Dielectric Relaxation in Amorphous Poly(ethylene terephthalate) and Poly(ethylene 2,6-naphthalene dicarboxylate) and Their Copolymers

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ABSTRACT: The dielectric loss spectra of poly(ethylene 2,6-naphthylene dicarboxylate) (PEN) and several copolymers of 2,6-naphthylene dicarboxylic acid and terephthalic acid with ethylene glycol have been studied over a wide range of frequency and temperature. Previously, Ezquerra, Balta-Calleja, and Zachmann have reported the presence, in isochronal temperature scans of dielectric loss, of a subglass process ( $\beta^*$ ) in PEN homopolymer in addition to the subglass process ( $\beta$ ) similar to that in poly(ethylene terephthalate) (PET). In the present work both the  $\beta$  and  $\beta^*$  processes in PEN and PET/PEN copolymers are resolved and characterized in isothermal frequency scans. It was found that the lower temperature  $\beta$  loss peak in PEN and the copolymers has a complex or composite frequency domain structure requiring two Cole–Cole processes in its representation. The  $\beta^*$  process in the copolymers is found to shift to higher frequency isothermally (or lower temperature isochronally) with increasing terephthalic acid content. Analysis of previous dielectric data for PET shows that its  $\beta$  subglass process is also complex in the log frequency axis but must be represented by three Cole–Cole processes. The two higher frequency components are essentially identical to the two Cole–Cole processes making up the  $\beta$  process in PEN. The third and lowest frequency component is interpreted as of the same origin as the  $\beta^*$  process in PEN and the copolymers but shifted to higher frequency isothermally (or lower temperature) isothermally (or lower temperature) isothermally (or lower temperature) with increasing up the  $\beta$  process in PEN. The third and lowest frequency component is interpreted as of the same origin as the  $\beta^*$  process in PEN and the copolymers but shifted to higher frequency isothermally (or lower temperature isochronally) to where it overlaps with the  $\beta$  process.

## Introduction

Poly(ethylene terephthalate) (PET) is a polymer of immense technological importance, finding wide use in molding, film, and fiber applications. As a consequence, it has been very widely studied scientifically. The relation between its physical properties and mechanical, dielectric, and NMR relaxational behavior has been of one the areas of study.<sup>1-10</sup> In the completely amorphous state obtained by quenching from the melt PET shows a dielectric relaxation process,  $\alpha$ , associated with the glass transition region that is typical of amorphous polymers. In addition, it shows a prominent  $\beta$  subglass process well separated in temperature from the  $\alpha$  region. It has often been conjectured that subglass processes have a role in the toughness of polymers. Thus, the nature of the subglass relaxation in PET is of some importance.

More recently, the counterpart of PET based on a naphthylenic moiety rather than phenyl, i.e., poly-(ethylene 2,6-naphthylene dicarboxylate) (PEN), has also come into some prominence. Its dielectric relaxation and mechanical behavior has been studied.11-14 PEN shows a typical amorphous polymer  $\alpha$  process associated with the glass transition. Not unexpectedly, based on the greater bulk of the naphthylenic units, the glass transition region in PEN is displaced to somewhat higher temperature than in PET ( $T_{\rm g}$  of ~120 °C vs ~80 °C in PET). It also shows a subglass  $\beta$  process whose time-temperature behavior is very similar to that for the  $\beta$  relaxation in PET. However, most interestingly, Chen and Zachmann<sup>11</sup> and Ezquerra et al.<sup>12</sup> also found in their isochronal temperature plots of mechanical or dielectric loss a prominent shoulder at the beginning of the rapid rise in loss with increasing temperature associated with the  $\alpha$  glass transition process. They considered this to be an additional subglass process at temperatures intermediate to those of the  $\alpha$  and  $\beta$ relaxations. It was denoted as  $\beta^*$  in order to preserve

the correspondence of the  $\alpha$  and  $\beta$  notation in PEN with similar processes in PET. The same convention is followed here (see Table 1).

Since PET and PEN have the same structure with respect to the bonds that are flexible in their ability to undergo conformational rotations and thus lead to dipolar relaxation, it is perhaps surprising that PEN should have two subglass processes and PET just one. On the other hand, if this difference can be rationalized, the circumstance should be important in the understanding the molecular nature of subglass relaxation in both polymers. This rationalization is the subject of the present study. To accomplish it, dielectric relaxation in PEN is studied experimentally under conditions where all three processes,  $\alpha$ ,  $\beta^*$ , and  $\beta$ , can be resolved isothermally in the frequency plane and thus well quantified with respect to phenomenological parameters. The effect of varying the chain structure toward that of PET is also studied via measurements on PET/ PEN copolymers. Analysis of previous wide frequency range data for the  $\beta$  relaxation in PET<sup>9</sup> is carried out, and the results are compared with the behavior of PEN and its copolymers with PET.

# **Experimental Details**

**Polymers Studied.** The amorphous PEN homopolymer studied dielectrically was obtained from Dr. J. C. Coburn of the DuPont Co. and was in unoriented film form. Differential scanning calorimetry (DSC) analysis indicated that it was completely amorphous. Three copolymers of PET and PEN were synthesized in our laboratory via condensation polymerization. This leads to random copolymers.<sup>15</sup> The mole ratios of terephthalic acid and naphthoic acid units of the three copolymers were 2/1, 1/1, and 1/2 and are designated for mnemonic simplicity as 2PET/1PEN, 1PET/1PEN, and 1PET/2PEN, respectively, in ensuing discussions. All chemicals were obtained commercially from Aldrich Chemical Co. The synthesis takes place in two stages: transesterification and polycondensation. In a typical synthesis reaction, 30 g total

 Table 1. Nomenclature Used To Denote Relaxation Processes

designation	process
α	glass transition region
eta	overall low-temperature subglass relaxation in PET, PEN, and their copolymers and which has a
	composite nature in these polymers
$\beta_1, \beta_2$	components of the composite $\beta$ process in PET, PEN, and their copolymers (order of frequency maximum
	of the three $\beta$ components is $1 \ge 2 \ge 3$ )
$\beta_3$	component of the composite $\beta$ process in PET
$\beta^*$	resolved subglass relaxation intermediate in temperature and frequency between the $\alpha$ and $\beta$ relaxations
	in PEN and copolymers but not found in PET

Table 2. Summary of the DSC Glass Transition, Endotherm, and Exotherm Temperatures for PET and PEN and Copolymers

sample	<i>T</i> g (°C)	$T_{\text{crystallization}}$ (°C)	$T_{\text{melt}}$ (°C)
PET	74	140	241
2PET/1PEN	90		
1PET/1PEN	96		
1PET/2PEN	99		
PEN	118	197	261

of dimethyl terephthalate (DMT) and dimethyl 2,6-naphthalate (DMN) in the appropriate mole ratio was placed in a reaction tube with 15 mL of ethylene glycol (EG), 0.07 g of manganese acetate, and 0.01 g of antimony trioxide. The final two components serve as catalysts in the transesterification and polycondensation stages, respectively. During the transesterification stage, DMT and DMN react with EG to form bis-(hydroxyethyl) terephthalate (BHET), 2,6-bis(hydroxyalkyl)naphthalate (BHAN), and methanol. To accomplish this, nitrogen gas was passed through the closed system as it was heated to 200 °C and held there until no more methanol was collected, requiring up to 2 h. During the polycondensation stage, the BHET and BHAN react to form copolymer and EG. This was accomplished in several steps. The pressure was reduced to 3-4 Torr with nitrogen gas still flowing. The temperature of the system was then increased 5-10 K and held for 10-17 h. This heating and holding process was repeated several times until the reaction mixture was very viscous and had formed a honeycomb-like structure. The system was then held at this final temperature for another 12-14 h. Finally, the system was cooled to room temperature, and the reaction tube was broken to remove the copolymer. Material balances indicated no significant loss of terephthalic or naphthalic units. The copolymers were cut into small pieces and melt-pressed into thin disks.

**Differential Scanning Calorimetery Analysis.** A Shimadzu Co. differential scanning calorimeter (DSC) was used to analyze the "raw" copolymer directly out of the reaction tube and the flash from the molded samples of the copolymers. In addition, films of amorphous PET (also obtained from Dr. Coburn) and PEN homopolymer were analyzed. A stream of nitrogen gas was passed through the sample chamber, and a heating rate of 10 °C/min was used. The scans were run from ambient temperature to about 300 °C, using alumina as a reference material. The scans were performed to determine the glass transition temperature ( $T_g$ ) of the polymers and to ensure that all of the polymers were amorphous.

Pure amorphous PET and PEN behaved in a manner similar to what is reported in the literature.<sup>14–16</sup> Both displayed a single glass transition, a large crystallization exotherm, and a melting endotherm. The values for temperatures associated with each of these phenomena are recorded in Table 2. The as-synthesized material and molded samples of the 1PET/ 1PEN and 1PET/2PEN copolymers behaved similarly. They both showed a glass transition and no hint of crystals either forming or melting. The as-synthesized 2PET/1PEN exhibited some evidence of crystallinity in addition to the glass transition. However, no evidence of crystallinity was noted in molded samples. The copolymer results are also listed in Table 2.

**Dielectric Measurements.** Dielectric specimens were circular disks coated with sputtered gold with a guard ring scribed near the outer diameter. The dielectric measurement apparatus was a time domain spectrometer (TDS) made by



**Figure 1.** Dielectric constant and loss vs log frequency in PEN homopolymer in the  $\beta$  relaxation region as a function of temperature at 5 K intervals from 165 to 195 K.

the Imass Co., Hingham, MA. The instrument is based on the design due to Mopsik.<sup>17,18</sup> The time domain data when Fourier transformed by the TDS apparatus to the frequency domain spans the 7 decades of  $10^{-3}-10^{+4}$  Hz. In implementing the transform process, Mopsik<sup>18</sup> paid careful attention to both the accuracy of the transform and the elimination of truncation effects within the selected frequency window. In our experience, within the levels of loss studied here, the transform is robust and does not give rise to transform artifacts. For some of the specimens the frequency range 1 kHz to 1 MHz was measured by means of a Hewlett-Packard model 4284A precision LCR meter. Although the LCR meter nominal high frequency is 1 MHz, it was found that for the subglass processes where the dielectric loss is rather low a spurious roll-off in dissipation factor occurred at high frequency, limiting the effective upper frequency to ~300 kHz.

Dielectric measurements below room temperature were carried out in a cryostat (Janis Research Co. Supertran B) with temperature controlled to  $\pm 0.1$  K. Above room temperature the same sample and dielectric cell were placed in a temperature chamber (Delta Design Co. model 9010) also controlled to  $\pm 0.1$  K. Care was taken in all of the measurements to equilibrate the specimen at room temperature in a flowing dry nitrogen atmosphere at reduced pressure and thus eliminate any absorbed moisture before commencing the measurement schedule.

# **Experimental Results and Phenomenological Analysis for Subglass Processes**

**PEN:** Subglass Processes Overview. Isothermal scans of dielectric constant (relative dielectric permittivity) and loss vs log frequency in the temperature region of the  $\beta$  relaxation in PEN homopolymer are displayed in Figure 1. In Figure 2 scans in the temperature region intermediate between the  $\beta$  and  $\beta^*$  regions are shown. In Figure 3 scans appropriate to the tem-



**Figure 2.** Dielectric constant and loss vs log frequency in PEN homopolymer as a function of temperature in the region intermediate to the  $\beta$  and  $\beta^*$  relaxations.



**Figure 3.** Dielectric constant and loss vs log frequency in PEN homopolymer in the  $\beta^*$  relaxation region as a function of temperature.

peratures where the  $\beta^*$  relaxation is resolved are given. It may be seen that both processes have significant regions of temperature where they are resolved in the frequency plane. Argand plots of loss vs dielectric constant of the data in Figure 1 and Figure 3 are displayed in Figure 4 and Figure 5.

**PEN:** Subglass  $\beta$  Process. Because of the very broad nature of subglass relaxations in the frequency domain, comparatively little is known concerning the shapes of such processes in log frequency. In restricted frequency scans it has been commonly supposed that such processes are symmetrical in log frequency about the maximum in the loss and the Cole–Cole<sup>19</sup> phenomenological equation utilized in their representation. However, the advent of broader experimental frequency windows allows investigation of this point. It may be seen for the  $\beta$  process, in Figure 1, that the loss process is skewed toward higher frequency. This situation is reminiscent of the well-known shape of the  $\alpha$  process associated with relaxation above the glass transition in



**Figure 4.** Argand diagram of loss vs dielectric constant in PEN homopolymer in the  $\beta$  relaxation region as a function of temperature.



**Figure 5.** Argand diagram of loss vs dielectric constant in PEN homopolymer in the  $\beta^*$  relaxation region as a function of temperature.

amorphous polymers. In the latter instance, the Havriliak-Negami (HN) equation<sup>20</sup> successfully represents the shape of the process. However, it can also be seen in the loss curves of Figure 1 that the situation is more complicated than permitted by the shape of the HN function. Over much of the temperature range (175– 195 K) a second inflection point in the curvature of the loss vs log frequency, where the curvature becomes downward, is present on the high-frequency side of the peak. Concomitantly, the Argand plot in Figure 4 shows upward curvature on the immediate high-frequency side. Neither of these features can be accommodated with the HN function. These observations suggest that rather than invoking a single asymmetrically broadened process the situation would be better represented as a composite of two overlapping processes, denoted here as  $\beta_1$  and  $\beta_2$  (see Table 1). In the interests of simplicity it is assumed that each of these processes is a symmetric Cole-Cole process and that they are additive. Thus, the composite Cole–Cole representation<sup>19</sup> is given by

$$\epsilon^* = \epsilon_{\rm u} + \frac{\Delta \epsilon_1}{\left(1 + (i\omega\tau_1)^{\bar{\alpha}_1}\right)} + \frac{\Delta \epsilon_2}{\left(1 + (i\omega\tau_2)^{\bar{\alpha}_2}\right)} \qquad (1)$$

where  $\epsilon_u$  is the unrelaxed dielectric constant,  $\Delta \epsilon$  is the dielectric increment or strength,  $\tau$  is the central relaxation time,  $\bar{\alpha}$  is the broadening parameter, and  $\omega$  is circular frequency. Subscripts 1 and 2 refer to the two components of the composite process, and 1 is taken to be the higher frequency one.



**Figure 6.** Fit of two Cole–Cole components to the PEN  $\beta$  process at 185 K. The upper panel is the fit to the Argand diagram, and the lower one is the fit to the loss vs frequency data. The dashed curves are the individual Cole–Cole components,  $\beta_1$  and  $\beta_2$ .

A fit of eq 1 to the  $\beta$  region dielectric data at 185 K is shown in Figure 6. Since both the real and imaginary  $\epsilon'$  and  $\epsilon''$  components of  $\epsilon^*$  in eq 1 have to be fit, application of nonlinear regression to carry out parameter determination is somewhat awkward since they ( $\epsilon'$ ,  $\epsilon''$ ) are to some degree independent numerically. That is, exact conversion between the two ( $\epsilon'$ ,  $\epsilon''$ ) via the Kramers-Kroenig relation requires the entire frequency spectrum.<sup>21</sup> In practice, it turned out to be convenient and effective to do successive trial and error fits on the Argand plots and  $\epsilon''$  vs log *f* plots. The position of the  $\epsilon''$ maximum in log *f* and the low-frequency shape of  $\epsilon''$  are largely determined by  $\tau_2$  and  $\bar{\alpha}_2$ , respectively. The shape of the inflection region between the 1 and 2 processes in both  $\epsilon''$  and the Argand diagram are very sensitive to the choice of both  $\tau_1$  and the relative  $\Delta \epsilon$  strengths of 1 and 2. Finally, the high-frequency tail of  $\epsilon''$  is largely determined by  $\alpha_1$ . Thus, there is a fair degree of parameter set uniqueness. It can be seen in Figure 6 that a good representation of the features of the data is achieved. Fits were made to the data at other temperatures as well, and these are summarized for the -log  $\tau$  and  $\alpha$  parameters in Figure 7 and for  $\Delta \epsilon$  strength parameters in Figure 8.

Some features that emerge (see Figures 7 and 8) from the fitting are the following. Although the higher frequency component, 1, is a shoulder on the lower frequency one, 2, the strength of the former is actually somewhat larger than the latter. The higher frequency component, 1, is considerably broader, however, especially at lower temperature, than component 2 although component 1 narrows strongly with increasing temperature. The activation energy for the central relaxation time parameter for component 1 is less than that for component 2. The strengths of processes 1 and 2 are relatively temperature independent. Although not shown in Figure 7, it was found that, because component 2 is considerably narrower than component 1, the experimental maximum in the loss vs frequency curve for the composite overall  $\beta$  process corresponds closely to the



**Figure 7.**  $\beta$  processes. Summary of the  $-\log \tau$  relaxation time and  $\bar{\alpha}$  width parameters from the fitting of the Cole–Cole components to the  $\beta$  processes in all of the polymers, including the  $\beta_3$  component in PET. All of the results are plotted vs reciprocal temperature. The upper panel shows the  $-\log \tau$ values. The middle panel shows the  $\bar{\alpha}$  parameter for the PET  $\beta_3$  component. The lower panel shows  $\bar{\alpha}$  for the  $\beta_1$  and  $\beta_2$ components for all the polymers.



**Figure 8.**  $\beta$  processes. The dielectric strength increments,  $\Delta \epsilon$ , from fitting of the Cole–Cole components to the  $\beta$  processes in all of the polymers, including the  $\beta_3$  component in PET. All of the results are plotted vs reciprocal temperature. The symbols for the polymers are the same as in Figure 7.

location dictated by  $\tau_2$  alone. Thus, the activation energy for the component 2 process is also that for the experimental composite overall  $\beta$  process.

**PEN:** Subglass  $\beta^*$  Process. The  $\beta^*$  region in PEN (Figures 3 and 5) is more symmetric in shape than the overall  $\beta$  process, and a single Cole–Cole function suffices to represent it. However, there is some overlap with the higher frequency  $\beta$  process. In the phenomenological fitting this was recognized by adding to the



**Figure 9.** Fit of a single Cole–Cole component to the PEN  $\beta^*$  process at 330 K. The upper panel is the fit to the Argand diagram, and the lower one is the fit to the loss vs frequency data. The dashed curves are the contribution of the  $\beta$  process as expressed by the Cole–Cole components,  $\beta_1$  and  $\beta_2$ .

Cole–Cole loss and dielectric constant functions the contributions of the  $\beta_1$  and  $\beta_2$  processes. The latter were obtained by extrapolation of the log  $\tau$  relaxation times (with Arrhenius temperature dependence),  $\bar{\alpha}$  breadth, and  $\Delta\epsilon$  strength parameters (both of the latter two with linear temperature dependence) for the  $\beta_1$  and  $\beta_2$  processes to the temperature of the  $\beta^*$  process being fit. The results of the fitting for the PEN  $\beta^*$  process at 330 K are shown in Figure 9. The parameters found are shown in Figure 10.

**PET/PEN Copolymers:** Subglass  $\beta$  Process. Dielectric loss vs frequency data in the  $\beta$  region for the three copolymers and PEN homopolymer are compared at 195 K in Figure 11. It may be seen that the composite nature of the processes in the copolymers is very similar to the situation in PEN homopolymer. Phenomenological fits for the copolymer data invoking two Cole–Cole processes were accomplished at a number of temperatures by the same procedures invoked above for PEN homopolymer. The results are shown in Figures 7 and 8.

**PET/PEN Copolymers:** Subglass  $\beta^*$  Process. Dielectric loss vs frequency data in the  $\beta^*$  region for the three copolymers and PEN homopolymer are compared in Figure 12. It is apparent that the  $\beta^*$  process is present in the copolymers as well. However, it may also be seen that for the 2PET/1PEN copolymer the process is only poorly resolved. This is in some degree due to overlap from the lower frequency  $\alpha$  glass transition process. As noted (see Table 2), the  $T_g$  value decreases with increasing PET content. This causes the separation between the  $\alpha$  process and the  $\beta^*$  process to decrease. There is a noticeable shift in the  $\beta^*$  loss location toward higher frequency with increasing PET content. The lower temperature for the 2PET/1PEN curve (320 K) compared to the other three curves (335 K) was selected to display the center of the process in the same window as the latter ones. This curve also indicates a continuation of the higher frequency progression with PET content when considered at the same temperature as the other curves. This progression, expressed as loss



**Figure 10.**  $\beta^*$  processes. Summary of the  $-\log \tau$  relaxation times,  $\bar{\alpha}$  width parameters, and dielectric strength increments,  $\Delta \epsilon$ , from the fitting of the Cole–Cole components to the  $\beta^*$  processes in all of the polymers (except PET). All of the results are plotted vs reciprocal temperature. The upper panel shows the  $-\log \tau$  values. The middle panel shows the  $\bar{\alpha}$  parameters The lower panel shows the  $\Delta \epsilon$  increments.



**Figure 11.** Dielectric loss vs frequency curves of the  $\beta$  processes in all of the polymers compared at 195 K. The PET data are from ref 9.

map of the maximum in the loss vs log frequency curve plotted in Arrhenius form, is displayed in Figure 13.

In the 1PET/2PEN and 1PET/1PEN polymers phenomenological fitting was carried out as for the PEN homopolymers. The parameter values are displayed in Figure 10 along with the PEN homopolymer values. Because of the poor resolution, no fitting was attempted for the 2PET/1PEN polymer. However, approximate values for log  $f_{\text{max}}$  were estimated from the loss curves (Figure 13). These values were converted to a log  $\tau$  basis through the relation  $1/\tau \sim 2\pi f$ . The values for 2PET/1PEN for  $-\log \tau$  in Figure 10 were determined in this fashion.

**PET Homopolymer:** Subglass  $\beta$  Process. The  $\beta$  process in PET homopolymer as represented by previously published data<sup>9</sup> is compared to those in PEN and



**Figure 12.** Dielectric loss vs frequency curves of the  $\beta^*$  processes in PEN and the copolymers compared. The 2PET/ 1PEN copolymer data are at 320 K rather than at 330 K as for the other polymers in order to show the process in the same frequency window.



**Figure 13.**  $\beta^*$  processes. Loss map of frequency of the maximum in the dielectric loss vs reciprocal temperature for PEN and the copolymers.

the copolymers studied in Figure 11. There is significant difference between PET and the other polymers. Although the higher frequency side of the  $\beta$  process appears to have similar structure to that in PEN and the copolymers, the overall  $\beta$  process is skewed toward *low* frequency rather than high. This suggests, and is borne out by phenomenological analysis, that the PET  $\beta$  process contains *three* components in its composite nature. Accordingly, the PET  $\beta$  process dielectric data were fit to eq 1 modified to contain three Cole-Cole terms, one for each of the processes  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$ . In the fitting process values for the parameters for the  $\beta_1$ and  $\beta_2$  components were taken as typical for these processes in PEN and copolymers, and only the  $\tau_3$ ,  $\bar{\alpha}_3$ , and  $\Delta \epsilon_3$  parameters varied. Following this, slight adjustments were made to  $\bar{\alpha}_1$  and  $\Delta \epsilon_2$  to improve the fits. The other  $\beta_1$  and  $\beta_2$  parameters are tightly clustered for PEN and the copolymers (Figures 7 and 8), and this was maintained for PET homopolymer. Figure 14 shows the fit achieved for PET at 203 K. The resulting relaxation time, width, and strength parameters,  $\log \tau$ ,  $\bar{\alpha},$  and  $\Delta\epsilon,$  respectively, for the three components are shown in Figures 7 and 8. From Figure 14 we conclude that the overall PET homopolymer  $\beta$  process can be well represented as a composite of the  $\beta_1$  and  $\beta_2$  components typical of PEN and the copolymers plus a third  $\beta_3$ component.

It is appropriate here to comment that resolution of the  $\beta$  process in PET into components is not a new proposal. Illers and Breuer<sup>2</sup> suggested three components on the basis of isochronal temperature scans of torsion



**Figure 14.** Fit of three Cole–Cole components to the PET  $\beta$  process at 203 K. The upper panel is the fit to the Argand diagram, and the lower one is the fit to the loss vs frequency data. The dashed curves are the individual Cole–Cole components,  $\beta_1$ ,  $\beta_2$ , and  $\beta_3$ .

modulus and damping, and Sacher<sup>3b</sup> proposed two components on the basis of dielectric loss scans.

# Experimental Results and Phenomenological Analysis for Glass Transition α Processes

**PEN: Glass Transition**  $\alpha$  **Process.** Dielectric loss as a function of frequency for PEN homopolymer is shown in Figure 15 over the temperature range of the glass transition. It is apparent that the loss curves have the high-frequency skewing that is typical of the glass transition region in amorphous polymers and that is well represented by the Havriliak–Negami (HN) function. It is also seen that at the lowest temperature shown the  $\beta^*$  relaxation is present as a resolved process at high frequency. As temperature increases, the  $\alpha$  and  $\beta^*$  relaxations merge. This coalescence with increasing temperature or bifurcation with decreasing temperature is a well-known phenomenon. However, direct observation in isothermal frequency scans as opposed to isochronal temperature scans is still a rather sparsely documented situation.<sup>7,22,23</sup>

The data in Figure 15 were fit to the Havriliak– Negami equation,<sup>20</sup> which is expressed as

$$\epsilon^* = \epsilon_{\rm u} + \frac{\Delta \epsilon}{\left(1 + (i\omega\tau)^{\tilde{\alpha}}\right)^{\tilde{\beta}}} \tag{2}$$

and where, in addition to the symbols in eq 1,  $\bar{\beta}$  is the asymmetric skewing parameter. The fitting was done by numerical regression. Because of the  $\beta^*$  process and conductance loss overlaps at high and low frequency, respectively, the data at the frequency extremes were unweighted. The fit achieved for PEN homopolymer at 398 K is shown in Figure 16.

**PET/PEN Copolymers:**  $\alpha$  **Processes.** The  $\alpha$  process loss data for PEN and the PET/PEN copolymers are compared at 398 K in Figure 17. The HN function was fit to the copolymer data at the various temperatures. The  $-\log \tau$ ,  $\bar{\alpha}$ , and  $\bar{\beta}$  parameters for all of the polymers from the fitting process at the temperatures studied are



Figure 15.  $\alpha$  process region. Dielectric loss vs log frequency for PEN homopolymer between 383 and 428 K at 5 K intervals.



**Figure 16.** Fit of the HN equation to the PEN  $\alpha$  process at 398 K. The upper panel is the fit to the Argand diagram, and the lower one is the fit to the loss vs log frequency data.



Figure 17.  $\alpha$  process region. Dielectric loss vs log frequency compared for PEN and the copolymers at 398 K.

shown in Figure 18. The PET data of ref 9 were also analyzed, and the results are also shown in Figure 18.

It is apparent in Figure 18 that the relaxation times have the expected and typical non-Arrhenius temperature behavior associated with the glass transition region. The Vogel–Fulcher (VF) equation<sup>24</sup> is traditionally invoked to represent this situation. The latter equation is expressed as



**Figure 18.**  $\alpha$  processes. Summary of the  $-\log \tau$  relaxation time and  $\bar{\alpha}$  width, skewing, and parameters from the fitting of the HN equation to the  $\alpha$  processes in all of the polymers including the PET data of ref 9. All of the results are plotted vs reciprocal temperature. The top panel shows the  $-\log \tau$  values. The curves shown are VF equation fits to the data. The next two panels show the  $\bar{\alpha}$  width and  $\bar{\beta}$  skewing parameters, respectively; the lowest panel shows the dielectric strength increments,  $\Delta \epsilon$ .

Table 3.  $\alpha$  Process: Parameters for the VF Equation and  $T_{\rm g}$  Values from  $\tau = 100~{\rm s}$ 

polymer	Α	В	$T_{\infty}$ (K)	<i>T</i> <sub>g</sub> (100 s) (K)	<i>T</i> <sub>g</sub> (100 s) (°C)
PEN	560	-11.41	351	389	116
1PET/2PEN	481	-11.14	341	379	106
1PET/1PEN	473	-11.20	336	372	99
2PET/1PEN	489	-11.71	332	367	94
PET	404	-11.07	318	353	80

where *A*, *B*, and  $T_{\infty}$  are constants chosen to fit the data. The curves in Figure 18 are VF fits to the data. The *A*, *B*, and  $T_{\infty}$  parameters are listed in Table 3. Table 3 also shows values of the glass transition temperature computed from the VF parameters according to the criteria that the relaxation time = 100 s. These values are in general accord with the DSC results (Table 2).

# Interpretation

As indicated in the Introduction, the center of interest in this study is the nature of the  $\beta^*$  relaxation in PEN and its relation to the lower temperature  $\beta$  relaxation in PEN and in PET. The salient facts found here are the following. First, the  $\beta$  relaxation when examined under broad-band isothermal frequency scans is not a single featureless process but has complex or composite structure. These features in PEN can be represented by two overlapping Cole–Cole processes ( $\beta_1$ ,  $\beta_2$ ). The  $\beta$ relaxation in PET is even more complex in its features and requires three Cole–Cole processes ( $\beta_1$ ,  $\beta_2$ ,  $\beta_3$ ) in its representation. The two components of the  $\beta$  relaxation ( $\beta_1$ ,  $\beta_2$ ) in PEN are very similar in behavior to their  $\beta_1$  and  $\beta_2$  counterparts in PET (see Figures 7 and 8). These observations seem to inescapably lead to the hypothesis that the  $\beta^*$  relaxation in PEN is related to the  $\beta_3$  component in PET, but the former is shifted to lower frequency isothermally or higher temperature isochronally compared to the latter.

There are two simple scenarios as to the nature of the shifting process from  $\beta^*$  to  $\beta_3$  as the PET content increases. The first would be that the process continuously moves to higher frequency or lower temperature. The other would be that the  $\beta^*$  process disappears at low frequency while the  $\beta_3$  process grows at high frequency without a frequency shift. The first scenario would imply on the molecular scale that the  $\beta^* \sim \beta_3$ mechanism involves some degree of cooperativity in groups of bond rotations or conformational jumps. The second scenario would be more appropriate to a highly localized association of the process to specific bond rearrangements.

The experimental data do not totally distinguish between the two scenarios above. As noted (section PET/ PEN Copolymers: Subglass  $\beta^*$  Process), because of the interference of the  $\alpha$  process, the phenomenological analysis of the  $\beta^*$  process was incomplete in that only log  $f_{\rm max}$  behavior was available for the lowest PEN content copolymer (2PET/1PEN). It does seem clear, however, that there is an actual shift in the  $\beta^*$  location with increasing PET content (Figure 13) with a decrease in activation energy toward that of the  $\beta_3$  component in PET (Figure 7). It also seems clear that there is no appearance of the  $\beta_3$  component at the position observed in PET homopolymer as PET content increases in the copolymers studied (Figures 11 and 14). These observations are consistent with the first scenario. However, the degree of shift in position over the compositions of the first two copolymers is rather slight (Figure 10).

Thus, it appears that the shifting scenario is basically correct. However, the slowing of the chain dynamics associated with the  $\beta^*$  process seems to be sensitive to naphthoic unit content in a manner that would indicate interaction over several monomeric units. That is, keeping in mind that the conformationally mobile bonds are in the ester moieties spanning two aromatic rings, suppose that the dynamics were sensitive to the composition of a pair of monomers units NN vs NT vs TT (where N = naphthoic, T = terephthalic) so that the dynamics were slowed by the N unit in either NN or NT pairs. Then it would follow that the relaxation would tend not to respond to T content until high T content, i.e., a predominance of T–T pairs.

Finally, it worth speculating on the occurrence of three subglass components ( $\beta_1$ ,  $\beta_2$ ,  $\beta_3 \sim \beta^*$ ). It is tempting but perhaps to some degree naive to associate these with the three conformationally flexible bonds in the structures that allow dipolar relaxation. Keeping in mind that the dipole is effectively directed along the ester carbonyl bond and that the ester unit is effectively conformationally rigid, the mobile bonds are the aromatic ring carbon (CA) to ester carbon (C) bond, the ester ether oxygen (O) to aliphatic carbon (C) bond, and the aliphatic carbon-carbon (C-C) bond. It is known with reasonable certainty that the CA-C bond has the highest rotational barrier, C-C is intermediate, and the

C-O bond has the lowest one.<sup>25,26</sup> Molecular dynamics (MD) simulations of PET show that dipolar relaxation responds to the bond types in this fashion.<sup>26</sup> The slowest component of relaxation is associated with the CA-C bonds, the next with the C-C bond, and the fastest component with the C-O bonds. It is also found in MD simulations that dipolar relaxation in PEN is slower than in PET a circumstance only attributable to the hindrance induced by the bulky naphthoic units. Although the situation is no doubt more complex, it seems to be useful to think of the three relaxation components as associated with the bonds as  $\beta_1 \sim C-O$ ;  $\beta_2 \sim C-C$ ;  $\beta^*, \beta^3 \sim CA-C.$ 

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#### **References and Notes**

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