus. This anisotropy is a result of chains alignment and the decrease in the mobility of molecules in the amorphous region due to the high constrains imposed on this region as a result of the drawing process. The Cole - Cole plot of the real component *versus* the imaginary component of electric modulus for both normal and parallel to the direction of chains alignment yields nearly perfect circles indicating that a certain polarization mechanism is dominant in die drawn isotactic polypropylene copolymer.

Keywords: Polypropylene; Die-draw; Dielectric measurements; Anisotropy

1. INTRODUCTION

There is a considerable interest in the effect of orientation on the structure and properties of semi-crystalline polymers. It was found that the mechanical properties of polymers can be modified significantly as a result of deformation [1-4]. As an example it was found that the tensile modulus is directly related to the draw ratio reached

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[5]. In general the uniaxial orientation can be achieved by various techniques such as conventional drawing [6], die drawing [7], hydrostatic extrusion [8], and by melt-spinning/hot drawing route [9]. The drawing process induces ordering in the crystalline region with the chain axes aligning in the draw direction. At draw ratio about 8, X-Ray [10] and birefringence measurements [11] show that the crystallites are nearly fully aligned. Upon increasing the draw ratio the constrains in the amorphous phase dramatically increase and the tie molecules posses some degree of orientation. Since the relaxation transition in isotactic polypropylene takes place in the amorphous region, it is expected that the dielectric relaxation will show some anisotropy in the drawn samples.

This paper describes a study of the effect of orientation introduced by die drawing technique on the electrical behavior of isotactic polypropylene copolymer. The measurements were performed in two directions parallel and normal to the chain alignment, on samples with different draw ratios in the frequency range 10 Hz to 10^6 Hz.

2. EXPERIMENTAL

2.1. Samples Preparation

The polymer used was propathane GSE 108, MFI 0.8, a polypropylene copolymer manufactured commercially by ICI plc (UK). Samples were prepared by a die drawing technique. An isotropic rod of polypropylene machined from a cast billet was drawn through a heated 4 mm die at various drawing speeds to obtain a range of molecular orientation. The draw temperature was controlled at 110°C to an accuracy of ± 1°C. Since control of draw ratio could be achieved by varying the diameter of the isotropic feedstock billet, the draw ratio of the drawn rod was determined as the ratio of cross sectional area of the isotropic billet to the drawn one.

2.2. AC Measurements

The ac measurements were carried out at room temperature (25°C) in the frequency range 10 Hz to 10^6 Hz using a Solorton -1260 impedance/gain phase analyzer (Schlumberger instrument). The apparatus is controlled by software packages which maximize the performance and data handling of the system. The measurements were performed on samples machined carefully in the directions parallel and normal to the draw direction. Silver electrodes were added on to each surface, and the sample set-up was then kept in a shielded cavity to improve low frequency measurements. Using this set-up the complex ac impedance and the phase angle were measured. From these measurements the real and imaginary components of dielectric permittivity and electric modulus were determined.

3. RESULTS AND DISCUSSION

Generally four electrical complex quantities were reported in terms of real and imaginary components in the literature [12, 13] as follows:

Complex impedance $Z^* = R_s - j/\omega C_s = Z' - jZ''$
Complex admittance $Y^* = 1/Z^* = R_p + j\omega C_p$
Complex permittivity $\varepsilon^* = \varepsilon' + j\varepsilon''$
Complex modulus $M^* = M' + jM''$.

Where the subscript p and s refer to the equivalent parallel and series circuits, ω is the angular frequency, R is the equivalent resistance and C is the equivalent capacitance. However, the measured values of the real and imaginary components of the ac impedance and admittance depend on the geometry of each sample and can't be used to study the effect of drawing on the electrical properties of die-drawn isotactic polypropylene if different samples have been used in the measurements; therefore, we will report the dielectric permittivity and electric modulus only.

To study the electrical anisotropy in die drawn isotactic polypropylene copolymers, the measurements were performed with the electric field both parallel and normal to the mean chain direction. The ac measurements give the complex ac impedance and the phase angle, where the real (Z') and imaginary components (Z'') of ac impedance can be calculated from the relations;

$$Z' = Z\cos\theta \quad \text{and} \quad Z'' = Z\sin\theta$$

The real component of dielectric permittivity (ε') and the imaginary component (loss factor) (ε'') using the following relation:

$$\varepsilon' = -Z'/\left(Z'^2 + Z''^2\right)\,\omega\, C_0$$
$$\varepsilon'' = -Z''/\left(Z'^2 + Z''^2\right)\,\omega\, C_0$$

where C_0 is the vacuum capacitance of the cell.

On the other hand the complex permittivity is a compliance as in the case of the mechanical compliance, and can be written to give an electric modulus, $M^* = 1/\varepsilon^*$, therefore, the real (M^*) and imaginary (M'') components of electric modulus can be determined from the relations:

$$M' = \varepsilon'/\left(\varepsilon'^2 + \varepsilon''^2\right) \quad \text{and}$$
$$M'' = \varepsilon''/\left(\varepsilon'^2 + \varepsilon''^2\right)$$

We emphasize here, that the complex permittivity and the complex electric modulus contain the same information. In M' relation, the real component of permittivity appears in the denominator to the second power, therefore, its tendency to overwhelm the loss function is minimized.

The general feature of the phase angle *versus* frequency as shown in Figure 1 for different draw ratio samples is nearly the same for all samples when the electric field is applied normal or parallel to the mean chains alignment. This feature is nearly identical to that observed in RC network in parallel [14], where the phase angle varies from −90° at 10^6 Hz to less than −10° at 10 Hz, for both types of samples.

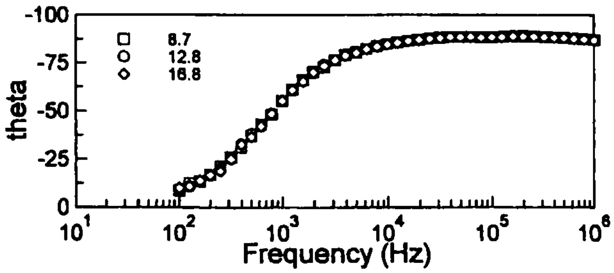

FIGURE 1 Phase angle (theta) *versus* frequency for die-drawn polypropylene at different draw ratios.

This indicates that the dependence of the sample and the cell are equivalent to RC network in parallel. Therefore, for such network it is expected that the following points should be observed in ac measurements.

- the complex plane plots of Z'' *versus* Z' and M'' *versus* M' should yield semi-circle,
- the angular frequency of the peak maxima and center of semi-circle coincide, and are given by the reciprocal of the conductivity σ and the relaxation time τ, where $\omega_{\max}=2\pi f_{\max}=1/\tau=\sigma/\varepsilon_0\varepsilon''$.

The calculated values of ε' and ε'' of the electric permittivity are shown in Figures. 2 and 3. The values of ε' and ε'' are nearly independent of frequency in the high frequency range. However, ε''

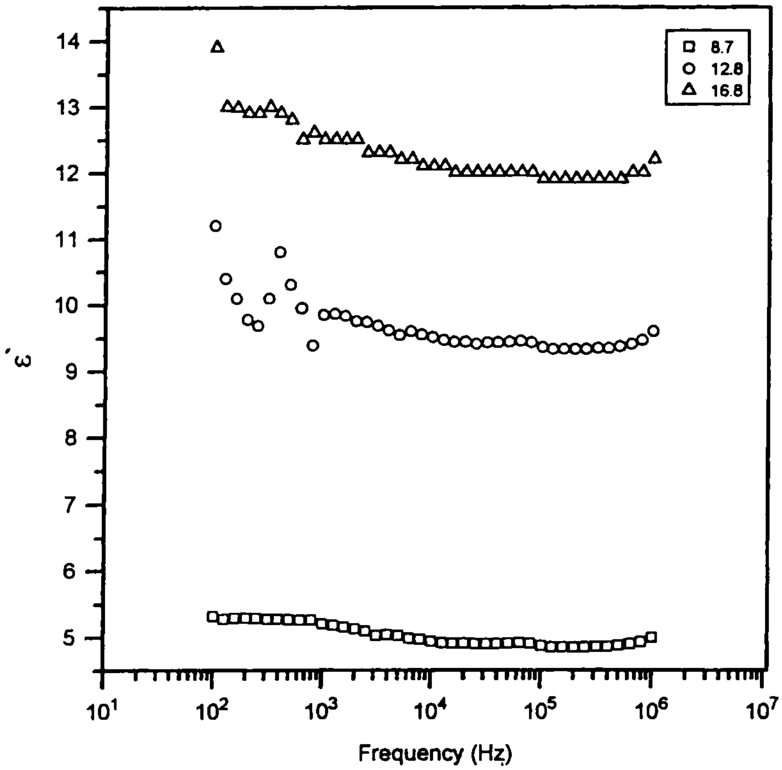

FIGURE 2a Real component of electric permittivity (ε') for die drawn polypropylene *vs.* frequency, electric field is parallel to the chain alignment.

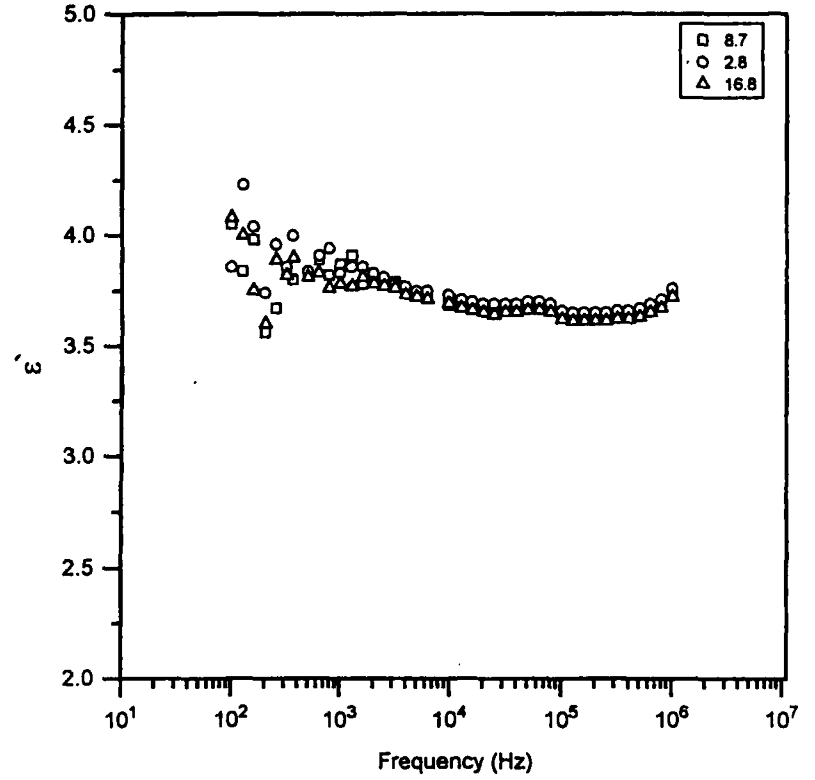

FIGURE 2b Real component of electric permittivity (ε′) for die drawn polypropylene *vs.* frequency, electric field is normal to the chain alignment.

increases dramatically at low frequency range indicating that the dc conductivity phenomenon plays an important role which mask any relaxation transition process in this region. In addition, the quality of the determined data at low frequencies may be influenced by contact effects, since the charge carriers may assemble around the electrodes. Therefore, no well defined relaxation peak was observed in the plot of ε″ *versus* frequency when the electric field is applied parallel or normal to the mean chains alignment. On the other hand the plot of *M*″ *versus* frequency as shown in Figures 4a and 4b reveals well defined relaxation peaks with pronounced decrease in intensity with increasing draw ratio when the electric field is applied parallel to the mean chain direction. This relaxation is associated with a dramatic drop in the real component of the electric modulus when the electric field was applied

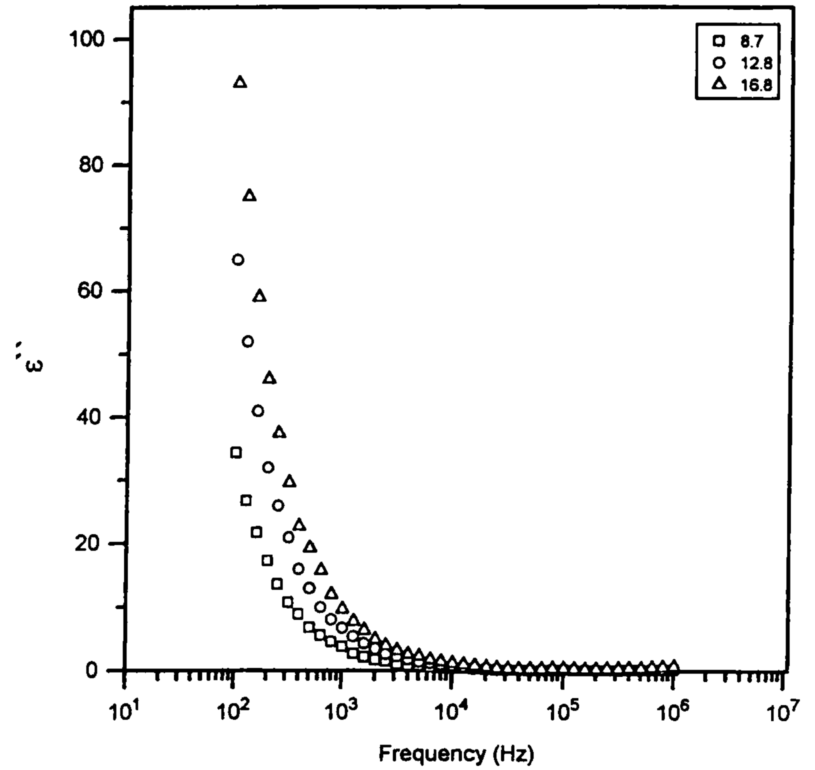

FIGURE 3a Imaginary component of electric permittivity (ε'') for die drawn polypropylene *vs.* frequency, electric field is parallel to the chain alignment.

normal to the mean chains orientation. In both cases, when the electric field is applied parallel or normal to the chain alignment the plot of complex plan M' *versus* M'' as shown in Figures 5a and 5b yields nearly perfect semicircles with different relaxation times when the electric field was taken parallel to the mean chain alignment as given in Table I.

As given in Table I the relaxation time is nearly independent of the draw ratio when the electric field is applied normal to the draw direction. However, a decrease in τ with increasing the draw ratio occurs when the electric field is applied in the draw direction.

This decrease in τ may indicate that the molecules become less mobile. On the other hand polypropylene is essentially a non-polar polymer. Curtis [14] has estimated that the net contribution of C—H

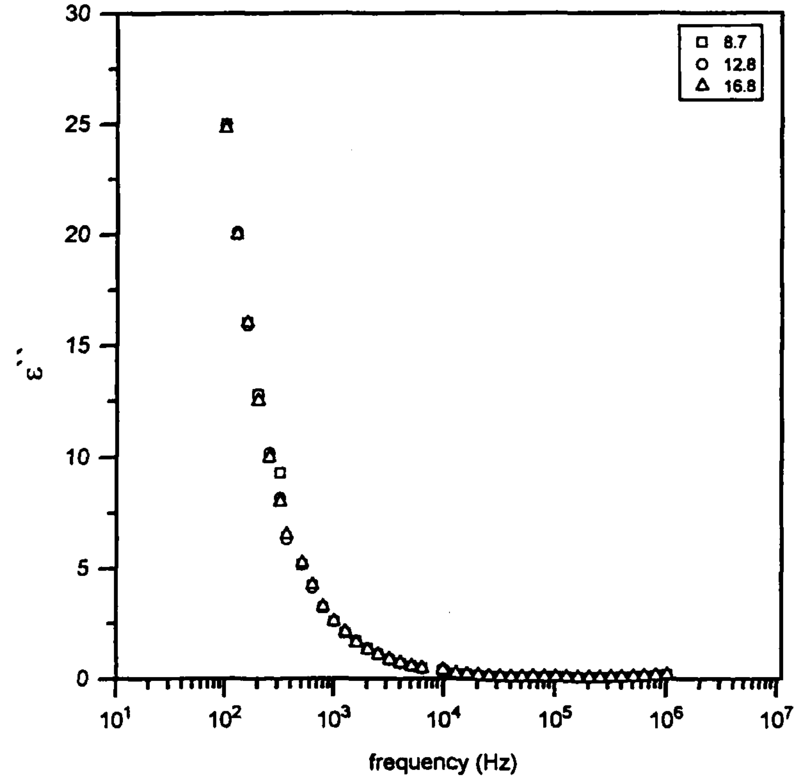

FIGURE 3b Imaginary component of electric permittivity for die drawn polypropylene (ε'') *vs.* frequency, electric, field is normal to the chain alignment.

dipoles is sufficient to account for the observed loss in the dielectric measurements. However, this relaxation occurs in the amorphous region, then the decrease in the intensity occurs in as shown in Figure 4a as a consequence of decrease in the number of molecules contributing to this relaxation. This is the case when a decrease in volume is due partially to the collapse of localized free volume, *i.e.*, high entropy regions which remain in an internal thermodynamic equilibrium [15].

Hus and Kwan [16] found that the intensity of the dielectric dissipation factor is a minimum when the electric field is applied in the draw direction. They concluded that the motion of dipoles would necessarily involve rocking of the chain backbone. This implies that a

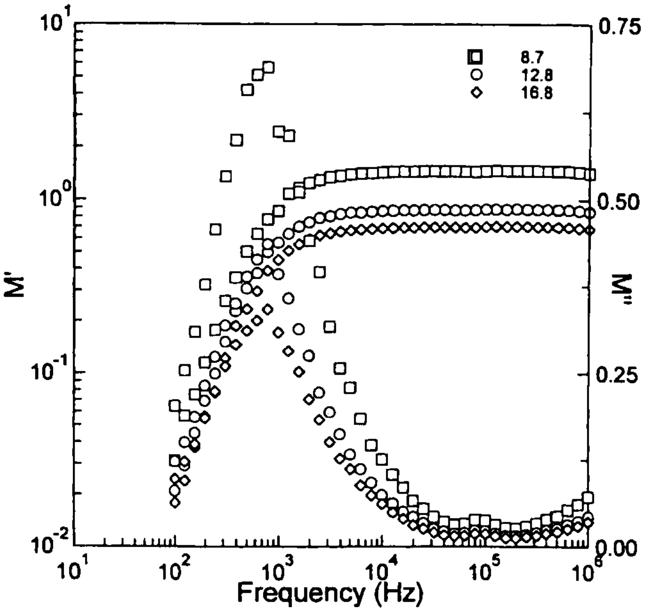

FIGURE 4a Real (M') and imaginary (M'') for die drawn polypropylene *vs.* frequency, electric field is parallel to the chain alignment.

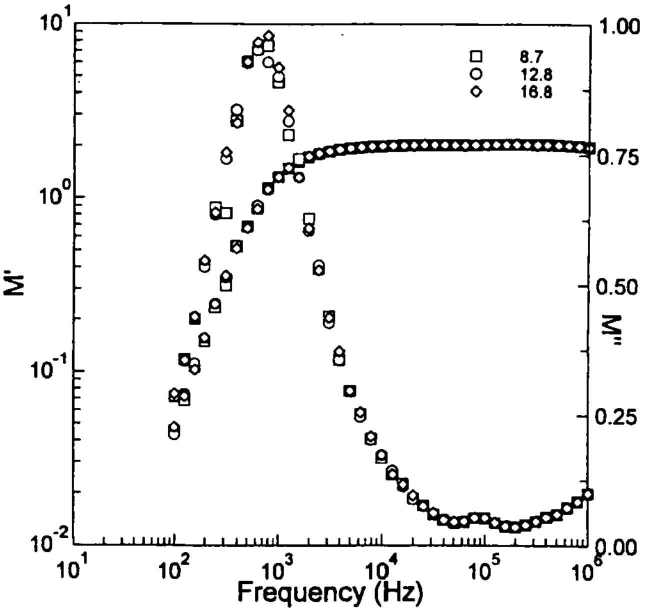

FIGURE 4b Real (M') and imaginary (M'') for die drawn polypropylene *vs.* frequency, electric field is normal to the chain alignment.

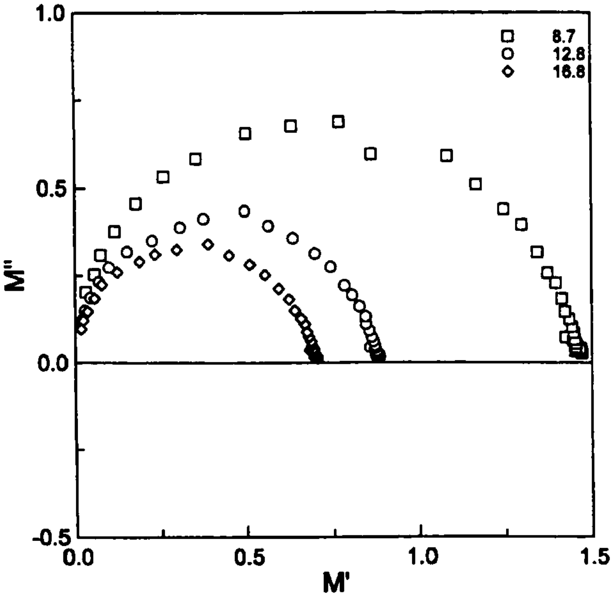

FIGURE 5a Imaginary component of electric modulus (M'') for die drawn polypropylene *vs*. real component of electric modulus (M'), electric field is parallel to the chain alignment.

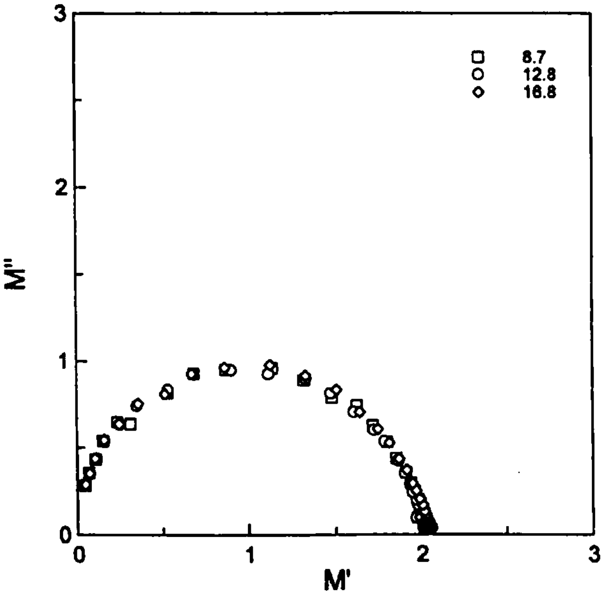

FIGURE 5b Imaginary component of electric modulus (M'') for die drawn polypropylene *vs*., real component of electric modulus (M'), electric field is normal to the chain alignment.

TABLE I Relaxation time (τ) for die-drawn polypropylene

	Relaxation time τ (ms)	
Draw ratio	*Parallel*	*Normal*
8.7	0.240	0.243
12.8	0.236	0.245
16.8	0.225	0.242

comparatively large activation energy is needed. Therefore, increasing the degree of orientation in the amorphous region, causes continuous increase of the fraction of taut-tie molecules axially connecting crystalline blocks and the constraint imposed on the amorphous region. These affect the molecular mobility in the direction of chains alignment, and as a result the intensity of the relaxation peak decreases with increasing the draw ratio.

On the other hand the increase in the crystallites orientation and the orientation of taut-tie molecules will affect the electronic polarizability and lead to an increase in the dielectric permittivity in the direction of chain alignment as shown in Figure 3, where no change was observed in ε' when the electric field was applied normal to the chains alignment.

4. CONCLUSIONS

The study of electrical behavior of highly oriented isotactic polypropylene copolymers in the direction parallel and normal to the mean chains alignment reveals the following results:

1. The electrical behavior shows high degree of anisotropy, where the dielectric permittivity increases with increasing draw ratio if the electric field is applied parallel to the chains alignment, and where it is nearly independent of draw ratio when the electric field is applied normal to the chain alignment.
2. The plot of the imaginary component of electric modulus *versus* frequency show well defined relaxation transition peak, with a decrease in its intensity with increasing draw ratio; however normal to the chains alignment no change in the intensity of the relaxation peak was observed.

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