

# Thermally Stimulated Depolarization Current Studies on Strain-Induced Relaxations in Polymers

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## Synopsis

Thermally stimulated depolarization current (TSD) method has been used to study the molecular relaxation from room temperature up to the glass-transition temperature for three plastically deformed polymers. A well-defined distinct  $\alpha'$  peak has been observed in the vicinity of 70°C for polycarbonate, polysulfone, as well as poly(ethylene terephthalate), that had been annealed above  $T_g$  and subsequently cold-rolled. Since this relaxation is not observed after the initial measurements, it is a nonequilibrium relaxation. In the case of polycarbonate, the nonreversible  $\alpha'$  process had an activation energy ranging from 1.22 to 1.75 eV and an intensity proportional to the degree of deformation resulting from cold-rolling. The spontaneous polarization in the rolled material was believed to originate from the initial anisotropy which was subsequently enhanced by the rolling process. Density measurements, as well as the birefringence observation, have been performed on the rolled specimens. All the studies led to the conclusion that the molecular motion responsible for this  $\alpha'$  peak was the disorientation of local chain segments from their aligned conformation frozen in during the cold-work.

## INTRODUCTION

Numerous studies of relaxation transitions in polycarbonate have reported the existence of a nonequilibrium shoulder on the dissipation curve over the intermediate temperature range of 50 to 100°C for low-frequency measurements. Since this intermediate relaxation, which is of interest here, relaxes out during the heating stage of the initial measurements and is absent in subsequent measurements, it has been designated a nonequilibrium relaxation. The intermediate temperature range designation stems from its location below the  $\alpha$  relaxation (glass transition) and above the local mode  $\beta$  transition. Details of the occurrence of the intermediate temperature relaxation process in polycarbonate have been summarized in Table I.<sup>1-23</sup> Because of the confusion existing in the literature on the designation of the relaxation transitions, they have been tabulated as peaks 1, 2, and 3. Where peak 1 designates the primary relaxation process at  $T_g$  and peak 3 the local mode transition which for frequencies of less than 70 Hz occurs at a temperature of about -100°C. The intermediate process, with several exceptions, generally manifests itself in the shape of a small shoulder in the 50 to 100°C range. There is some uncertainty as to the origin of the intermediate relaxation in that it has been observed in both "untreated" and mechanically stretched films and also that heat treatments below  $T_g$  tend to broaden the relaxation.

As indicated in Table I, there exists considerable discrepancies among the designations assigned the peaks by various authors other than the primary  $\alpha$  transition. This lack of uniqueness in peak designation is a source of some

TABLE I  
Summary of Relaxation Studies on Polycarbonate

Reference	Technique <sup>a</sup>	Frequency (Hz)	Peak temperature (°C) and peak designation (if any)			Remarks
			1	2	3	
1	M	0.5-1.2	150		-110	
2	M	1	150		-100 with a shoulder at -10	
3	M	867	(data not available in this region)		-53( $\gamma$ )	flexural vibrations
4	M	1	150 ( $T_g$ )		<100	
5	M	1 K	140-160 ( $T_g$ )	80	ca. -90	stretch-oriented solvent-cast film
6	M		160 ( $\alpha$ )	80 ( $\beta$ )	-110 ( $\gamma$ )	$\beta$ depressed and sharpened when specimen heat-treated at 130°C
7	M	70	150	100-120	-100	compression-moulded samples in forms of tuning forks
8	M	1	(incomplete data)	60-80	(incomplete data)	for untreated and drawn films
9	M	110	$\alpha$	100 ( $\beta$ )	-60 ( $\gamma$ )	as-received Lexan sheet
10	D	1 K	175	80	-80	stretched film
11	D	10 <sup>-4</sup> -10 <sup>5</sup>	110-164 ( $\alpha$ )	room temperature-60( $\alpha'$ )	-70--80( $\beta$ )	drawn film

12	D	10	150 ( $\alpha$ )	>80 (intermediate)	-100 ( $\beta$ )	intermediate process less prominent in annealed (120°C) sample than in the as-moulded sample
13	D	3 K	170 ( $\alpha$ )	120( $\beta$ ), 65( $\beta'$ )	(not available)	annealed and drawn film
14	M		ca. 150	a shoulder at 80	-100	
15	M	1	ca. 150 ( $\alpha$ )	a shoulder 60-80	-100	injection-moulded film, shoulder depressed on annealing at 120°C
16	M	1	ca. 150	ca. 70	-100	compression-moulded sample
17	D	1 K	(data not available in this region)		-71.5 ( $\beta$ )	moulded sample
	M	1	150 ( $\alpha$ )	a shoulder at 80	-100 (4 $\beta$ )	containing 0.37% H <sub>2</sub> O
18	M	1	ca. 150 ( $\alpha$ )	60-100 (intermediate)	<-80 ( $\beta$ )	intermediate process observable in the extruded sheet
19	M	0.5-1.24	150 ( $\alpha$ )		-108 ( $\gamma$ )	and the annealed (120°C) film
20	D	100	(not reported)	141.8( $\beta$ ), 39( $\gamma$ ) 155 ( $\alpha'$ , 100 kHz)	-114.3 ( $\delta$ )	extruded sheet
21	T		170	151,55	-120	unoriented sample
22	T		ca. 160	ca. 70		cold-drawn sample
23	N		197 ( $\alpha$ )	12( $\beta$ ), -53( $\gamma$ )	-117 ( $\delta$ )	

<sup>a</sup> M denotes dynamic mechanical method; D denotes dielectric method; T denotes thermomechanical method; N is the NMR method.

confusion in the literature. We have adapted the procedure of designating the peaks according to their appearance on the temperature scale in TSD measurements. This means that the primary transition at ca. 150°C is designated the  $\alpha$  relaxation and the second equilibrium relaxation, which occurs between -23 and -173°C, is the  $\beta$  relaxation. More recent TSD cryogenic measurements revealed that the  $\beta$  relaxation has a broader temperature range of -23 to -228°C and a  $\gamma$  relaxation centered at about -256°C (17°K).<sup>24</sup> Since the intermediate nonequilibrium relaxation was observed after both the  $\alpha$  and  $\beta$  transitions were found, it has been designated the  $\alpha'$  transition. While the TSD  $\alpha'$  transition may be the same as some of the other observed intermediate transitions, in this work the designation applies specifically to the transition that is associated with plastically deformed state due to cold-rolling.

Aside from its frequent occurrence, the intermediate relaxation may also play an important role in the performance of the finished product. This is because the temperature range of this relaxation is in accord with the end-use temperature range of polycarbonate products. As a result, property characteristics may be modified during its service life due to the underlying molecular relaxation. Nevertheless, up to the present, little is known about the origin of the intermediate relaxation other than that somehow it is associated with residual stress frozen in the polymer glass.

In this paper, we report the appearance of the  $\alpha'$  relaxation peak in three uniaxially cold-rolled phenylene-containing polymers: polycarbonate, polysulfone, and poly(ethylene terephthalate) via thermally stimulated depolarization current method (TSD) under *zero bias voltage*. Results of a systematic study in the case of polycarbonate, in which the  $\alpha'$  process was initially observed in a previous TSD study in this laboratory,<sup>25</sup> are presented to elucidate its origin. In addition, qualitative observation of the change of birefringence, as well as the density measurements, are also utilized to complement our TSD study.

## EXPERIMENTAL

LEXAN (General Electric) polycarbonate sheet 0.015 in. thick was used throughout. Viscosity measurement determined  $\bar{M}_v$  as 30,000. No change in this value was observed as a result of thermal and mechanical treatments employed in this work. The amorphous commercial sheets were first annealed in a vacuum oven at 160°C (10°C above  $T_g$ ) to eliminate the existing residual stresses as revealed by crossed-polaroids. The annealed sheets were then uniaxially cold-rolled to different degrees of deformation at room temperature. The cold-rolled samples were stored in a vacuum desiccator prior to measurements of TSD, density and birefringence. Infrared spectra of the cold-rolled PC (measured on a Perkin-Elmer 180 spectrometer) indicated no trace of water content at 3620  $\text{cm}^{-1}$ .<sup>26</sup>

Test specimens of the cold-rolled PC for TSD measurements were cut in the form of a flat disk of 1 1/8 in. diameter and 3/4 in. Au electrodes were vacuum evaporated onto both sides. Details of the TSD set-up in this laboratory have been described elsewhere.<sup>27</sup> Measurements proceeded as follows: the cold-rolled specimen was placed in the capacitor-type sample holder under short-circuit condition for at least 2 h. Heat was then applied to warm up the specimen from room temperature to about  $T_g$  at constant rate, 3°/min, and the released

current was registered at the same time. Note that during this process, *no* external poling field was applied at any temperature, in contrast to the conventional TSD measurement; orientation of the dipoles was achieved by cold-rolling. TSD theory gives the following expression for the released current density

$$J = \frac{P_0}{\tau_0} \exp\left(-\frac{E}{kT} - \int_{T_0}^T \frac{dT}{b\tau}\right) \quad (1)$$

where  $P_0$  is the initial polarization, in the present work, induced by the cold-rolling,  $b$  is the heating rate, and  $\tau$  is the relaxation time given by

$$\tau = \tau_0 \exp(E/kT) \quad (2)$$

At the low-temperature tail, we have

$$J = (P_0/\tau_0) \exp(-E/kT) \quad (3)$$

Thus,

$$\ln J = \ln \frac{P_0}{\tau_0} - \frac{E}{kT} \quad (4)$$

Equations (3) and (4) contain the substance underlying the partial heating method<sup>28</sup> which utilizes the initial rising part of the current during each heating cycle. The activation energy  $E$  is determined from the slope of a semi-logarithm plot of  $\ln J$  vs.  $1/T$ .

Temperature-dependence birefringence of the rolled specimen was measured on a Leitz transmittal light microscope in conjunction with a Mettler FP 52 hot stage. The light source was filtered with a green interference filter. Specimens were placed on the stage with the rolling direction at an angle of 45° to the crossed polarizer and analyzer. Light intensity coming out of the analyzer was recorded continuously via a photometer as a function of temperature during the subsequent linear heating. The heating rate was set at 3°/min, the same as that in TSD measurements. Densities of rolled specimens were determined using a SGA density column of  $\text{ZnCl}_2 + \text{H}_2\text{O}$  maintained at 20°C.

In addition to polycarbonate, TSD measurements were also performed on two commercial sheets of polysulfone and poly(ethylene terephthalate) following their annealing (above the respective  $T_g$ ) and cold-rolling.

## RESULTS

### $\alpha'$ Relaxation

Typical  $\alpha'$  peaks in the 60–80°C temperature range for the three as cold-rolled polymers are shown in Figure 1. Here, the thickness reductions due to the uniaxial rolling are 32%, 32%, and 20% for carbonate, polysulfone, and poly(ethylene terephthalate), respectively. It is seen that the three temperatures of peak maxima are in an order parallel to the glass transition temperature:  $T_m$  (PET) <  $T_m$  (PC) <  $T_m$  (PS). It is also to be noted in Figure 1 that on a second TSD measurement of the same specimens, the  $\alpha'$  peaks were absent, indicating the nonreversible nature of this process. In the following, further results will be concerned primarily with polycarbonate only. While the  $\alpha'$  peak temperature for polycarbonate occurs at  $(69 \pm 1)^\circ\text{C}$  and appears to be invariant to the degree

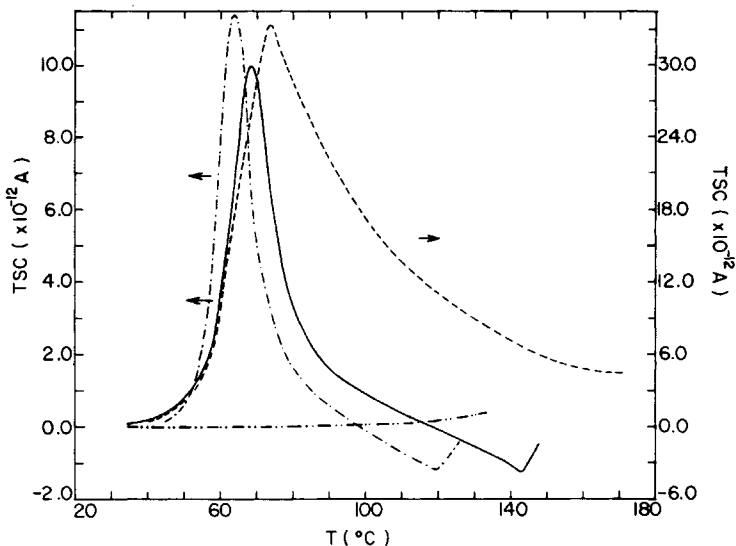


Fig. 1.  $\alpha'$  peaks in TSD measurements under zero bias voltage for three cold-rolled polymers: (—) polycarbonate; (---) poly(ethylene terephthalate); (-·-) polysulfone; and (···) polycarbonate, second run.

of deformation, the peak temperature does vary with the thickness of the specimen. The peak polarity is chosen as positive here, although it may reverse depending on the configuration of the specimen relative to the electrodes. A small peak, opposite in polarity, follows the  $\alpha'$  peak immediately and extends toward the glass transition temperature. Note that the thermogram in Figure 1 was obtained without any external voltage being applied; therefore, no perturbation is created in the specimen other than the initial deformation.

It has been found that the small peak near  $T_g$  is essentially constant in its magnitude, whereas  $\alpha'$  peak exhibits a strong, linear dependence on the degree of rolling. Figure 2 depicts this characteristic in a plot of the maximum current of  $\alpha'$  peak against the percentage reduction in thickness for two sets of rolled specimens preannealed at 160°C for 30 min and 2 h, respectively. The two straight lines pass through the data points quite well including the origin point where measurements are taken on as-annealed specimens subjected to no deformation. The influence of the preannealing treatment at 160°C is shown in Figure 3. Here, despite zero bias voltage, peaks corresponding to the glass transition are observed even in as-annealed specimens, although the  $\alpha'$  peak is absent in the as-annealed material.

In order to obtain the activation energy associated with the  $\alpha'$  process, the partial heating method was applied and the results are shown in Figure 4. It is seen that  $\alpha'$  peak is a distributed relaxation process with a spectrum of activation energy ranging from 1.22 to 1.75 eV.

### Birefringence Measurement

The transmitted light detected by the photometer displayed a constant intensity from room temperature up to ca. 60°C from which a fluctuation began

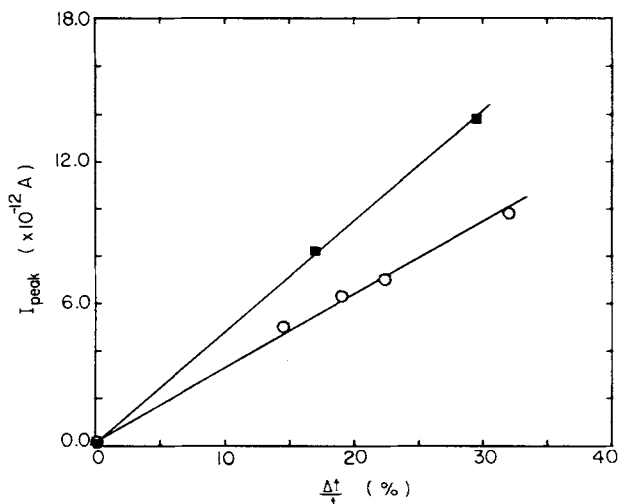


Fig. 2. Linear dependence of the  $\alpha'$  peak intensity on the degree of deformation for two sets of polycarbonate preannealed at 160°C for 30 min (■) and 2 hr (○), respectively.  $t$  is the initial thickness of the polymer and  $\Delta t$  is the thickness reduction resulting from cold-rolling.

to appear. When the rolled specimen was heated over  $T_g$ , the intensity dropped to zero, indicating the recovery of the isotropic state in the specimen.

### Density Measurement

Figure 5 depicts the variation of density of PC as a result of cold-rolling: an initial rapid increase followed by a plateau. The total change in density is less than 0.2%, although the thickness reduction amounts to 37%. In order to investigate the effect of  $\alpha'$  process on the density, one set of the rolled specimens were placed in an oven maintained at 70°C and annealed for times of 0.25–200 h. Their densities were essentially constant, as shown in Figure 6.

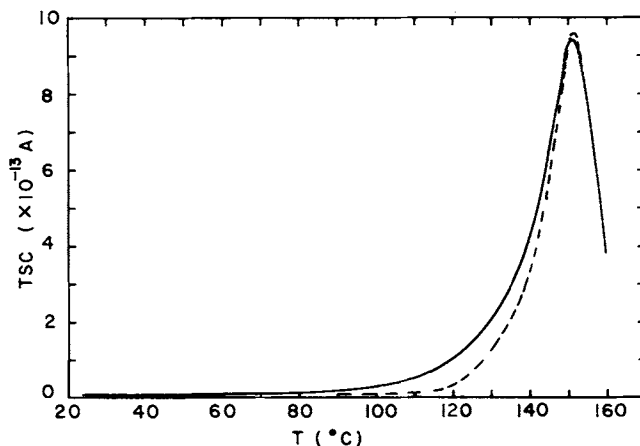


Fig. 3. Relaxation peaks at  $T_g$  in TSD measurements under zero bias voltage for two as-annealed polycarbonates: (—) 160°C, 30 min; (---) 160°C, 2 h.

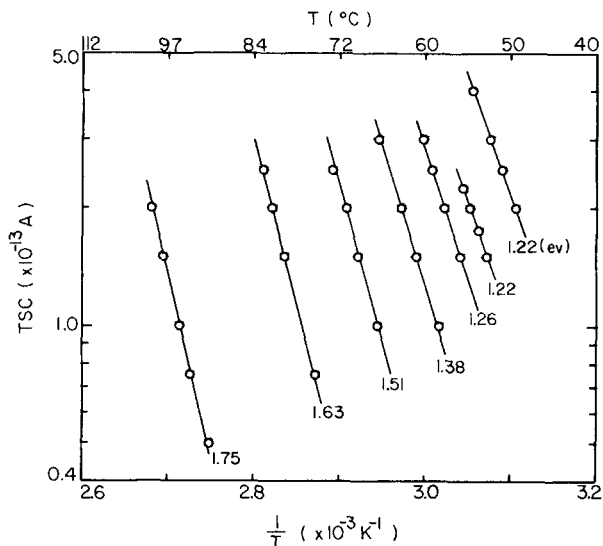


Fig. 4. Log (current) vs.  $1/T$  in the partial heating measurements for  $\alpha'$  peak. The activation energy determined from the slopes of the fitted lines is indicated. For convenience, temperatures are shown on the top scale.

## DISCUSSION

Figure 3 reveals that even in specimens annealed above  $T_g$  for 2 h, anisotropy associated with the prior processing of the PC is still in existence. Although it is too small to be visible in polaroids, a more sensitive method such as TSD can detect its presence in the relaxation at  $T_g$ . Sacher<sup>29</sup> also found in undeformed commercial PET a TSD peak at  $T_g$  under zero bias and attributed it to the orientation induced by high mechanical stresses during manufacturing process. In the present case, it appears that annealing the material above  $T_g$  cannot eliminate all the initial orientation, although 2 hr are more effective than 30 min

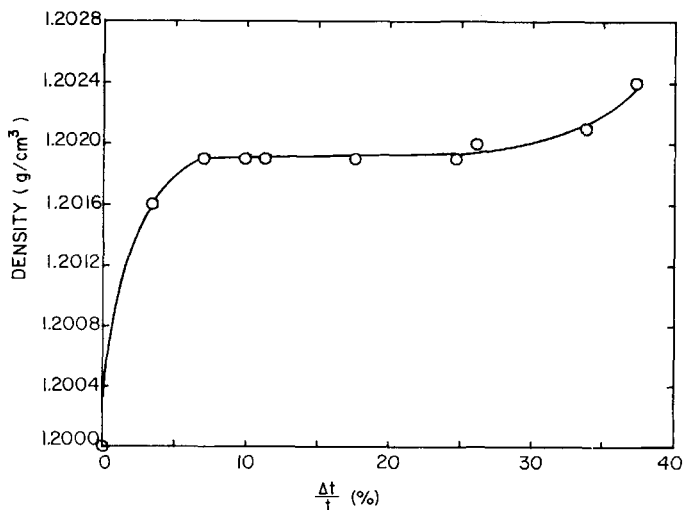


Fig. 5. Variation of density with respect to the degree of deformation for cold-rolled polycarbonate.



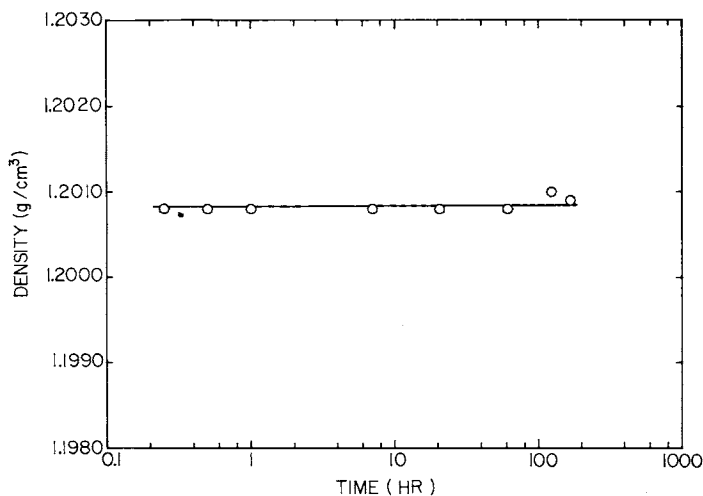


Fig. 6. Density variation as influenced by the annealing time at 70°C,  $\alpha'$  peak temperature.

as the area under the  $\alpha$  transition (Fig. 3) is smaller than that under the latter one.

A unique  $\alpha'$  relaxation process can be associated with the uniaxial rolling process for each of the three polymers studied (Fig. 1). The order of the peak temperatures are seemingly in accord with the degree of stiffness among the three polymer chains. The magnitude of this peak in the case of polycarbonate can be 10 times as large as that at  $T_g$  (Fig. 3), when both relaxations are observed via TSD without the use of an external poling field. Figure 2 reveals that for the same degree of deformation the higher the initial anisotropy, the higher the  $\alpha'$  peak. In addition, for the same initial anisotropy the  $\alpha'$  peak is higher, the larger the degree of deformation. These observations suggest that the  $\alpha'$  relaxation observed in the TSD measurements in the absence of bias voltage originate from the orientation stemming from the initial anisotropy and enhanced by the plastic deformation. The invariance of the peak temperature with respect to the degree of deformation illustrates that the same molecular mechanism is responsible for the various specimens deformed in this work.

The origin of the small, opposite in polarity, peak following the  $\alpha'$  peak, which manifests itself in both polycarbonate and poly(ethylene terephthalate), is not known at this stage.

Compared to a range of activation energy from 2.0 to 4.1 eV for glass transition,<sup>25</sup> the 1.22 to 1.75 eV values associated with  $\alpha'$  process (Fig. 4) imply that the latter involves only a small fraction of molecular motions occurring at  $T_g$ . Lunn and Yannas,<sup>30</sup> in their observation of molecular motion below  $T_g$  in the stretched polycarbonate film, reported an onset temperature of disorientational motion detectable to infrared dichroism measurements to be at 81°C, 10°C higher than the  $\alpha'$  peak temperature here. This further indicates that  $\alpha'$  process is, in fact, a localized motion which serves to disorient the aligned local constituent groups without causing any large scale motion in the chain backbone. The activation energy for  $\alpha'$  process obtained by Kato<sup>22</sup> in his thermomechanical measurements was 1.46 eV, in good agreement with the average value reported in Figure 4.

Further evidence for the localized nature of  $\alpha'$  process is provided by the isothermal behavior of density at 70°C, i.e.,  $\alpha'$  peak temperature. Polycarbonate has been found to manifest some increase in density when annealed at temperatures below  $T_g$ ,<sup>6,31</sup> especially when the annealing temperature is above 120°C. This is indicative of large scale motion taking place during annealing. Accordingly, the absence of density change in Figure 6 is in agreement with the above described mechanism associated with  $\alpha'$  relaxation process.

Furthermore, as stated before the birefringence observation for the rolled polycarbonate reveals a change in the light intensity beginning at the temperature region which is in coincidence with the onset of the intermediate process observed in the TSD measurements. Since the birefringence arises from the molecular alignment, the observation is thus in support of the idea that  $\alpha'$  process is associated with the initial localized disorientational motion of chain segments.

Finally, despite the considerable difference in the glass-transition temperatures for the three polymers studied, the strain-induced relaxation processes occurred in close proximity to one another as shown in Figure 1. This suggests that the constituent groups in the localized segmental motion of the relaxation are common to all three polymers, namely, the phenylene groups along the chain backbones.

## CONCLUSION

(i) A well-defined distinct  $\alpha'$  peak has been generated in the plastically deformed polycarbonate, polysulfone, and poly(ethylene terephthalate), making possible an independent study on its characteristic property.

(ii) The spontaneous polarization in the material stems from its initial anisotropy and is enhanced by the subsequent deformation process. The precise nature of this enhancement is not known at this stage.

(iii) The molecular mechanism responsible for this  $\alpha'$  peak is the disorientation of local chain segments from their aligned configuration frozen in during the cold-work.

(iv) Birefringence and density measurements have been shown to support the above molecular origin associated with the  $\alpha'$  process.

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