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Dielectric Characterization of a Thermotropic Liquid Crystalline Copolyesteramide: 2. Orientation and Crystallinity

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ABSTRACT: The dielectric characterization of a thermotropic liquid crystalline copolyesteramide was extended. The influence of orientation and crystallization was studied. An effect of the draw ratio on the dielectric properties in the transverse direction was hardly found. However, the orientation of the sample in the electric field (parallel or perpendicular) showed a significant effect. The birefringence predicted from the dielectric data at high frequencies agrees well with the optical value. Annealing of extruded and compression-molded samples resulted in an increase of the α relaxation peak.

I. Introduction

Dielectric spectroscopy on the thermotropic liquid crystalline copolyesteramide Vectra B950, discussed in the previous paper, ¹ revealed the existence of four relaxations. The effect of orientation and crystallization on the relaxations was not discussed. However, it is known that these parameters can have a large influence on the magnitude and position of the relaxations. In the present paper we will deal with this influence.

Several authors have discussed the influence of the draw ratio on the mechanical properties of main chain LCPs. For instance, Choy et al.² correlated the molecular orientation, obtained by X-ray diffraction, to the elastic moduli as a function of the draw ratio. The dependence of the dielectric properties on the molecular orientation in main chain LCPs is described by only a few authors (e.g. Liu³ and Willems⁴). They both found an increase of the relaxation strength perpendicular to the orientation direction with increasing draw ratio.

II. Theory

Relation between Relaxation Strength and Order Parameter. Liquid crystalline polymers are by nature highly anisotropic materials. For the interpretation of dielectric data of liquid crystalline polymers, it is important to consider the molecular orientation with respect to the applied electric field. Several authors have published experimental and theoretical results on side-chain LCPs. The papers on main chain LCPs considering molecular alignment are however limited.

For side-chain LCPs it is common to account for orientation phenomena, but for main-chain LCPs not many data are available. An interesting approach has been suggested by Attard et al.⁵ They assumed that the polymer is built up of domains and derived expressions for the dielectric permittivity as a function of the order parameter, under the assumption that the orientation is uniaxial.

$$\epsilon_z = \epsilon_{\parallel} (1 + 2S_d)/3 + \epsilon_{\perp} 2(1 - S_d)/3 \tag{1}$$

$$\epsilon_x = \epsilon_y = \epsilon_{\parallel} (1 - S_{\rm d})/3 + \epsilon_{\perp} (2 + S_{\rm d})/3$$
 (2)

where ϵ_x , ϵ_y and ϵ_z are the dielectric permittivities in the x, y and z directions. The z axis is parallel to and

the x and y axis are perpendicular to the draw direction of the samples (Figure 1). ϵ_{\parallel} and ϵ_{\perp} are the permittivities parallel to and perpendicular to the director of the domains. The order parameter of the director S_d is related to the angle θ between the director and the z-axis by Hermans's relation $S_d = (3\langle\cos^2\theta\rangle - 1)/2$.

Equations for the low frequency or static permittivities $\epsilon_{\parallel}{}^s$ and $\epsilon_{\perp}{}^s$ of the domains were derived by Maier et al.⁶ as a function of the local order parameter inside the domains.

$$\epsilon_{\parallel}^{\rm s} = \epsilon_{\parallel}^{\infty} + \frac{G_{\parallel}\mu^2}{3kT} [1 - S_{\parallel}\langle 1 - 3\cos^2\Psi\rangle] \tag{3}$$

$$\epsilon_{\perp}^{\rm s} = \epsilon_{\perp}^{\infty} + \frac{G_{\perp}\mu^2}{3kT} [1 + S_{\parallel}\langle 1 - 3\cos^2\Psi \rangle/2] \qquad (4)$$

in which μ is the permanent dipole moment, Ψ the angle between each dipolar vector and the director of the domains. $S_{\rm l}$ the local order parameter inside the domains, and $G_{\rm ll}$ and G_{\perp} combine the number of dipoles, the cavity field factor and the reaction field factor in the parallel and perpendicular direction, respectively. Maier et al. derived these equations neglecting the influence of the dielectric anisotropy on both the cavity and the reaction field, thus using G instead of $G_{\rm ll}$ and G_{\perp} . Furthermore, since we are dealing with a semi-crystalline polymer, the effect of the crystallinity is also incorporated in the parameter G. Combination of eqs 1-4 leads to the following equations for the three dielectric permittivities:

$$\epsilon_{z}^{s} = \epsilon_{||}^{\infty} \frac{1 + 2S_{d}}{3} + \epsilon_{\perp}^{\infty} \frac{2(1 - S_{d})}{3} + \frac{G_{z}\mu^{2}}{3kT} [1 - S_{d}S_{l}\langle 1 - 3\cos^{2}\Psi\rangle]$$
 (5)

$$\epsilon_{x}^{s} = \epsilon_{y}^{s} = \epsilon_{\parallel}^{\frac{1 - S_{d}}{3}} + \epsilon_{\perp}^{\frac{2 + S_{d}}{3}} + \frac{G_{xy}\mu^{2}}{3kT} \left[1 + \frac{S_{d}S_{l}}{2} \langle 1 - 3\cos^{2}\Psi \rangle \right]$$
(6)

The parameters G_z and G_{xy} incorporate the cavity and reaction field in the direction of respectively the z and

Figure 1. Coordinate system for calculating the orientation-dependent relaxation strength of extruded samples. The draw direction (and thus molecular orientation) is in the *z* direction. Note that electrical measurements are usually carried out with the electric field in the *x*-direction

x or y axis. The parts on the far right in eqs 5 and 6 are due to the dipole contributions. Now we can calculate the dipole relaxation strengths in the x and z direction: $\Delta \epsilon = \epsilon^s - \epsilon^\infty$.

$$\Delta \epsilon_z = \frac{G_x \mu_z^2}{kT} = \frac{G_x \mu^2}{3kT} [1 - S_d S_l \langle 1 - 3 \cos^2 \Psi \rangle] \quad (7)$$

$$\Delta \epsilon_{x} = \frac{G_{xy} \mu_{xy}^{2}}{kT} = \frac{G_{xy} \mu^{2}}{3kT} \left[1 + \frac{S_{d} S_{l}}{2} \langle 1 - 3 \cos^{2} \Psi \rangle \right]$$
 (8)

The overall order parameter (S) can be represented by the product of S_d and S_l . In anisotropic dielectrics the values of G_z and G_{xy} are not the same. We can approximate the maximum ratio of G_z and G_{xy} from eqs 7 and 8 and the Onsager equation:

$$\Delta \epsilon = \epsilon^{s} - \epsilon^{\infty} = \frac{\epsilon^{s} (\epsilon^{\infty} + 2)^{2}}{2\epsilon^{s} + \epsilon^{\infty}} \frac{N \mu_{k}^{2}}{9\epsilon_{0} kT}$$
 (9)

 $\mu_{\it k}$ is the dipole component along the z or xy axis: $\mu_{\it z}$ or $\mu_{\it xy}$

$$\left[\frac{G_z}{G_{xy}}\right] = \frac{\epsilon_x^s (\epsilon_z^\infty + 2)^2 (2\epsilon_x^s + \epsilon_x^\infty)}{\epsilon_x^s (\epsilon_x^\infty + 2)^2 (2\epsilon_z^s + \epsilon_z^\infty)} \tag{10}$$

For a more comprehensive calculation of the xy and z components of the permittivity, we refer to De Jeu. ²² For isotropic dielectrics the ratio of G_z/G_{xy} is equal to 1.

Application of Orientation Measurements to Main Chain Liquid Crystalline Polymers. The relations between the relaxation strengths and order parameters given in the previous section were derived for side chain LCPs. For these LCPs the orientation of the domains is easily changed in various directions, so the relaxation strengths in all directions are significant. However, for main chain LCPs the orientation can only be modified by an increase or decrease in the draw ratio of the molten polymer. So, the domains are always planarly oriented in the z direction. Therefore, the relaxation strength in the z direction gives more information about the order parameter. For example, changing the order parameter from 0.8 to 0.85 results in a 2% difference in $\Delta \epsilon_x$, but a 25% difference in $\Delta \epsilon_z$. Admittedly, dielectric measurements are seldom carried out in the z direction. Yet, it is very important to perform dielectric experiments in the z direction of the sample. We have achieved this by preparing a special sample wherein the draw direction runs parallel to the electric field (cf. Figure 2). Another option would have been the use of comb electrodes.

The equation for calculating the order parameter from the measured relaxation strengths perpendicular and

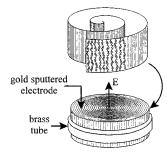


Figure 2. Schematic representation of the special sample P15, which is prepared in such a way that the draw direction and therefore the molecular orientation line up parallel to the electric field between the measuring electrodes.

parallel to the orientation can be found by combining eqs 7 and 8.

$$\frac{\Delta \epsilon_z}{\Delta \epsilon_x} = \frac{G_z}{G_{xy}} \frac{2 - 2S\langle 1 - 3\cos^2 \Psi \rangle}{2 + S\langle 1 - 3\cos^2 \Psi \rangle}$$
(11)

We should point out that Wissbrun et al. ⁷ gave another explanation for the small influence of the orientation on the properties in the *x*-direction. LCPs already consist of small domains, having a high degree of local order, even in the absence of a macroscopic orientation. Macroscopic stretching only results in a change in orientation direction and not in an enhancement of the local order parameter. Since the electrical techniques only focus on the microscopic alignment, the differences between drawn and undrawn samples can be expected to be minimal.

III. Experiments

Materials and Sample Preparation. The polymer used was a random liquid crystalline copolyesteramide composed of three monomer units, viz. 60% 2,6-hydroxynaphthoic acid (HNA), 20% *p*-aminophenol (AP) and 20% terephthalic acid (TA) (see ref 1, Figure 6). This polymer is commercially available from Hoechst-Celanese as Vectra B950. The polymer was dried for 4 h at 180 °C in a nitrogen atmosphere to remove residual water and kept under vacuum at 60 °C. From the dry polymer three kinds of samples were prepared.

Samples for the dielectric analysis were made by compression molding of polymer granules at 300 °C and quenching the films afterward. The thickness of the samples was approximately 100 μ m (C samples).

A second type of sample was made by film extrusion using a Collin laboratory extruder (diameter = 20 mm; length/diameter = 20), to analyze the influence of the orientation of the sample on the dielectric response. The films were drawn at the extrusion temperature (300 °C) until a certain draw ratio was reached. The resulting films varied in thickness between 10 and 200 μm . Films with various draw ratios could be prepared in this way (E samples).

The third type consisted of a stack of extruded films having a draw ratio of about 15 rolled together tightly and put inside a brass tube. The orientation of the films was parallel to the tube. From this tube, slices were sawn. Electrodes were applied on the top and bottom of the sample. This special preparation resulted in samples of about 4 mm thick having the draw direction (z axis) virtually **parallel** to the electric field (Figure 2). The overall density of these samples was about 1.29 g/cm³ instead of the 1.36 g/cm³ for the extruded films. The results were corrected for this difference (P samples). Table 1 summarizes the samples made using the different techniques and treatments.

It turned to be impossible to make isotropic samples, because compression molding and extrusion always involve flow of the liquid crystalline polymer and therefore induce a

Table 1. Samples Used in the Dielectric Analysis

name		draw ratio	thickness (µm)	comments
E15	extruded	15	50	field \perp orientation
E20	extruded	20	17	field \perp orientation
$P15^a$	extruded	15	3850	field orientation
C1	compression	1	90 - 130	quenched after
	molded			molding

^a Sample P15 was prepared according to Figure 2.

planar orientation. Even melting of the polymer did not produce isotropic samples.

DSC Experiments. The glass transition, degrees of crystallinity, and melting temperatures of the samples were determined using a Perkin-Elmer differential scanning calorimeter (DSC 7).

Dielectric Measurements. The dielectric measurements were performed on two-sided gold-sputtered films (3 cm in diameter for the E and C samples; 2 cm in diameter for the P type sample). The sputtered samples were put between two thick brass electrodes inside a sample holder. This sample holder was then placed inside a Novocontrol temperature control unit, which regulated the temperature by means of a heated nitrogen gas flow. A Pt100 (a temperature-dependent resistor) implemented in one of the electrodes measured the temperature and ensured a temperature gradient as small as

The dielectric experiments were conducted using a Hewlett-Packard 4284A precision LCR-meter for frequencies between 1 and 500 kHz and a combination of a Schlumberger SI 1260 impedance gain-phase analyzer and a dielectric electrometer (developed by TNO) for frequencies between 0.5 and 1000 Hz.

Dielectric measurements were done at constant temperature by taking frequency scans (0.5 Hz to 500 kHz) every 5 $^{\circ}\text{C}$ between -100 and $+300\,^{\circ}\text{C}$. The upper temperature was just above the melting point of the polymer (which is 284°C, determined from DSC measurements at 10 °C/min). The applied AC voltage was 1 V.

IV. Results and Discussion

Influence of Main Chain Alignment on the Relaxation Strength. The angle between the direction of the electric field and the orientation of the sample has a large influence on the dielectric response of liquid crystalline polymers. We have evaluated this influence by performing measurements on two types of samples. The draw ratio was equal for both samples (=15), but the direction of the electric field was quite different: one perpendicular to the main chain orientation (E15) and one more or less parallel to the orientation (P15). The latter was achieved by using a specially prepared sample (cf. Figure 2). The temperature loss data for both samples at 125 Hz is shown in Figure 3. The dielectric loss curves were fitted using the parameters described in the previous paper¹ (Table 1). We could fit the curve of sample P15 using the same parameters as E15 and with only the relaxation strengths as variable. The fitted values of $\Delta\epsilon$ for sample P15 are given in Table 2. It is obvious that for all the relaxations the values of $\Delta \epsilon$ are much smaller for the parallel sample (P15) than for the perpendicular sample (E15). This is caused by the anisotropy of the polymer after extrusion. The main chain alignment clearly disfavors the orientation of the polar groups in the parallel direction.

From the data of the parallel and perpendicular sample, we can calculate the order parameter using eqs 10 and 11. It is then necessary to know the angle between the rotating dipole and the director and the value of $G_{\mathbb{Z}}/G_{xy}$. The β relaxation is the most suitable

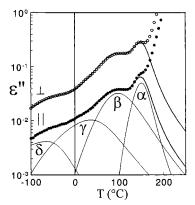


Figure 3. Dielectric loss at 125 Hz: (O) electric field perpendicular to the draw direction (E15); (●) electric field parallel to the draw direction (P15).

Table 2. Relaxation Strengths of the Four Relaxations of a Parallel (P15) and Perpendicular (E15) Oriented Sample Having a Draw Ratio of 15

	α	β	γ	δ
$\Delta \epsilon_{x}(E15)$	2.07	1.11	0.34	0.26
$\Delta \epsilon_z (P15)$	0.47	0.23	0.10	0.07

for this evaluation. The most favorable conformation of the HNA group is shown in Figure 6 of the previous paper, in which the two rotating bonds are in line. If we assume that the rotating bonds are parallel to the chain direction, this results in an angle ψ between the dipole moment and the director of about 90°. This causes the $\cos \psi$ terms to disappear from the equation. The maximum value of $G_{\mathbb{Z}}/G_{xy}$ is 1.74, which is calculated using eq 10 and $\epsilon_z^{\rm s} = 6.43$, $\epsilon_z^{\infty} = 6.20$, $\epsilon_x^{\rm s} = 5.14$, and $\epsilon_{\scriptscriptstyle X}^{\scriptscriptstyle \infty}=$ 4.03 for the β relaxation.

Using the data from Table 2, the ratio $\Delta \epsilon_z / \Delta \epsilon_x$ (= $\Delta \epsilon_{P15}/\Delta \epsilon_{E15}$) calculated for the β relaxation is 0.21. Inserting this in eq 11 and taking $G_z/G_{xy} = 1.74$ and Ψ = 90°, the order parameter of the extruded sample (S) has a value of 0.83 (S = 0.72 if $G_z = G_{xy}$ as was assumed by Maier et al.⁶ in their derivation). Choy et al.² used X-ray diffraction to obtain an order parameter of 0.88 for draw ratios above 5. A few possible explanations for this difference could be found. The first one assumes an imperfect sample preparation. It turned out that it was not possible to prepare P type samples having the orientation perfectly aligned in the direction of the electric field. This introduces an error in the order parameter.

A second explanation is that for this random copolyesteramide the angle Ψ is not 90°. If this would be the only reason for the difference between the calculated and theoretical order parameter, the angle Ψ would have a value of 82° for the β relaxation. The angles for the γ and δ relaxation would be even smaller. This means that the rotating groups of the two low temperature relaxations are less oriented in the direction of the main chain. This is quite likely since these groups disturb the chain packing of the HNA groups.

A third reason for the deviation might be that the actual order parameter of the sample is smaller than 0.88. This is in fact a high value for a liquid crystalline polymer. For instance, Butzbach et al.⁸ calculated an overall order parameter of 0.81 for a HNA-HBA copolymer. This is in better agreement with our results. The difference between the measurements and the calculations is probably a combination of the three reasons given.

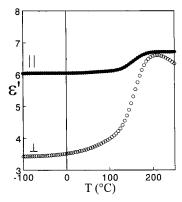


Figure 4. Dielectric permittivity at 125 kHz: (○) electric field perpendicular to the draw direction (E15); (●) electric field parallel to the draw direction (P15).

High-Frequency Limit of the Dielectric Constant and Refractive Indices. Besides the decrease in relaxation strength, due to the less effective orientation of the polar groups, when the electric field changes from perpendicular to parallel, the dielectric permittivity at very high frequencies and/or very low temperatures (ϵ^{∞}) also changes with the molecular orientation. Figure 4 shows the curves of the real permittivity at 125 kHz for the two samples E15 and P15.

Two things emerge from this figure. The first was already mentioned in the previous section. This is the marked difference in the dipolar relaxation strengths between the two samples. The second is the large difference in the two values of ϵ^{∞} . From this graph we obtained a value for ϵ^{∞} (E15) of 3.43 and for ϵ^{∞} (P15) of 6.02. Since ϵ^{∞} is merely caused by electronic and atomic polarization, this induced polarization is much higher when the electric field is parallel to the polymer chains. This is just the opposite of the dipole polarization, which is higher in the x direction. Maxwell's identity relates this induced polarization at high frequencies, ϵ^{∞} , to the refractive index, n:

$$\epsilon^{\infty} = n^2 \tag{12}$$

A noteworthy application of the dielectric high-frequency data is the calculation of the birefringence. The calculated values for the refractive indices are $n_{\perp}(E15)$ = 1.85 and $n_{\parallel}(P15)$ = 2.45. The birefringence obtained from these values is $\Delta n = n_{\parallel} - n_{\perp} = 0.6$. Direct birefringence measurements have been performed as well on the extruded samples using a method described by Beekmans.⁹ The measured birefringence for a sample having a draw ratio of 15 was about 0.55. The same value for the birefringence was derived using Brewster's angle (tan $\Theta = n$, in which Θ is the angle of total extinction).¹⁰ These optical values compare well with the value of Δn from the dielectric measurements.

It is not easy to obtain the values for the two refractive indices of liquid crystalline polymers separately. Hamza et al. 11 have done some work on the optical anisotropy of poly(p-phenylene terephthalamide) fibers. They found values for n_{\parallel} of about 2.3 and for n_{\perp} of about 1.6, which resulted in a birefringence of 0.7. This is comparable with our results, although the respective refractive indices are a little higher in our measurements.

Influence of Orientation, Crystallinity, and Annealing on the Dielectric Properties. In the previous sections we discussed the possible influence of

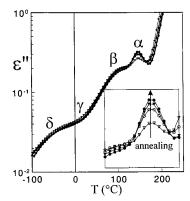


Figure 5. Effect of annealing on the dielectric loss vs temperature at 500 Hz. Extruded samples (E20): (\bullet) annealed; (\bigcirc) unannealed. Compression molded samples (C1): (\blacktriangledown) annealed; (\triangledown) unannealed. The insert shows an enlargement of the α relaxation.

orientation on the dielectric properties. We did not consider the crystallinity of the samples. This was permitted since the permittivity at high frequencies hardly depends on the crystallinity, under the presumption that the density does not change. From experimental data on the copolyesteramide and other liquid crystalline polymers published in the literature, ¹² it can be concluded that the density indeed hardly depends on the crystallinity.

The measurements with the electric field perpendicular (E15) and parallel (P15) to the draw direction were performed on samples having the same crystallinity. So the crystallinity did not have an influence on the outcome of the comparison between these measurements.

Studying the influence of different draw ratios after extrusion on the dielectric response, we should not ignore the crystallinity any longer. The way in which the various samples are produced has a significant influence on the crystallinity. The orientation itself can have a positive influence on the crystallinity, since the molecules are already more aligned. On the other hand, under similar extrusion conditions, an increased draw ratio results in more oriented, thinner samples. Thinner samples cool more rapidly and may show a lower crystallinity. It was shown however, using DSC that the melt enthalpy increases with increasing draw ratio. So, we can conclude that the orientation of the samples has a larger influence than the cooling rate.

To determine the genuine effect of crystallinity, we have annealed both a compression molded sample (C1) and an extruded sample (E20). We have performed dielectric measurements before and after annealing for 90 min at 260 °C in a nitrogen atmosphere. The curves of the dielectric loss at 500 Hz vs temperature are shown in Figure 5. The first striking fact is the small influence of the orientation. Despite the difference in draw ratio (1 vs 20) the curves of the unannealed samples show only a very small difference below 100 °C. In fact, the dielectric loss of the sample (C1) is a little higher than that of the highly oriented extruded sample (E20).

The dielectric loss of a higher oriented sample should be higher than the loss of a less oriented sample, because of the better orientation of the dipoles in the electric field. The discrepancy between measurements and theory can be explained by the orientation induced during compression molding of the samples. The samples were produced by compression molding granules of a

few millimeters into a mold of about 100 μ m thick. The flow resulting from this procedure provokes a planar orientation of the domains radial to the normal axis of the film. This causes the film to be macroscopically isotropic in the y and z direction (this was verified using X-ray diffraction), but not in the *x* direction. The main chain directors in all domains are likely to be oriented parallel to the plane of the film. This results in the same dielectric response as the extruded samples, because dielectric spectroscopy cannot detect any difference in orientation perpendicular to the electric field. As already mentioned in the theory section, dielectric measurements, which normally take place perpendicular to the orientation are therefore not suitable for the determination of in-plane orientations. This was verified by measurements on samples having different draw ratios (not shown here). There was no significant change in the dielectric response as function of the draw ratio. The best samples for research on oriented films should therefore have their draw direction parallel to the electric field. This prompted us to prepare the special sample P15, using the approach illustrated in Figure 2.

The experiments on samples E15 and P15 have shown clearly that changing the orientation from perpendicular to parallel to the electric field results in a decrease of all the relaxations strengths. It is therefore plausible that the observed increase in the relaxation strength of the α relaxation and the decrease of the other relaxations upon annealing of samples E20 and C1 is caused by the change in crystallinity of the samples. Annealing of the samples produces an increase of the degree of crystallinity.^{8,13} From Figure 5 we can conclude that the compression molded sample is less crystalline, but that its crystallinity increases during annealing. The same occurs for the oriented sample E20, although its crystallinity is already higher than that of the compression molded sample before anneal-

A decrease in the relaxation strengths of the β , γ , and δ relaxations upon annealing can be expected, because of the decreased mobility of the polymer chains. The increase of the α peak during postcrystallization is somewhat remarkable, since crystallization of thermoplastic polymers usually gives rise to a decrease of the α relaxation. This is explained by the incorporation of the main chains in the crystals, which reduces their mobility.

This discrepancy in relaxation strength of the α relaxation between conventional thermoplastic polymers and main chain liquid crystalline polymers was observed earlier in the literature. Several authors have done research on the effect of annealing. Again, most of these papers are based on HNA-HBA copolymers. Troughton et al.¹⁴ and Sarlin et al.¹⁵ performed dynamic mechanical experiments and found that the intensity of the α relaxation peak showed a slight increase upon annealing, whereas the intensity of the β relaxation did not change. Troughton did not give any explanation for this phenomenon, but Sarlin explained it by the introduction of large scale movements, which can create long chain sequences that are more mobile than quenched

It is also known from the literature that the crystallization of the HNA-HBA copolymers can be described by a fast process which is characterized as solidification into a pseudohexagonal structure and a slow process in

which an orthorhombic structure is formed (Biswas¹⁶ and Cheng^{13,17}). In the hexagonal structure there is rotational disorder, which results in a certain rotational freedom of the chains. The hexagonal packing changes to the orthorhombic structure as a result of annealing above 230 °C (Kaito et al.18).

The effect of annealing of an LCP composed of HBA, TA, hydroxybiphenol, and isophthalic acid on the dielectric properties is small according to Hong et al.¹⁹ Closer examination of their results, however, shows a small increase in the relaxation strength upon annealing. The same results were found by Kalika et al.²⁰ and Bechtoldt et al.²¹ They explained the minimal influence of the crystallinity on the dielectric properties, by the appearance of a relaxation process having the same relaxation strength in both the quenched nematic (hexagonal) and the three-dimensionally ordered (orthorhombic) state.

From these references, we can deduce an explanation for our dielectric results. The mobilities of the chains are not dramatically different in the different crystal structures of the polymer. During annealing (and thus crystallization), noncrystallizable material is rejected from the crystals, which results in a higher mobile "amorphous" fraction and therefore in a higher relaxation strength of the α relaxation. Since the β , γ , and δ relaxations correspond to local motions of individual chain moieties, the decrease in relaxation strength upon crystallization is caused by the difference in mobility in the crystal structures. However, this turns out to be a very small effect.

V. Conclusions

The influence of the orientation and crystallinity of the copolyesteramide Vectra B950 on the dielectric properties was studied. A change in draw ratio of the extruded samples did not have a significant impact on the dielectric properties, whereas the change of the electric field from perpendicular to parallel to the draw direction clearly did. From the difference in the dielectric constant at high frequencies of the two sample orientations, we could predict the birefringence of the oriented anisotropic sample, and we found that it corresponds well to the optically measured value.

Annealing of compression-molded and extruded samples resulted in an increased crystallinity. The secondary relaxations showed the expected small decrease, whereas, in contrast to conventional thermoplastic polymers, the α relaxation peak of the copolyesteramide increased upon annealing.

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