Dielectric Relaxation Studies of Poly(4-hydroxybenzoic acid) and Copolyesters Based on 4-Hydroxybenzoic Acid and 6-Hydroxy-2-naphthoic Acid

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ABSTRACT: Dielectric relaxation measurements have been performed for two samples of 4-hydroxybenzoic acid homopolymer (PHBA) of different molecular weight and copolymers composed of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) with molar ratios of 73/27, 58/42, and 30/70 HBA/HNA, respectively; the materials were investigated at frequencies ranging from 0.4 kHz to 4 MHz at temperatures ranging from −100 to +480 °C (homopolymer) and −100 to +250 °C (copolymers). The homopolymer displays two dipolar relaxations with increasing temperature: a shallow, frequency-dependent relaxation process at low temperatures, which corresponds to motion of the HBA ester dipoles in noncrystalline regions of the material, and a stepwise increase in dielectric constant for all frequencies at ca. 340 °C, which corresponds to the first high-temperature transition in DSC. The characteristics of the latter transition are in excellent agreement with existing X-ray diffractometry and NMR results. The copolymers display two (frequency-dependent) relaxation processes with increasing temperature over the investigated frequency range: the lower temperature γ relaxation follows an Arrhenius-type behavior that is virtually identical with that observed for the low-temperature relaxation in the PHBA homopolymer and that corresponds to rotation of the HBA units, while the higher temperature β relaxation displays isochronal loss maxima that can be described by a WLF-type relationship and that appears to correspond to a combination of both rotational and translational motions. Applications of the Onsager equation based on a model of full, unhindered ester dipole rotation for the various relaxations described above reveals measured dielectric strengths that are well below those expected for free rotation, indicating local conformational ordering that restricts the orientation of successive ester groups. Comparison of the (normalized) relaxation strengths for the γ transition in the copolymers with that observed at the high-temperature PHBA transition indicates that the local conformations and rotational motions of the HBA moieties in the copolymers are nearly identical with those present in the high-temperature phase of PHBA above ca. 340 °C. The increased dipolar relaxation strength observed for the β relaxation relative to the γ relaxation reflects a decrease in such conformational constraints at higher temperatures.

Introduction

The homopolyester of 4-hydroxybenzoic acid (PHBA) and its associated copolyesters have been the subject of considerable study in both industrial and academic research settings, as investigators seek to understand structure–property relationships and develop optimum processing techniques that take full advantage of the outstanding high-temperature characteristics of these materials.[2,3] One of the most prominent groups of polymers in this class is the copolyesters based on 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) developed by Celanese, which is the basis for their Vectra family of resins.[4] In this work, dielectric relaxation measurements have been performed for samples of the PHBA homopolymer and for a series of HBA/HNA copolymers over a wide range of frequency and temperature in order to examine polymer chain dynamics in the solid phase. Specifically, the dielectric properties of two PHBA samples of varying molecular weight were investigated at frequencies of 0.4 kHz to 4 MHz over a temperature range of −100 to +480 °C. In addition, three copolymer compositions of 73/27, 58/42, and 30/70 HBA/HNA were investigated at temperatures of −100 to 250 °C. The PHBA homopolymer, which is a highly crystalline material, displays a shallow relaxation at low temperature and a stepwise increase in dielectric constant for all frequencies at the high-temperature crystal-to-smectic E transition, while the copolyesters display two solid-phase relaxations with increasing temperature that appear to correlate with localized rotations of the HBA units and combined rotations and translations of chain segments, respectively. These results are consistent with previously reported (lower frequency) dielectric and dynamic mechanical data for the copolymers and are in qualitative agreement with existing NMR studies on the PHBA homopolymer.

Background

PHBA Homopolymer. The highly crystalline PHBA homopolymer is very difficult to process by conventional methods.[2] The material displays two high-temperature transitions at 340 and 430 °C[5] (the upper transition has also been reported at 445 °C[6]); Yoon and co-workers[5] have identified these transitions as crystal-to-smectic E and smectic E-to-smectic B, while Economy et al.[6] have described the two high-temperature phases as a plastic crystal (or highly ordered smectic) and a nematic mesophase. The transition at 340 °C is accompanied by a dramatic increase in the volume of the unit cell as measured by X-ray diffractometry, the phenyl groups packing locally in an orthorhombic herringbone array with successive phenyl planes staggered by approximately 120° along the chain axis.[5] At 430 °C, Yoon et al.[5] report the loss of long-range orthorhombic coherence in the phenyl packing, which is consistent with a smectic E-to-smectic B (orthorhombic-to-hexagonal) transition; no nematic structures are observed. Coulter et al.[7] have also reported X-ray results and modeling analyses that are very close to those of Yoon et al.,[5] although somewhat different in the choice of local torsional angles around the phenylene groups. More recently, Kricheldorf and Schwarz[8] reported X-ray patterns obtained with synchrotron radiation at temperatures up to 500 °C that confirm the previous results of refs 5 and 7.

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NMR investigations have probed the possibility of localized motions occurring in the PHBA homopolymer over a wide range of temperatures.[9-11] At 25 °C, both ^1H NMR and ^{13}C (CP/MAS) spectra reflect a highly rigid structure, but above 120 °C, a significant narrowing of the proton spectrum is observed, indicating the onset of molecular motion about the twofold axis of the phenylene units. Over the temperature range 120–260 °C, progressive narrowing of the proton spectrum continues, with evidence of considerable motional heterogeneity; by 300 °C, the entire population of rings is undergoing rapid flipping motions. The ^1H NMR results contrast the ^{13}C investigations, in which the carbonyl carbon was enriched in order to determine whether the carbonyl group moves in concert with the phenyl ring reorientations. From −196 to +340 °C, no change is observed in the ^{13}C spectrum, thus indicating that the phenyl rings are moving independently of the carbonyl groups, which remain fixed. At the high-temperature (340 °C) transition, the lattice expands, and the entire repeat unit is seen to participate in 180° jumping motions about the chain axis which are consistent with the twofold orientational disorder proposed above.[5,7] Limited dielectric data reported by Yoon et al.[5] and Economy et al.[12] are also consistent with these results, as they indicate virtually no dipolar relaxation response below the 340 °C transition temperature, with a significant increase in measured dielectric constant once the transition temperature is reached.

HBA/HNA Copolymers. The thermal transition characteristics of the HBA/HNA copolymers are well established. Results by Cheng[13] detail kinetic studies of the mesophase transitions for copolymers composed of 75/25, 58/42, and 30/70 HBA/HNA; these materials display melting temperatures of 291, 248, and 306 °C, respectively. Combined thermal and compositional analysis by Mühlebach and co-workers[14] reveals a crystal-to-nematic transition temperature for the Vectra 73/27 HBA/HNA copolymer of 285 °C.

Dielectric studies on samples of composition 73/27 and 30/70 HBA/HNA at frequencies of 1 Hz to 10 kHz (−80 to +150 °C) by Alhaj-Mohammed et al.[15] reveal three relaxation processes with increasing temperature that correspond to localized motion of the HBA units (γ relaxation), localized motion of the HNA units (β relaxation), and a glass transition (α relaxation); the α and β relaxations appear to merge at frequencies above 100 Hz. These data are consistent with dynamic mechanical results reported by Troughton and co-workers[16] for the same compositions and dielectric data reported by Takase et al.[17] for 75/25 HBA/HNA. In the case of the dynamic mechanical data, which were recorded at 10 mHz to 10 Hz, the low-temperature γ transition is very weak.

The assignment of the γ and β relaxations to motions involving distinct HBA and HNA segments, respectively, is based on observed changes in the relative intensities of these two relaxations with varying composition;[15,16] both the dielectric and mechanical loss data indicate a decrease in the intensity of the γ transition and an increase in the intensity of the β transition with increasing HNA content. As suggested by Hummel and Flory,[18] if one assumes that resonance stabilization at the carbonyl sites is sufficient to prevent rotation about the carbonyl–aromatic carbon bonds, then motion of the permanent dipoles about the polymer chains is possible only when rotation occurs at the ether oxygen–aromatic carbon linkages. Thus, the relevant dielectric rotational entities will be entire HBA or HNA units, which is consistent with the observations described above. The assignment of the HBA/HNA relaxations, which was originally proposed by Yoon and Jaffe,[19] was confirmed for the β relaxation via combined dielectric and mechanical studies by Blundell and Buckingham[20] on three HBA/HNA-type copolymers in which the naphthyl group–ester linkage was varied, thereby removing the permanent dipole associated with naphthyl motion for two of the samples. The three polymers, which contained the same proportions of naphthalene and phenyl units, each displayed three separate dynamic mechanical relaxations with increasing temperature. However, the two samples for which no net dipole moment was expected with naphthyl group rotation showed a systematic absence of the β transition, thus establishing a direct relationship between that relaxation and localized motion of the HNA-based ester groups.

Experimental Methods

Two samples of PHBA homopolymer were investigated: a commercial material obtained from Polysciences, Inc. (catalog no. 4306), and a sample of slightly lower molecular weight that was synthesized from established methods.[12] Both homopolymer samples were in powder form. Differential scanning calorimetry (DSC) was performed on the PHBA materials under an inert atmosphere using a Du Pont 910 calorimeter; typical sample size was 10 mg, with a heating rate of 20 °C/min. The copolymer samples were obtained through the courtesy of Hoechst-Celanase, with molar compositions of 73/27 (designated Vectra A-900),[14] 58/42, and 30/70 HBA/HNA; these materials were supplied as pellets.

Dielectric relaxation measurements were carried out over the frequency range 0.4 kHz to 4 MHz through the combination of the Hewlett-Packard multifrequency LCR meter Models 4274A and 4275A; the test amplitude at lower frequencies (Model 4274A, 0.4–100 kHz) was 5 V, while the test amplitude at higher frequencies (Model 4275A, 10 kHz to 4 MHz) was 1 V. The homopolymer samples were prepared for dielectric investigation by compression molding plaques from the as-received powder at 440 °C according to the method described by Karis et al.[21] The resulting disks were 25 mm in diameter with a thickness of 1 mm; gold electrodes of 15 mm in diameter were evaporated directly on the samples. The copolyesters were prepared by pressing individual resin pellets at flow temperature between glass slides upon which aluminum test electrodes had been previously evaporated; the samples were then quenched to room temperature. The electrode diameter was 11 mm, with a sample thickness of approximately 0.1 mm. At least three test samples were prepared for each copolymer composition, with a reproducibility of ±2% observed for the measured values of the dielectric constant and loss at room temperature.

Dielectric constant (ϵ') and loss (ϵ'') were measured over the temperature range −100 to +480 °C for the homopolymer samples, −100 to +200 °C for 73/27 and 58/42 HBA/HNA, and −100 to +250 °C for 30/70 HBA/HNA. All samples were placed in a brass testing cell that included a thermocouple mounted at the sample and were heated from below in a nitrogen atmosphere using a hot plate and controller assembly: the heating rate in all cases was 10 °C/min. In order to cover the full frequency range offered by the two HP LCR meters, two successive heating sweeps were required. Over the temperature range of investigation employed for the copolymers, the dielectric data showed no influence of annealing. The PHBA homopolymer does tend to degrade above 450 °C, however, so dielectric sweeps for these samples were performed initially over the range −100 to +200 °C, with a final (high-frequency) sweep taken to the highest temperatures.

Results

The DSC sweeps for the two PHBA homopolymers are provided in Figure 1. The Polysciences sample displays two distinct transitions at 350 and 440 °C, which are characteristic of high molecular weight samples as reported previously.[5,6,8] The sample synthesized in-house shows similar features, with endothermic peak minima of 345

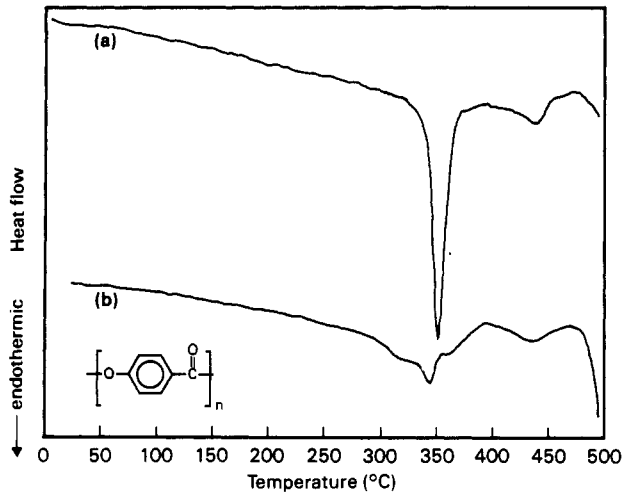

Figure 1. Differential scanning calorimetry (DSC) curves for PHBA homopolymers measured at 20 °C/min heating rate: (a) commercial Polysciences sample; (b) sample prepared in-house.

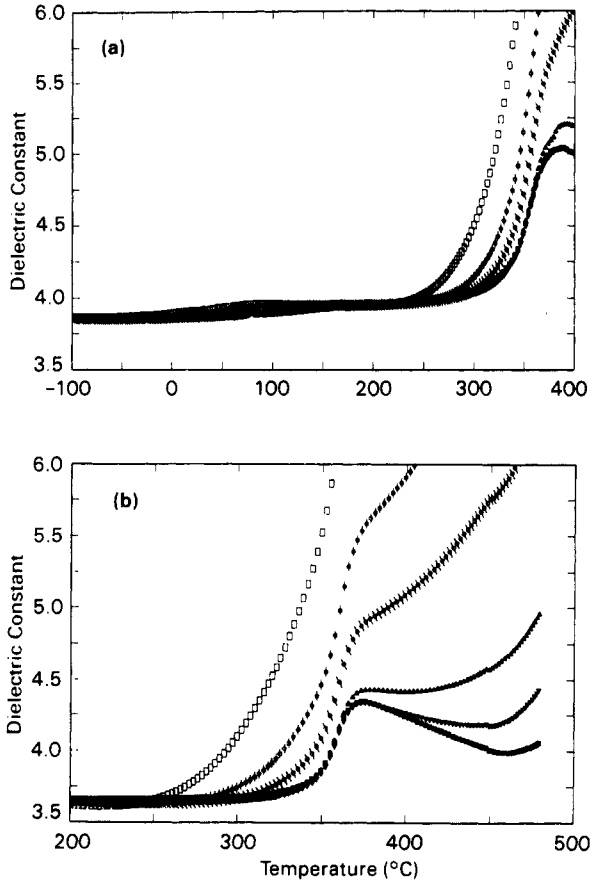

Figure 2. Dielectric constant (ϵ') versus temperature (°C) for Polysciences PHBA samples: (a) −100 to +400 °C; (b) 200 to 480 °C. (□) 10 kHz; (ϕ) 40 kHz; (⊗) 100 kHz; (▲) 0.4 MHz; (▼) 1 MHz; (■) 4 MHz.

and 435 °C; the downward shifting and increased breadth of the endotherms for the latter case suggest a lower overall degree of polymerization and a somewhat higher polydispersity as compared to the commercial material.[6]

Dielectric results for the Polysciences PHBA are provided as plots of dielectric constant versus temperature in Figure 2. In Figure 2a, data are shown for a sample heated from −100 to +400 °C. Below 250 °C, ϵ' is virtually independent of temperature and frequency, with only a shallow (frequency-dependent) relaxation process evident from 0 to 150 °C. Above 250 °C, the dielectric constant measured at 10, 40, and 100 kHz begins to increase due

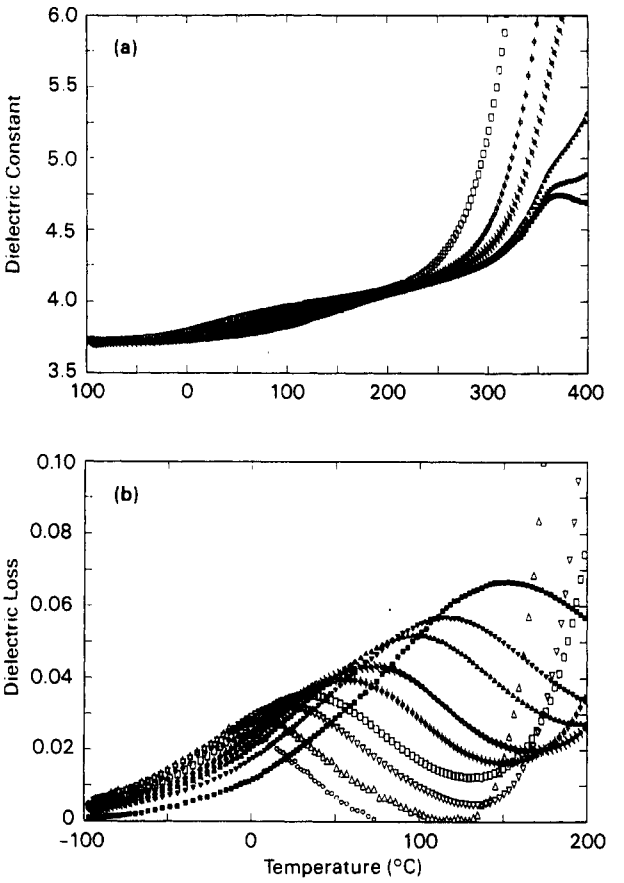

Figure 3. Dielectric results for PHBA sample prepared in-house: (a) dielectric constant (ϵ') versus temperature from −100 to +400 °C; (b) dielectric loss (ϵ'') versus temperature from −100 to +200 °C. (○) 0.4 kHz; (△) 1 kHz; (▽) 4 kHz; (□) 10 kHz; (ϕ) 40 kHz; (⊗) 100 kHz; (▲) 0.4 MHz; (▼) 1 MHz; (■) 4 MHz.

to ionic conduction. The higher frequency data (0.4, 1, and 4 MHz) remain nearly constant until approximately 325 °C, at which temperature a stepwise increase in ϵ' is observed for all frequencies. The magnitude of this increase is identical for the two highest frequencies (1 and 4 MHz) for which the ionic conduction effect appears negligible. The apparently larger increases at lower frequencies seem to reflect more serious contributions of the conduction effects. Dielectric data for an additional Polysciences PHBA sample that extend to higher temperatures are shown in Figure 2b. These data are consistent with those described above, with no obvious transitions observed in the high-frequency dielectric constant over the range 370–480 °C.

Dielectric results for the lower molecular weight PHBA are provided in Figure 3. These data display a significant relaxation over the range −100 to +200 °C (see Figure 3a) as well as the high-temperature increase in dielectric constant observed for the Polysciences material. In order to fully investigate the lower temperature relaxation, successive low-frequency (0.4–100 kHz) and high-frequency (10 kHz to 4 MHz) heating sweeps were performed on an additional sample over the range −100 to +200 °C; the corresponding loss data are shown in Figure 3b. Finally, a full (high-frequency) sweep was carried out up to 400 °C. The loss data display a single relaxation of relatively low intensity, which is most likely due to dipolar motions occurring in noncrystalline regions of the sample. When the loss maxima from the isochronal sweeps are plotted in an Arrhenius manner, a linear result is obtained with a corresponding activation energy of approximately 14 kcal/mol. These PHBA loss maxima are represented

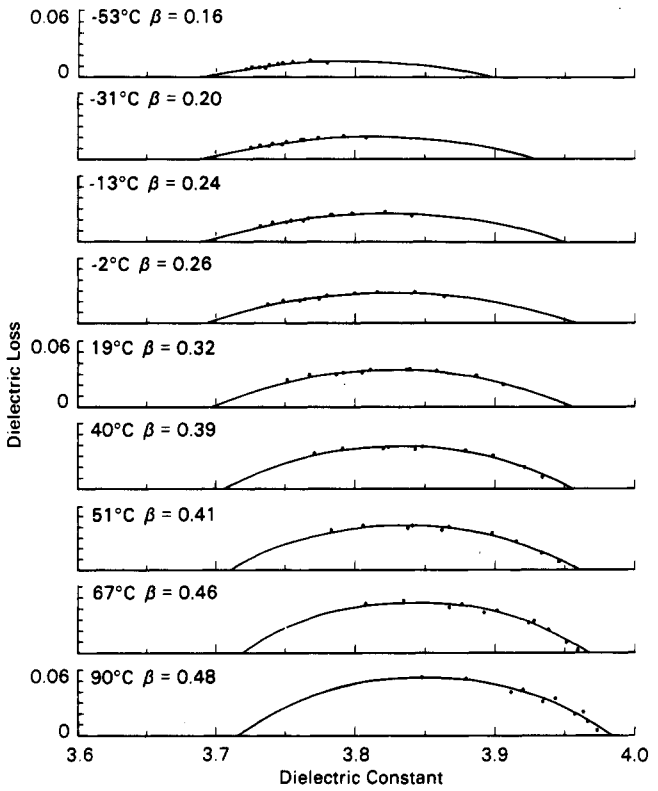

Figure 4. Argand plots for PHBA sample prepared in-house at different temperatures between −53 and +90 °C. Semicircular arcs represent the least-squares fits to the Cole–Cole equation.

by the (best fit) dashed line in Figure 9.

Argand plots of dielectric loss versus dielectric constant in the region of the low-temperature PHBA relaxation reveal a symmetric behavior with considerable Cole–Cole broadening (Figure 4). These data can be described by the Cole–Cole equation

$$\epsilon^* = (\epsilon_r - \epsilon_u)/(1 + (i\omega\tau)^{\beta}) \quad (1)$$

where ϵ^*, the complex dielectric constant, is related to the relaxed and unrelaxed values of the dielectric constant (ϵ_r, ϵ_u), the frequency (ω), a central relaxation time (τ), and a symmetric broadening parameter (β); the semicircular arcs in Figure 4 represent least-squares fits. The broadening parameter is found to be a strong linear function of temperature for this relaxation, β varying from 0.16 (−53 °C) to 0.48 (90 °C; refer to Figure 4); a β value of unity corresponds to the single relaxation time Debye case.

The measured values of the dielectric constant (ϵ') and loss (ϵ'') plotted as a function of temperature are provided for the copolymers in Figures 5–7. The dielectric constant displays a broad, frequency-dependent increase for each copolymer over the range −100 to +200 °C (see values of the dielectric increment, $\Delta\epsilon$, Table Ia), with an additional increase observed at higher temperatures due to the onset of ionic conduction. Examination of the loss data reveals two overlapping dipolar relaxations with increasing temperature; these two relaxations merge into a single feature at the highest frequencies investigated. The dramatic increase in dielectric loss that is observed above the second relaxation is the result of ionic conduction, which is particularly strong for the 30/70 copolymer composition. Comparison of the intensities of the two relaxations as a function of composition reveals that the lower temperature relaxation (designated the γ relaxation) decreases in intensity with decreasing HBA content relative to the higher temperature (β) relaxation. Quantitative assessment of the two relaxations is difficult at this point,

Table I
Summary of Dielectric Relaxation Strength for HBA/HNA Copolymers as a Function of Copolymer Compositions

(a) Total Dielectric Increment[a] and Separated Values for the γ and β Relaxations

composition HBA/HNA	$\Delta\epsilon$ (total)	γ	β
73/2	1.31	0.70	0.61
58/42	1.11	0.47	0.64
30/70	0.94	0.20	0.74

(b) Fraction of "Fully Mobile" Dipoles Based on the Onsager Equation

composition HBA/HNA	fraction of "fully mobile" dipoles	
	γ	β
73/27	0.25	0.63
58/42	0.24	0.52
30/70	0.22	0.42

[a] Based on measurements at 1 kHz.

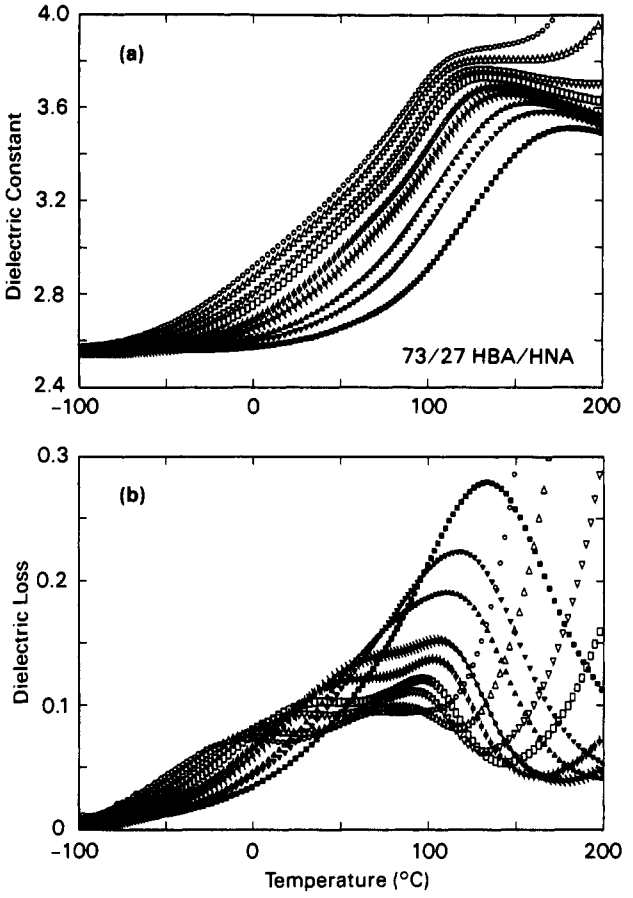

Figure 5. 73/27 HBA/HNA: (a) dielectric constant (ϵ') versus temperature; (b) dielectric loss (ϵ'') versus temperature. (○) 0.4 kHz; (△) 1 kHz; (▽) 4 kHz; (□) 10 kHz; (◇) 40 kHz; (◇) 100 kHz; (▲) 0.4 MHz; (▼) 1 MHz; (■) 4 MHz.

however, owing to the overlap of the loss peaks and the high level of conduction that is encountered at the lower frequencies.

The ionic conduction contribution can be satisfactorily removed from the copolymer loss data by fitting the values of the dielectric loss measured above the β relaxation to an Arrhenius functionality. Specifically, when log (ϵ'') is plotted against reciprocal temperature for the lower frequency data over the range where ionic conduction dominates, a linear result is obtained. This function can be used to remove the ionic conduction contribution over the temperature range where the dipolar loss and the

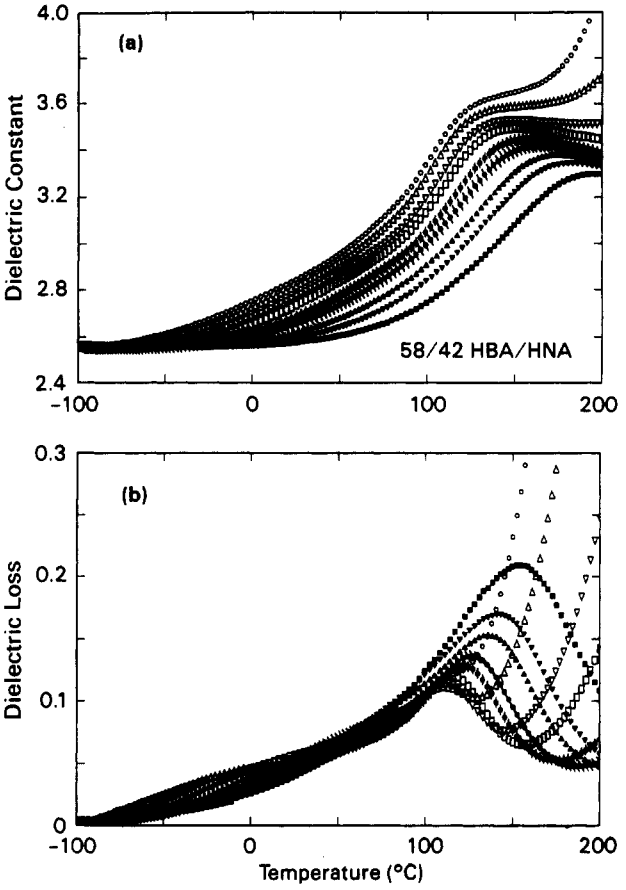

Figure 6. 58/42 HBA/HNA: (a) dielectric constant (ϵ') versus temperature; (b) dielectric loss (ϵ'') versus temperature. (○) 0.4 kHz; (△) 1 kHz; (▽) 4 kHz; (□) 10 kHz; (◇) 40 kHz; (◇) 100 kHz; (▲) 0.4 MHz; (▼) 1 MHz; (■) 4 MHz.

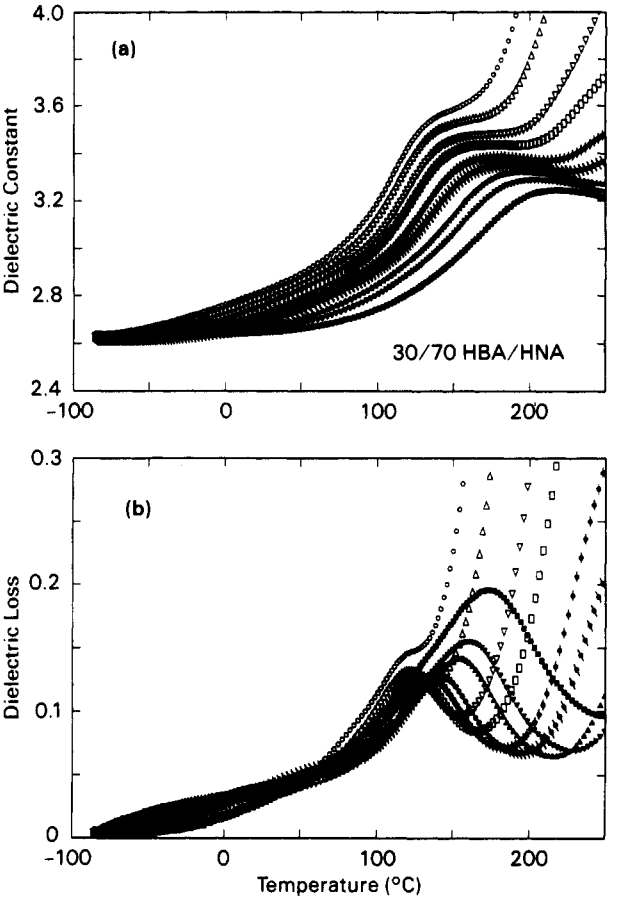

Figure 7. 30/70 HBA/HNA: (a) dielectric constant (ϵ') versus temperature; (b) dielectric loss (ϵ'') versus temperature. (○) 0.4 kHz; (△) 1 kHz; (▽) 4 kHz; (□) 10 kHz; (◇) 40 kHz; (◇) 100 kHz; (▲) 0.4 MHz; (▼) 1 MHz; (■) 4 MHz.

conduction loss are of comparable magnitude. In addition, the lower frequency data can be used to establish the conduction contribution–frequency relationship, which follows a power-law expression of the form $\epsilon'' \rightarrow \omega^a$; the value of the exponent $\{a\}$ is found to lie between –0.65 and –0.70 for the three copolymers. This result is used to correct the higher frequency data for conduction, as the temperature range of the experiments does not extend high enough to allow Arrhenius fitting at all frequencies. An example of the application of the conduction correction is shown in Figure 8a for the 73/27 HBA/HNA copolymer (4 kHz), where both the conduction contribution and resulting loss data are plotted as a function of temperature; conduction-corrected loss data for the 73/27 composition at all frequencies are provided in Figure 8b. While the application of the conduction correction helps to clarify the position of the loss maxima for the β relaxation at the lower frequencies, it does not reveal any additional relaxations.

An Arrhenius plot of frequency versus loss maxima based on the isochronal sweeps for the three copolymers is shown in Figure 9. The positions of the maxima for the γ relaxation are independent of composition and follow a linear relationship with an activation energy equivalent to that observed for the low-temperature PHBA relaxation (note dashed line, Figure 9). The loss maxima associated with the β relaxation are composition dependent, however, with the β relaxation occurring at progressively higher temperatures for the 73/27, 58/42, and 30/70 HBA/HNA copolymers, respectively. These data can be described by a single WLF-type expression

$$\log(\omega) = 28(T - T_0)/\{58 + (T - T_0)\} \quad (2)$$

where the reference temperature T_0 corresponds to a frequency of 1 Hz; T_0 = 66.2 °C (73/27 HBA/HNA), 89.1 °C (58/42 HBA/HNA), and 102.4 °C (30/70 HBA/HNA). The activation energy associated with these data ranges from 33 kcal/mol (73/27 HBA/HNA, 4 MHz) to 85 kcal/mol (30/70 HBA/HNA, 1 kHz).

Argand diagrams for the 73/27 copolymer composition in the temperature range of the γ relaxation are provided in Figure 10, where the semicircular arcs represent least-squares fits to the Cole–Cole equation and are largely representative of the results obtained for the 58/42 and 30/70 HBA/HNA materials, with the data showing a significant degree of Cole–Cole broadening. The limiting values of the dielectric constant (ϵ_r, ϵ_u), the broadening parameter (β), and the central relaxation time (τ) based on the Cole–Cole equation are plotted as a function of temperature for the three copolymers in Figure 11. ϵ_r and ϵ_u are temperature independent, β varies linearly with temperature, and τ can be described by an exponential functionality

$$\tau/\tau_0 = \exp(H/RT) \quad (3)$$

At higher temperatures, there is a sizable overlap between the γ and β relaxations, with the data no longer following symmetric Cole–Cole behavior.

The introduction of the expressions for the various Cole–Cole parameters (ϵ_r, ϵ_u, β, τ) as a function of temperature in eq 1 affords a means for separating the overlapping γ and β relaxations. Specifically, values of the dielectric

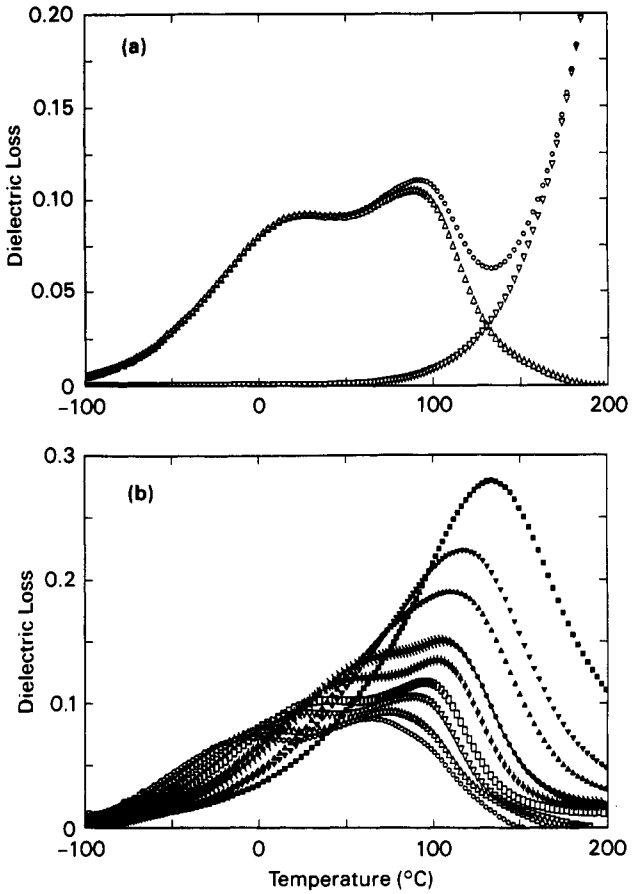

Figure 8. 73/27 HBA/HNA: (a) dielectric loss (ϵ'') versus temperature at 4 kHz corrected for ionic conduction ((○) measured data; (▽) conduction contribution; (△) net dielectric loss); (b) dielectric loss corrected for ionic conduction at various frequencies (see caption of Figure 7 for symbol–frequency correlations).

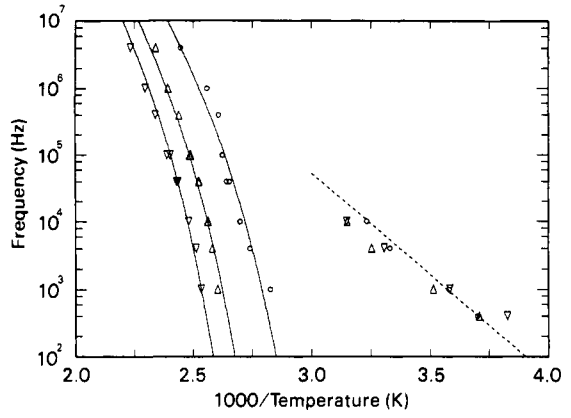

Figure 9. Arrhenius plot for HBA/HNA copolymers based on isochronal temperature sweeps: (○) 73/27; (△) 58/42; (▽) 30/70 HBA/HNA. Broken line represents data from low-temperature PHBA relaxation; solid curves represent WLF fit (see text).

loss are calculated for the γ relaxation over the entire temperature range based on the (low-temperature) parameters developed above and then subtracted from the measured values of ϵ''; the separated result for the copolymers at 10 kHz is shown in Figure 12. The relationship between loss intensity and composition is now clarified, particularly in the case of the β relaxation, which shows a progressive increase in maximum loss intensity with increasing HNA content that is not immediately evident from the raw data. No attempt was made to fit the β relaxation independently through the use of Cole–Cole plots, owing to the broad temperature range across which the γ and β relaxations overlap.

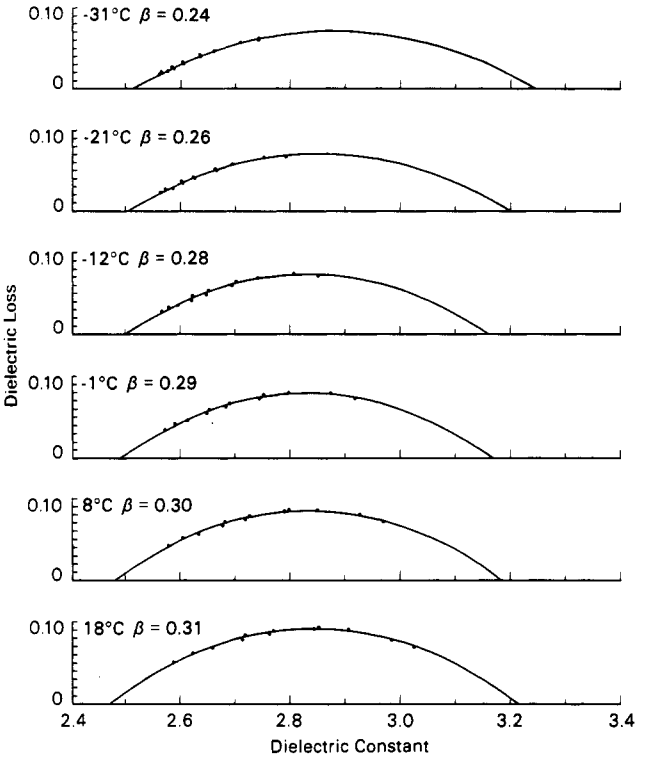

Figure 10. Argand plots for 73/27 HBA/HNA copolymer over the temperature range of the γ relaxation. Semicircular arcs represent the least-squares fits to the Cole–Cole equation.

Discussion

PHBA Homopolymer. The dynamic behavior that is observed for the PHBA homopolymer is consistent with its highly crystalline rigid structure, as only very limited dipolar mobility is evident prior to the first high-temperature DSC transition. The shallow relaxation that is encountered at low temperatures corresponds to motions of the ester groups that occur in noncrystalline regions of the sample; the lower molecular weight, more polydisperse (in-house) PHBA sample displays a higher relaxation strength as compared to the commercial Polysciences PHBA. The locations of the isochronal loss maxima and the corresponding activation energy for this low-temperature relaxation agree remarkably well with the data obtained for the γ relaxation in the copolymers.

Beginning at 325 °C, the highest frequency PHBA data display a stepwise increase in dielectric constant that indicates mobilization of the ester dipoles throughout the sample; this result is most sharply defined for the Polysciences PHBA, which displays a lower degree of ionic conduction as compared to the "in-house" material. The observed stepwise increase is independent of frequency and corresponds to the crystal-to-smectic E transition, as discussed above;[5] this transition is thermodynamic in nature, and as such the temperature at which it is observed does not depend on the frequency of investigation.[22] The dielectric strength associated with the transition is measured to be between 0.7 and 1.0; this range represents the reproducibility for multiple samples. The measured value of the dielectric strength can be compared to that expected for a system undergoing free rotation by application of the Onsager equation, which provides an estimation of the relaxation strength for a mobile, isotropic system with no correlations: i.e., the relaxation strength based on full, unhindered dipolar mobility.[23] The motion associated with the high-temperature transition is assumed to be purely rotational, as suggested by the X-ray diffraction results,[5,7,8,12] which indicate the persistence of a well-

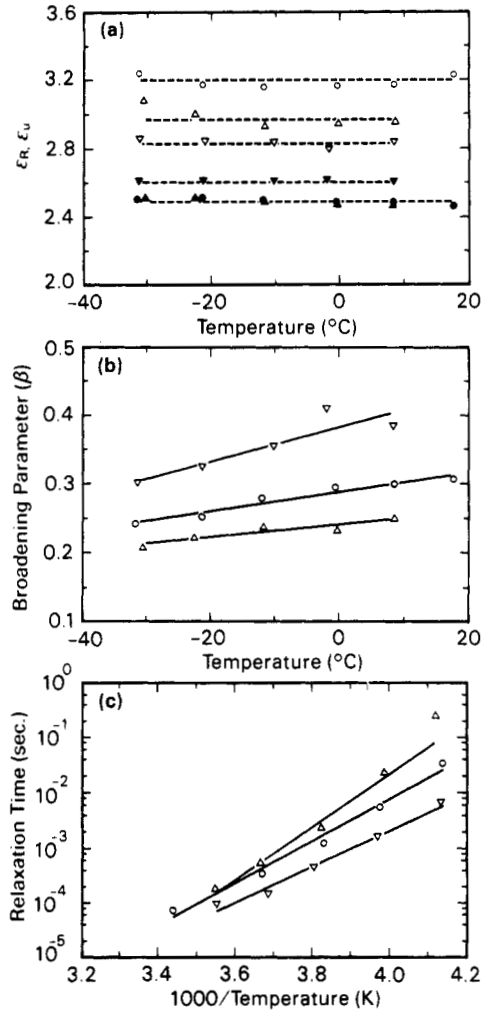

Figure 11. Cole–Cole parameters as a function of temperature for HBA/HNA copolymers based on Argand plots: (a) relaxed (open symbols) and unrelaxed (filled symbols) limits of the dielectric constant versus temperature (°C); (b) Cole–Cole broadening parameter (β) versus temperature (°C); (c) central relaxation time (τ, s) versus 1000/temperature (K). (○) 73/27; (△) 58/42; (▽) 30/70 HBA/HNA.

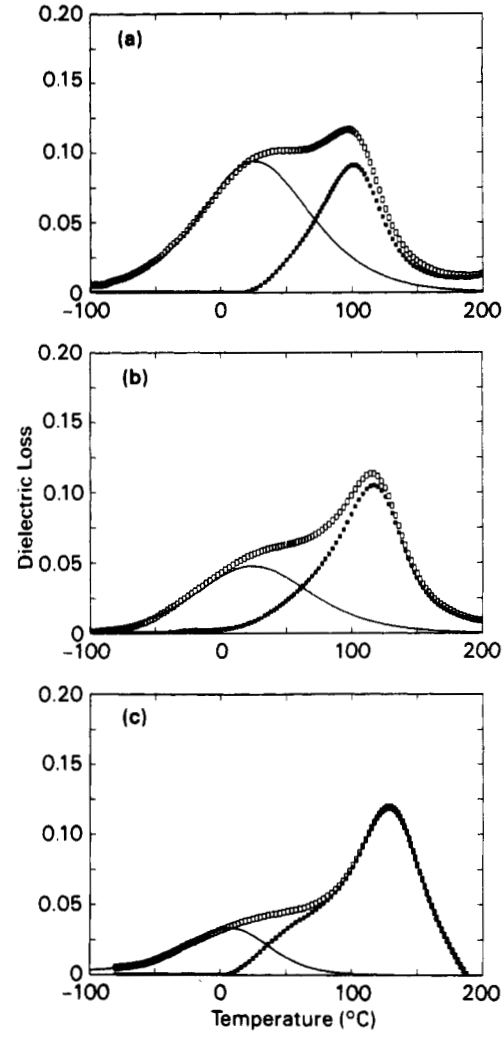

Figure 12. Dielectric loss (ϵ'') versus temperature at 10 kHz: (a) 73/27; (b) 58/42; (c) 30/70 HBA/HNA. (□) measured values; solid line represents Cole–Cole-based curve fit for low-temperature (γ) relaxation; (■) data for β relaxation obtained by difference.

defined lattice across the transition. The condition of global isotropy is satisfied for these samples, as they were formed by compression molding of as-synthesized powders. Adopting the results of Saiz et al.[24] for the magnitude (μ_e = 1.7 D) and orientation (ψ_ϵ = 123°) of the ester dipole vector, a value of 1.43 D is introduced for the ester group dipole moment perpendicular to the chain axis. The PHBA plaque density is taken to be 1.40 g/cm^3,[21] and using a value of 1.0 for dielectric strength, the fraction of "fully mobile" rotating dipoles (measured dielectric strength normalized by calculated dielectric strength) based on the Onsager equation is found to be 0.25. This relatively low value reflects significant cancellation of the ester dipole moments along the polymer chains; in the extreme limit of a 2_1 screw configuration along the chain axis,[25] the dipole vectors would cancel completely. Hence, the value of 0.25 indicates a considerable deviation from this limit for the successive dipole orientations. No additional dielectric relaxation is evident at the higher PHBA transition (~440 °C; see Figure 1), indicating no apparent change in the chain conformations; this result is consistent with the identification of the transition as smectic E-to-smectic B as discussed previously.[5]

HBA/HNA Copolymers. The dielectric data for the HBA/HNA copolymers over the investigated frequency range reveal two relaxations with increasing temperature. The γ relaxation, a secondary transition, is characterized by a frequency dependence that corresponds to an Arrhenian-activated process and that is composition independent. The designated β relaxation corresponds to the merging of an additional secondary process with a glass transition over the investigated frequency range and displays non-Arrhenian behavior that can be described by the WLF equation; the position of the β relaxation is dependent on composition. These data are in excellent agreement with existing results obtained at lower frequency for the same materials[15] and which display a separation of the higher temperature relaxation process.

The individual relaxation strengths of the two loss processes for all compositions are provided in Table Ia; the values for the γ relaxation are obtained from the Argand plots, while the values for the β relaxation are obtained by difference from the overall values of the dielectric increment. The strength of the γ relaxation correlates linearly with the HBA content of the copolymers, while the strength of the β relaxation is less sensitive to composition. An estimate of the relative dipolar mobility of these two relaxations can be obtained by using the Onsager equation in the same manner as was implemented above for the PHBA case. The motion associated with the relaxations is assumed to be purely rotational, which is not unreasonable for highly ordered rigid molecules

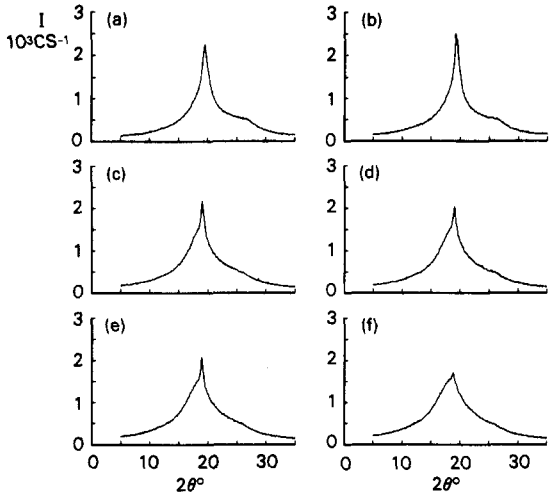

Figure 13. X-ray diffraction results (intensity (10^3 counts/s) versus 2θ°) for 50/50 HBA/HNA: (a) 25 °C; (b) 110 °C; (c) 205 °C; (d) 220 °C; (e) 245 °C; (f) 265 °C.

which are assembled largely parallel to one another. The condition of global isotropy is again satisfied, as these thermotropic materials are typically composed of domain-like microstructures that are highly oriented on a local level but display little long-range order. Introducing a sample density of 1.40 g/cm³ for all copolymer compositions and assuming that the γ relaxation is due entirely to rotations of the HBA units and the β relaxation is due entirely to rotations of the HNA units, one can estimate the fraction of "fully mobile" dipoles for each loss by normalizing the values reported in Table Ia with those calculated from the Onsager equation; these results are provided in Table Ib. The temperature basis for each Onsager calculation is the appropriate loss maximum at 1 kHz (refer to Figure 9).

An examination of the fraction of "fully mobile" dipoles calculated above as a function of composition and relaxation reveals measured relaxation strengths significantly lower than the "fully mobile" values. In the case of the γ relaxation, a strength of approximately one-fourth the free rotation value is realized for all compositions; the linear scaling of the measured relaxation strength with HBA content is consistent with the assignment of this relaxation to motion of isolated HBA units. It is somewhat surprising that the normalized γ relaxation strength is independent of composition. As these materials are random copolyesters,[14] one would expect different degrees of conformational constraint with varying HBA composition; this is not reflected in the results, however. Equally interesting is the observed agreement in the values of the normalized relaxation strength for the γ relaxation of the copolymers as compared to the high-temperature relaxation of the PHBA homopolymer. This result implies that the local conformational constraints and the nature of the reorientational motions in the copolymers are identical with those of the PHBA homopolymer above the first high-temperature transition.

In this regard, comparison of X-ray diffraction patterns recorded for a copolymer of composition 50/50 HBA/HNA originally prepared by Mühlebach[14,26] with the high-temperature results for PHBA[5,7,8] indicates that the analogy between these materials holds for static structural observations as well. Specifically, the diffraction pattern recorded at 25 °C for the copolymer (at which temperature the HBA units are rotationally active) contains the same features as are observed for PHBA above the 340 °C transition (Figure 13a), with a broad peak centered at 19.50° (2θ, d = 4.55 Å), and a shoulder evident at approximately 27° (d = 3.3 Å); these peaks correspond to the 110/200 and 211 reflections of the rotationally disordered orthorhombic cell. (No 00l reflections are expected for the random copolymer.) Upon heating, the copolymer shows little change in structure at 110 °C (Figure 13b), but order is progressively lost as the nematic melt is approached (~250 °C, Figure 13c–f). Moreover, the dynamics of the HBA ester groups, as investigated by Lyerla et al.[27] for a 73/27 HBA/HNA copolymer sample using ^{13}C NMR methods, are found to be consistent with the occurrence of 180° rotational jumps (100 °C); the dynamic characteristics of the copolymer at this temperature are found to be nearly identical with those observed for PHBA above ca. 340 °C.

Examination of the relaxation strengths and fraction of "fully mobile" dipoles for the β relaxation indicates a different situation. The measured values of the dielectric increment (obtained by difference), while increasing with increasing HNA content, do not correlate linearly with composition, thus leading to calculated values of relative dipolar mobility that decrease with increasing HNA fraction. This reflects the fact that the designated β relaxation represents the combination of a secondary transition and a glass transition, the inclusion of translational dipolar contributions offering an explanation for the overall higher values of relative dipolar mobility observed for the β relaxation as compared to the γ relaxation. The X-ray diffraction results are consistent with this apparent increase in conformational freedom, as a decrease in packing order is observed at high temperatures (Figure 13). Linear extrapolation of the calculated fraction of "fully mobile" HNA dipoles to a composition of 0/100 HBA/HNA (PHNA) provides a value of 0.27, which is very close to the values obtained for both the high-temperature PHBA transition and the γ relaxation in the copolymers. This result is important given the similarities in structure and thermal properties observed for the PHBA[5] and PHNA[28] homopolymers.

Examination of the shape of the separated β loss peak at 10 kHz with varying composition (Figure 12) reveals a low-temperature shoulder that becomes more prominent at the higher HNA compositions and that may correspond to isolated HNA rotations. The identification of this feature as an additional relaxation is tentative, however, as both the ionic conduction correction and the γ relaxation Cole–Cole curve fit are required for its observation over the investigated frequency/temperature range. Additional relaxation studies on copolymers of higher HNA content (and PHNA) would be required in order to fully elucidate this aspect of the dielectric loss results.

Conclusions

The dielectric relaxation results obtained for two samples of PHBA homopolymer are in excellent agreement with both thermal and NMR characterizations, and display a number of correlations with data recorded for the HBA/HNA copolymers. A weak, frequency-dependent relaxation is observed at low temperatures for the PHBA, with the isochronal loss maxima following an Arrhenius relationship; the increased strength of this low-temperature PHBA relaxation encountered for the lower molecular weight "in-house" sample indicates that the dipolar motion is most likely occurring in noncrystalline regions of the material. At the first high-temperature transition at ca. 340 °C, a stepwise increase in dielectric constant is observed for all frequencies, with its magnitude independent of frequencies in the range devoid of ionic conduction effects.

This is consistent with existing X-ray diffraction results[5,7,8] for the material that indicate a significant increase in the volume of the unit cell across the transition and the occurrence of 180° rotational jumps of two-monomer repeats around the chain axis.[5] Calculation of the relative dipolar mobility above this transition based on a free-rotation Onsager model provides a fraction of "fully mobile" dipoles of approximately one-fourth, indicating a large degree of conformational constraint that leads to significant cancellation of successive ester dipole moments. The second DSC high-temperature transition at ca. 440 °C is not detected by dielectric measurements, indicating that this transition involves little change in chain conformations and reorientational motions.

The dielectric relaxation measurements performed for the copolymer samples composed of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid reveal two well-defined relaxations in the solid phase with increasing temperature. The lower temperature γ relaxation reflects localized rotational motion of the HBA units. The positions of the isochronal loss maxima and corresponding activation energy for the γ relaxation are in agreement with those observed for the (shallow) low-temperature PHBA relaxation, with a calculated fraction of "fully mobile" dipoles of approximately one-fourth, independent of composition. This value is the same as the result noted above for the high-temperature PHBA transition and suggests that the nature of the local conformations and rotational motions of the HBA esters in the copolymers are essentially the same as those observed for PHBA in the high-temperature (smectic E) phase above ca. 340 °C. The higher temperature β relaxation that is observed for the copolymers appears to reflect a combination of localized HNA rotations and a glass transition that is accompanied by reduced conformational constraints. The isochronal loss maxima follow a WLF-type functionality, and both the positions of the loss maxima and the calculated fraction of "fully mobile" dipoles are dependent upon composition. A complete description of the β relaxation would require additional studies on both copolymers containing a higher HNA content (above 70 mol %) and the PHNA homopolymer.

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