Dielectric Relaxation Studies of Bisphenol A Polyarylates

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ABSTRACT: The dielectric relaxation characteristics of two polyarylates based on Bisphenol A and isophthalic (ISO) and terephthalic (TA) acids have been examined across both the glass–rubber (α) and sub-glass (β) relaxations. The two polymers differ in the relative proportion of isophthalic to terephthalic acid units incorporated in the chain backbone: resins comprised of 75/25 and 50/50 isophthalic/terephthalic ratios were investigated. The higher isophthalate content in the 75/25 ISO/TA polymer resulted in a lower α relaxation temperature as compared to the 50/50 sample and a stronger dielectric relaxation response; this latter result is consistent with a lower degree of dipolar cancellation in the 75/25 material owing to its lower terephthalic acid content. Examination of the (α) dielectric relaxation intensity as a function of temperature for the 50/50 ISO/TA sample indicated an increase in the relaxation intensity which reflects an apparent decrease in local dipolar correlation at higher temperatures. In the case of the sub-glass (β) relaxation, the measured dielectric intensity was found to be nearly identical for the two polyarylates which is consistent with a highly-localized, noncorrelated origin for this relaxation.

Introduction

Since their initial commercial development nearly 2 decades ago, aromatic polyarylates have been utilized in a wide range of high-performance engineering applications. These amorphous thermoplastics, based on the copolymerization of Bisphenol A and isophthalic and terephthalic acids, display excellent thermal resistance and toughness in combination with clarity and ultraviolet stability (see Figure 1).[1] Bisphenol A polyarylates have been introduced into a wide range of blend formulations: one combination which has been of considerable academic and commercial interest is polyarylate (PAr) and poly(butylene terephthalate) (PBT). PAr/PBT blends are miscible at all compositions,[2] with PBT acting as the sole crystallizable component. A number of detailed studies of PAr/PBT crystallization[3,4] and morphology[5–7] have recently appeared.

The highly-aromatic nature and resulting stiffness of the Bisphenol A polyarylate backbone is responsible for its exceptional thermal properties (i.e., high glass transition temperature). The overall conformation of the polyarylate chain backbone can be considered in terms of primary kinks located at the bridge carbon of the bisphenol group in combination with the phenyl ester segment (Ph–OOC–Ph–COO–Ph; where Ph = phenyl ring). Energy minimization calculations for polyarylate chains based on Bisphenol A and terephthalic acid (only) indicate that the phenyl ester segment assumes a linear, *trans* conformation with the phenyl rings in a planar arrangement: the overall conformation of these 100% terephthalic acid polyarylate chains is of a crankshaft nature.[8] The introduction of the unsymmetrical *meta*-connected isophthalic acid group adds a kink to the phenyl ester segment and results in a systematic decrease in the glass transition temperature relative to the wholly terephthalic acid composition.[9] At intermediate ratios of isophthalic acid to terephthalic acid, amorphous materials with high solubility are obtained. Currently available commercial polyarylate resins contain 50–75 mol % isophthalic acid as a fraction of the total dicarboxylic acid content.

To date, the investigation of relaxation phenomena in Bisphenol A polyarylates using dielectric relaxation spectroscopy has been limited. Alegria and co-workers[10,11] reported the characteristics of the glass–rubber (α) relaxation for a polyarylate sample based on a 50/50 ratio of isophthalic to terephthalic acids (50/50 ISO/TA) and observed that the relaxation could be described by the Havriliak–Negami modification of the single relaxation time Debye equation (see below).[12] Starkweather and Avakian[13] reported frequency–temperature data for the sub-glass (β) relaxation in 50/50 ISO/TA polyarylate which displayed a linear Arrhenius behavior. The resulting apparent activation energy corresponded to an activation entropy close to zero, which is consistent with highly-localized dipolar motions of a noncooperative nature.[14] Also, dielectric methods have been used to examine phase morphology and composition in crystallized PAr/PBT blends.[5,6]

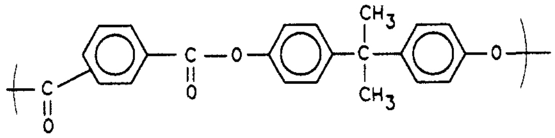

Figure 1. Repeat unit structure for the polyarylate copolymer based on Bisphenol A and isophthalic and terephthalic acids.

In this work, the dielectric relaxation behaviors of two Bisphenol A polyarylates are reported for both the glass–rubber (α) and sub-glass (β) relaxations. Specifically, the relaxation characteristics of two commercial polyarylates are contrasted: these materials differ in the ratio of isophthalic to terephthalic acid moieties present in the chain backbone. The polymers examined are the Unitika U-100 resin (Unitika Ltd., Japan) based on Bisphenol A and a 50/50 mixture of isophthalic and terephthalic acids and Hoechst-Celanese Durel-400 based on Bisphenol A and a 75/25 ratio of isophthalic to terephthalic acid. The relative quantity of the *meta*-connected isophthalic moiety in the chain backbone has a significant impact on the relaxation characteristics of the materials as manifested in their respective relaxation temperatures (i.e., central relaxation times), relaxation intensities, and relaxation temperature dependence.

Experimental Methods

The polyarylate samples were obtained through the courtesy of Unitika Ltd., Japan (U-100) and Hoechst-Celanese (Durel); both materials were supplied in pellet form. As noted above,

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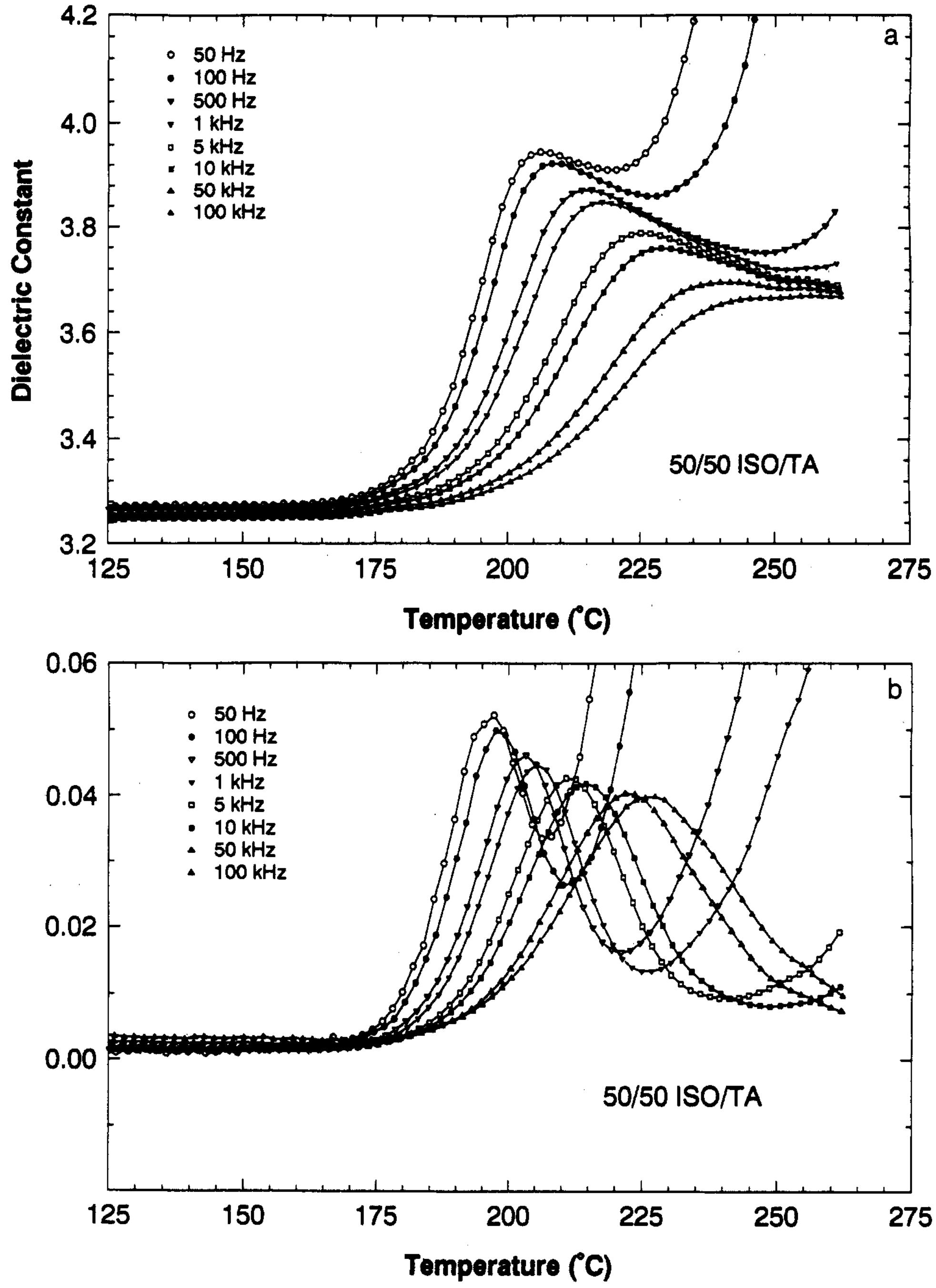

Figure 2. Dielectric results for polyarylate based on 50/50 isophthalic/terephthalic acids: α relaxation region. (a) Dielectric constant (ϵ') versus temperature (°C); (b) dissipation factor (tan δ) versus temperature (°C). (○) 50 Hz, (●) 100 Hz, (▽) 500 Hz, (▼) 1 kHz, (□) 5 kHz, (■) 10 kHz, (△) 50 kHz, (▲) 100 kHz.

these resins are copolymers based on Bisphenol A and isophthalic and terephthalic acids, with the relative proportion of isophthalic to terephthalic units equal to 50/50 in the U-100 and 75/25 in the Durel. Polymer films for the purpose of dielectric measurement were obtained by compression molding the resin pellets in a Carver melt press at 300 °C for short times; the resulting film thickness was approximately 0.23 mm. All films were subsequently dried under vacuum at 40 °C for a minimum of 24 h prior to measurement to remove residual moisture.

Dielectric spectroscopy measurements were accomplished using a Polymer Laboratories dielectric thermal analyzer (PL-DETA) comprised of a GenRad Digibridge interfaced with a Polymer Laboratories temperature controller. Concentric silver electrodes (33 mm) were vacuum evaporated directly on the samples, which were mounted between polished platens in the temperature-controlled test oven; all measurements were carried out under an inert (N_2) atmosphere. The dielectric constant (ϵ') and dissipation factor (tan δ) were recorded at frequencies ranging from 50 Hz to 100 kHz across a temperature range of −150 to +300 °C. Temperature scans for the β and α relaxation regions were typically carried out independently: the heating rate was 2.0 °C/min for the β relaxation scans and 0.75 °C/min for the α relaxation scans.

Results and Discussion

Dielectric results for the 50/50 ISO/TA polyarylate sample are provided for the α and β relaxation regions in Figures 2 and 3, respectively. These data, which are plotted isochronally as dielectric constant and dissipation factor versus temperature, are representative of both polyarylates. A stepwise increase in the dielectric constant is evident at the two relaxation events which corresponds to the mobilization of constituent dipoles in the polymer chains and which is accompanied by a maximum in the dissipation factor (tan δ). The relatively narrow α relaxation reflects the large-scale, cooperative motions inherent to the glass transition, while the broad (sub-glass) β relaxation reflects primarily local, noncooperative mo-

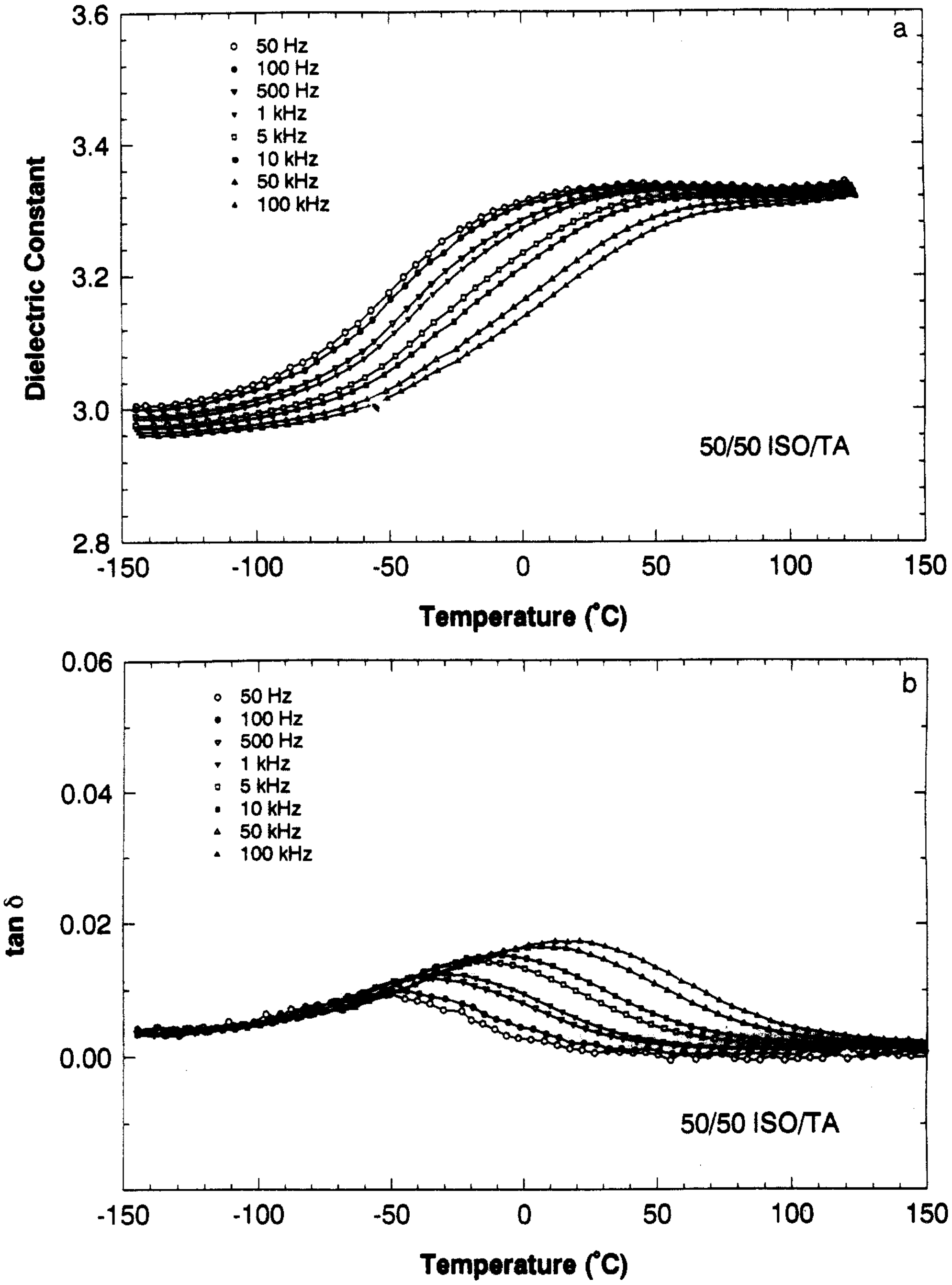

Figure 3. Dielectric results for polyarylate based on 50/50 isophthalic/terephthalic acids: β relaxation region. (a) Dielectric constant (ϵ') versus temperature (°C); (b) dissipation factor (tan δ) versus temperature (°C). Same symbols as in Figure 2.

Table 1. Dielectric Relaxation Temperatures and Relaxation Intensities ($\Delta\epsilon = \epsilon_R - \epsilon_U$) for the β and α Relaxations[a]

	T_β (°C)	$\Delta\epsilon(T_\beta)$	T_α (°C)	$\Delta\epsilon(T_\alpha)$
50/50 ISO/TA	−34	0.39	205	0.75
75/25 ISO/TA	−18	0.39	193	0.82

[a] T_β and T_α are based on the maximum in tan δ at a frequency of 1 kHz.

tions along the polymer backbone. The strong increase in dielectric constant and dissipation factor evident at temperatures above the glass transition (low-frequency measurements) corresponds to the onset of ionic conduction in the sample. The influence of conduction was removed from the dielectric loss data in the region of the glass transition prior to analysis by methods described previously.[15]

A comparison of the relaxation temperatures T_α and T_β (evaluated at 1 kHz) for the 50/50 and 75/25 ISO/TA polyarylates is provided in Table 1. The higher isophthalate content in the 75/25 material results in a decrease in the measured glass transition temperature as compared to the 50/50 resin, presumably owing to an increased disruption in chain packing with the increased fraction of *meta*-connected units. This trend is reversed for the β transition, with the sub-glass relaxation occurring at lower temperatures (i.e., shorter central relaxation times) for the 50/50 ISO/TA sample as compared to the 75/25 composition. Thus, the localized motions responsible for the observed β relaxation response appear to occur more readily in those chains which incorporate a lower fraction of isophthalic units. Complete time–temperature behavior across the frequency range of investigation is provided as an Arrhenius plot of log[frequency] versus $1000/T_{\max}$ in Figure 4; these data correspond to the measured temperature maxima in dissipation factor based on the individual isochronal curves. The α relaxation data for both polymers can be satisfactorily described using a WLF-type expression,[16] the relative offset in the position of the two data

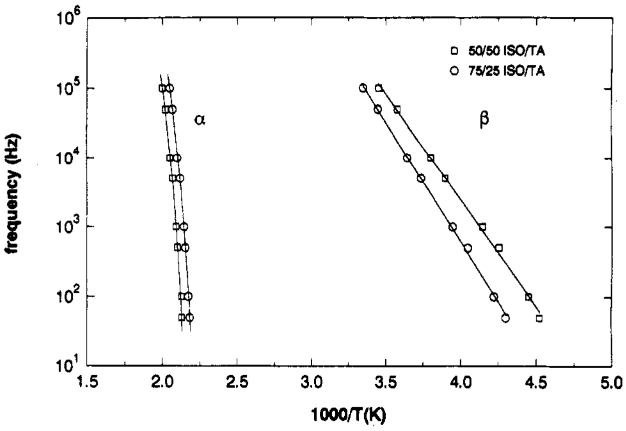

Figure 4. Arrhenius plot of frequency (Hz) versus 1000/*T* (K) based on isochronal temperature sweeps. (□) 50/50 ISO/TA and (○) 75/25 ISO/TA polyarylate compositions.

sets reflecting the sensitivity of the glass transition temperature to the isophthalate content. Apparent activation energies for the α relaxation range from 825 kJ/mol (50 Hz) to 300 kJ/mol (100 kHz), which is consistent with the highly-cooperative nature of this relaxation. The β relaxation data display a linear Arrhenius dependence which is in agreement with the results reported by Starkweather and Avakian[13] and which is characteristic of sub-glass relaxations in general.[17] The apparent activation energy for the 50/50 ISO/TA sample is 59 kJ/mol, while the apparent activation energy for the 75/25 ISO/TA specimen is 66 kJ/mol: these values are somewhat higher than the figure reported by Starkweather[13] of approximately 45 kJ/mol for a 50/50 ISO/TA sample.

Dielectric measurements for both samples were analyzed using the Havriliak–Negami modification of the single relaxation time Debye expression:[12]

$$\epsilon^* = \epsilon_U + \frac{(\epsilon_R - \epsilon_U)}{[1 + (i\omega\tau)^{\beta'}]^{\alpha'}} \tag{1}$$

where ϵ_R and ϵ_U represent the relaxed ($\omega \rightarrow 0$) and unrelaxed ($\omega \rightarrow \infty$) values of the dielectric constant, ω is the frequency, τ is the central relaxation time, and β' and α' represent the broadening and skewing parameters, respectively. When $\beta' = 1$, eq 1 reduces to the Davidson–Cole[18] expression corresponding to a dispersion in the shape of a skewed semicircle, while for $\alpha' = 1$, a symmetric arc results (Cole–Cole[19] form). When both β' and α' are equal to unity, the Debye expression is recovered. Argand diagrams plotting dielectric loss ($\epsilon'' = \epsilon' \tan \delta$) versus dielectric constant were constructed at selected temperatures in the vicinity of both the α and β relaxations and are shown in Figures 5 and 6 for the 50/50 ISO/TA sample. The five parameters inherent to eq 1 [ϵ_R, ϵ_U, τ, β', α'] were determined at each temperature of interest by a least-squares curve-fitting approach, with initial values for the parameters estimated using the method outlined in ref 12; the best-fit curves which resulted are included in Figures 5 and 6. The dielectric relaxation intensity ($\Delta\epsilon = \epsilon_R - \epsilon_U$) is plotted versus temperature for both polymers in Figure 7, and the values of the broadening and skewing parameters (β' and α') are provided in Figure 8.

Examination of Figure 5 reveals a high-frequency skewing in the case of the α relaxation which corresponds to values of the Havriliak–Negami parameters which are less than unity; the data shown for the 50/50 ISO/TA sample are representative of the results obtained for both polyarylate compositions and are consistent with the dielectric data reported by Alegria et al.[10] In the vicinity of the α relaxation, the broadening and skewing parameters show an initially strong temperature dependence for both polymers and approach constant values at the highest temperatures examined: for 50/50 ISO/TA, $\alpha' \rightarrow 0.30$ and $\beta' \rightarrow 0.90$, while for 75/25 ISO/TA, $\alpha' \rightarrow 0.35$ and $\beta' \rightarrow 0.80$ (Figure 8). These values are similar to Havriliak–Negami parameters reported for Bisphenol A polycarbonate[12] and amorphous poly(ethylene terephthalate),[20] for example.

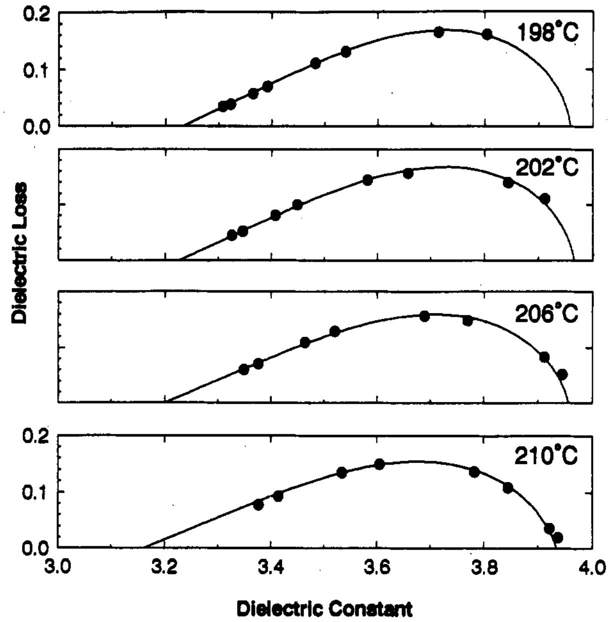

Figure 5. Argand diagrams for 50/50 ISO/TA polyarylate in the vicinity of the α relaxation. Solid curves represent best fits to the Havriliak–Negami equation.

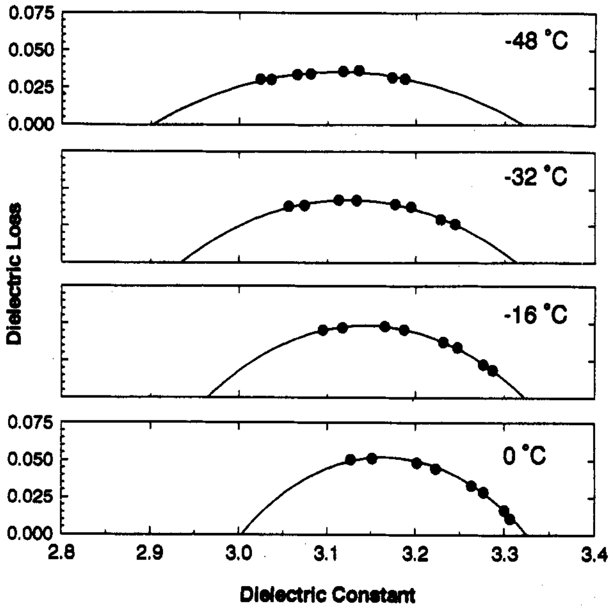

Figure 6. Argand diagrams for 50/50 ISO/TA polyarylate in the vicinity of the β relaxation. Solid curves represent best fits to the Cole–Cole equation.

For the sub-glass β relaxation, a symmetric response is observed so that the dispersion can be described by the Cole–Cole form of eq 1 ($\alpha' = 1$; see Figure 6). The values obtained for the broadening parameter are comparable for both polyarylates and range from $\beta' \sim 0.20$ to $\beta' \sim 0.40$; the steady increase in the broadening parameter with temperature reflects a gradual narrowing of the relaxation (narrowing distribution of relaxation times) and is accompanied by a systematic decrease in the dielectric relaxation intensity (see below).

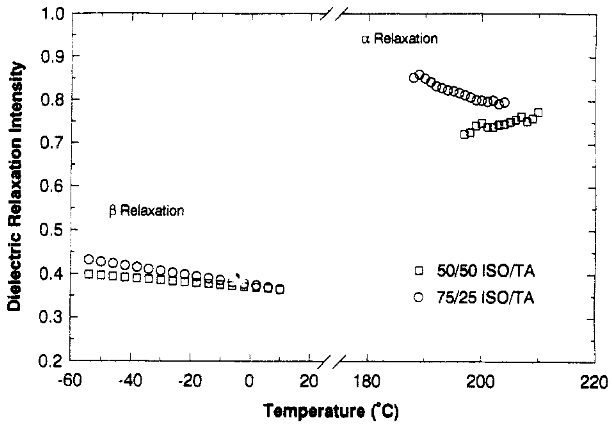

Figure 7. Dielectric relaxation intensity versus temperature (°C) for the α and β relaxations. (□) 50/50 ISO/TA and (○) 75/25 ISO/TA polyarylate compositions.

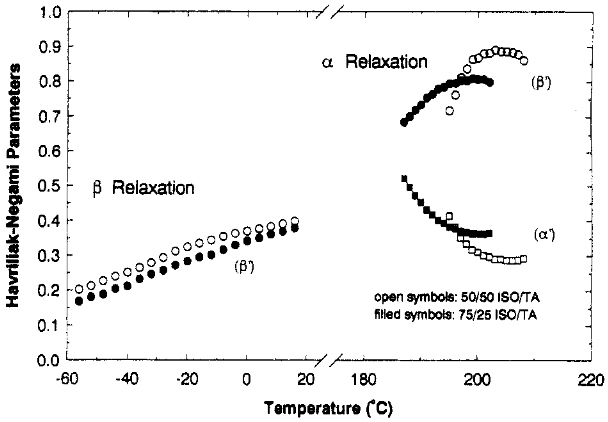

Figure 8. Havriliak–Negami parameters versus temperature (°C) for the α and β relaxations. (○/●) broadening parameter, β′; (□/■) skewing parameter, α′. Open symbols: 50/50 ISO/TA polyarylate. Filled symbols: 75/25 ISO/TA polyarylate.

Consideration of the dielectric relaxation intensity as a function of polymer composition and temperature (α relaxation; Figure 7) reveals a stronger dipolar response for the 75/25 ISO/TA polyarylate sample as compared to the 50/50 material (see also values of $\Delta\epsilon(T_\alpha)$; Table 1). This result corresponds to an overall lower value of the Onsager–Kirkwood correlation factor (g)[17] for the 50/50 ISO/TA specimen and is consistent with the presence of local dipolar cancellations in those terephthalic acid units which maintain a correlated, *trans* conformation along the polymer backbone. In addition, contrasting intensity–temperature behavior is observed for the two materials, the dielectric relaxation intensity decreasing with increasing temperature for the 75/25 ISO/TA sample and increasing with temperature for the 50/50 composition. In the case of the 75/25 ISO/TA sample, the decrease in the relaxation intensity with temperature reflects a gradual decrease in the orientational polarizability of the responding dipoles with increasing thermal energy: above the glass transition, increasing temperature leads to a disruption or randomization in the orientation of the dipoles relative to the alternating electric field, and this results in a net reduction in measured dipolar response. For the 50/50 ISO/TA polyarylate, two competing effects appear to influence the intensity–temperature behavior. First, the decrease in orientational polarizability with increasing temperature which dominates for the 75/25 material should similarly impact the 50/50 ISO/TA result. Second, however, it appears that increasing temperature may ultimately lead to a decrease in local dipolar correlations (i.e., cancellations) in the terephthalic acid groups, thus producing a net increase in the measured dipolar response. In fact, the two phenomena are likely occurring simultaneously in both polymers in the temperature range above the glass transition. For the 75/25 ISO/TA polyarylate (lower TA content) the orientational polarizability effect is dominant, while in the 50/50 ISO/TA sample (higher TA content) the reduction in local dipolar correlations governs the observed response.

The dielectric relaxation intensity values obtained for the β relaxation display relatively little sensitivity to polymer composition, with the measured relaxation intensities nearly superimposable for the two polyarylates. This result is consistent with a highly-localized, noncorrelated origin for the relaxation, the constituent dipoles responding independent of polymer chain microstructure. Both polymers display a decrease in the β relaxation intensity with increasing temperature.

Conclusions

A detailed investigation of the dielectric relaxation characteristics of two amorphous Bisphenol A polyarylates has been accomplished for both the glass–rubber (α) and sub-glass (β) relaxations; the two polymers differed in the relative proportion of isophthalic to terephthalic acid groups incorporated in the chain backbone. Introduction of a high fraction of the *meta*-connected isophthalic acid moiety resulted in a decrease in the glass–rubber relaxation temperature based on comparison of the 75/25 and 50/50 ISO/TA compositions and an increase in the measured dielectric relaxation intensity ($\Delta\epsilon$); this latter result was consistent with the presence of correlations across the terephthalic acid units which lead to local dipolar cancellations and thus a weaker response for the 50/50 material. Examination of the dielectric relaxation intensity as a function of increasing temperature revealed an increase in $\Delta\epsilon$ for the 50/50 composition which suggested a gradual reduction in the degree of local correlation at temperatures above T_g.

The dielectric results for the β relaxation were consistent with highly-localized, noncooperative motions along the polymer chains. The β dispersion was symmetric in shape when plotted on a Cole–Cole basis, in contrast to the skewed appearance of the α relaxation. The difference in composition for the two polyarylates was manifested in a lower sub-glass relaxation temperature for the 50/50 ISO/TA sample as compared to the 75/25 material. Both polymers displayed an Arrhenius frequency–temperature dependence, with the measured apparent activation energies reflecting an essentially noncooperative process. The measured β relaxation intensities for the two materials were virtually indistinguishable (i.e., composition independent), suggesting a lack of ester dipole correlation for the local motions inherent to the sub-glass relaxation.

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Registry Nos. Author Supplied. Bisphenol A–isophthalic acid–terephthalic acid (copolymer), 26590-50-1; Bisphenol A–isophthalic acid–terephthalic acid (SRU), 39281-59-9.