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Study of relaxation mechanisms in structurally related biomaterials by thermally stimulated depolarization currents

Nery Suárez[a,*], Stephen Brocchini[b], Joachim Kohn[b]

[a]*Department of Physics, Universidad Simón Bolívar, Caracas 1081, Venezuela*
[b]*Department of Chemistry, Rutgers, The State University of New Jersey, New Brunswick, NJ 09803, USA*

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Abstract

Thermal-stimulated depolarization current (TSDC) experiments were performed on a series of tyrosine-derived polyarylates with different number of methylene groups in the backbone. The low temperature TSDC spectra (80–240 K) were analyzed at two different degrees of hydration to assess the effects of small amounts of loosely and tightly bound water in the observed complex β band. Higher temperature TSDC spectra (250–350 K) provided the α relaxation peaks associated with the glass transition temperature. The direct signal analysis (DSA) method allowed the deconvolution of the peaks into elementary processes and the determination of their mean relaxation parameters. The variations in the low and high temperature polarization with the number of backbone methylene groups were interpreted as a combination of flexibility and entanglement phenomena. The dielectric manifestation of the disentanglement effects was observed for the case of the longest polymer. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Structurally related polyarylates; Relaxations; Hydration effects

1. Introduction

A better understanding of the structure–property relationships of biodegradable polymers is necessary to facilitate their development for medical applications such as drug delivery and bone fixation. Currently, comparative studies of the structure–property relationships of biodegradable polymers in medicine have not been widely described because of the disparate structures of the polymers used. Recently, a combinatorial library of promising biopolymers comprising 112 tyrosine-derived polyarylates **3** (Fig. 1) was synthesized to examine the structure–property relationship resulting from precise changes in the chemical structure of the polymers [1]. This polyarylate **3** family of polymers was specifically designed for medical applications. The polyarylates **3** are amorphous, strictly alternating copolymers prepared from the polyesterification of tyrosine-derived diphenols **1** and acyclic aliphatic diacids **2** (Fig. 1). Modifications of the polyarylate **3** pendent chain and backbone are accomplished through the choice of diphenol **1** and diacid **2** used in the polymerization reaction, thereby systematically varying the polymer structure in a controlled and predictable manner. These controlled structures were used to determine the influence of structural changes on the local and bulk molecular relaxation processes [2–4]. The molecular relaxations have been shown to affect the numerous properties of the polymer including the hydration effects and material properties such as elastic modulus, mechanical creep and thermal expansion coefficients [4–7].

Thermally stimulated depolarization current (TSDC) is one of several techniques useful for studying secondary relaxation processes and phase transitions over a wide range of temperatures [3,7–14]. The TSDC technique consists of measuring the thermally stimulated discharge currents resulting from the release of polarizations that were frozen in during a previous electric field poling of the dielectric. Key advantages of this technique are its high sensitivity, leading to the detection of very low dipole or carrier concentrations, and its very low equivalent frequency (~1 mHz), allowing multicomponent peaks to be resolved accurately. Low temperature TSDC spectra exhibits a broad peak associated with secondary β relaxation processes while high temperature TSDC spectra results in a sharper α relaxation peak that is associated with the glass transition of the polymer. Using the TSDC technique at temperatures below the freezing point of water, it is possible to identify the position of water molecules within

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* Corresponding author. Address: CCS 90285, P.O. Box 025323, Miami, FL 33102-5323, USA. Tel.: +1-58-2122-840-565; fax: +1-58-2122-862-692.

E-mail address: nsuarez@usb.ve (N. Suárez).

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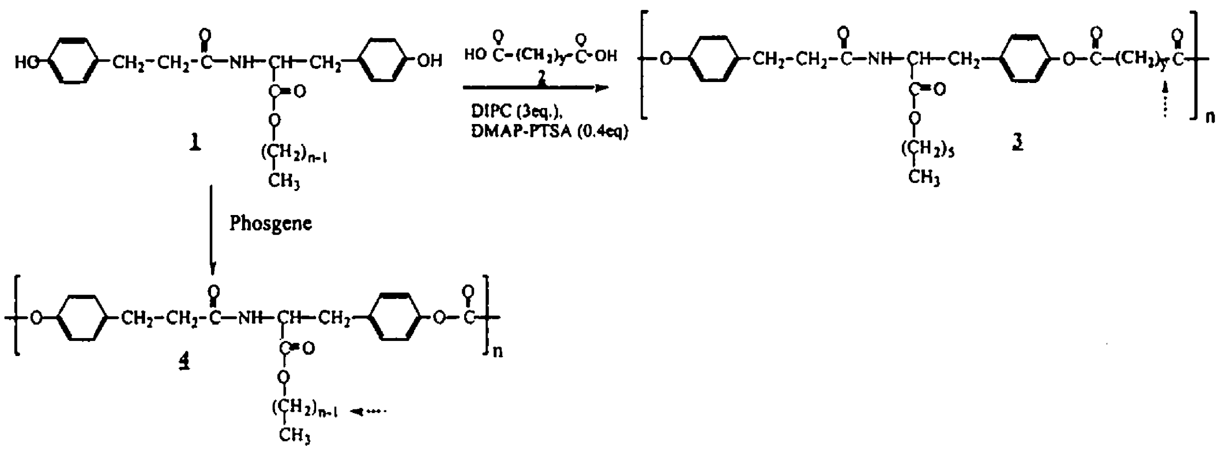

Fig. 1. Tyrosine-derived polyarylates **3** and polycarbonates **4**. The four polyarylates used in this study were modified along the polymer backbone and were derived from the hexyl ester ($n = 6$) of the tyrosine-derived diphenol **1** and the four diacids **2** with $y = 2$, 4, 6 and 8 methylene groups. The polycarbonates **4** used in a previous TSDC study [17] were modified along the pendent chain ($n = 2$, 4, 6 and 8).

the polymeric matrix and to distinguish between tightly and loosely bound water.

There have been several investigations of the fundamental relaxation properties of the polyarylates **3** so that their polymer structure could be tailored to specific applications. A prior study of polyarylates **3** established that the rate of enthalpy relaxation increased with increasing number of methylene groups in the polymer backbone, but was independent of the number of methylene groups in the pendent chain [15,16]. An investigation using TSDC studied hydration effects in poly(DTH succinate) **3** (Fig. 1; $n = 6$, $y = 2$) [7].

This study is designed to complement a prior TSDC study [17] of a related family of tyrosine-derived polycarbonates **4** (Fig. 1) that correlated secondary relaxation processes to increasing numbers of methylene groups in the polycarbonate pendent chain, and to supplement a prior detailed TSDC hydration study of poly(DTH succinate) **3** (Fig. 1; $n = 6$, $y = 2$) [7]. In the present study, high and low temperature TSDC spectra were used to study and correlate relaxation processes with the number of methylene groups in the backbone of the polyarylates **3**. Each of the four polyarylates were used in this study was derived from the hexyl ester of desaminotyrosyl-tyrosine **1** ($n = 6$) which is abbreviated as 'DTH'. The polymers differed only in the number of methylene groups in the backbone due to the precursor diacid **2** ($y = 2$, 4, 6, and 8) (Fig. 1). Each polymer is denoted by combining the abbreviation, DTH and the common name of the precursor diacid **2**, e.g. poly(DTH adipate) was the polymer prepared from succinic acid ($y = 4$). The low temperature TSDC spectra were also analyzed at two different degrees of hydration to assess the effects of small amounts of water. Thus, structural modifications made only in the polymer backbone provided a means to observe differences in the TSDC spectra that could be correlated to these specific changes in polymer properties and compared to the prior studies [7,17].

2. Materials and methods

2.1. Polymer synthesis

The polyarylates were prepared and characterized according to a previously published procedure [18]. Briefly, an exactly equimolar amount of desaminotyrosl tyrosine hexyl ester (**1** in Fig. 1) and the appropriate diacid (**2** in Fig. 1) were suspended in methylene chloride under nitrogen. To this suspension was added dimethyl aminopyridium-*p*-toluenesolfonate (0.4 equiv.) followed by the syringe addition of diisopropylcarbodiimide (2.5 equiv.) after which the reaction generally became clear. After about 1 h, a precipitate became evident. The reaction was stirred for 24–36 h and then was transferred to a separatory funnel and slowly added to a stirred solution of 10 volumes of methanol to precipitate the polymer (**3** in Fig. 1). For further purification, the polymer was dissolved in methylene chloride and twice reprecipitated from isopropanol. The polymer was then dried in vacuum to constant weight.

2.2. Film preparation

Transparent compression molded films were fabricated by placing 0.8 g of the polymer into a mold which was then heated to 50°C above the T_g whose values ranged from 19 to 55°C. A pressure of 2 MPa was applied using a Carver Laboratory Press Model 2625. Pressure was increased to 41 MPa and maintained for 10 min. The plates were water-cooled to room temperature before releasing the pressure on the mold.

2.3. Sample preparation and hydration cycle

Round disc shaped specimens (20 mm in diameter and 400 μm thick) were cut from the polyarylate films. These specimens were coated with evaporated aluminum on both surfaces to diminish the contact resistance between the electrodes and films while collecting the TSDC spectra. Coating also eliminated spurious currents due to electrostatic charges present at the sample surfaces. The discs were then stored in the refrigerator at 283 K four weeks, weighed, and a series of TSDC spectra were obtained. The degree of hydration (h) for these specimen was $h = 0.5\%$ (w/w). Dehydration was accomplished by storing the disc specimen in vacuum (10^{-6} Torr) at 300 K for 24 h. The specimens were weighed and TSDC spectra were obtained. Exposure of dried specimens to a water-saturated atmosphere at 300 K for 24 h was followed by reweighing the discs and obtaining a series of TSDC spectra. Percent hydration was calculated from the weight differences obtained at each step of the hydration cycle. The accuracy of the gravimetric measurements (±0.1 mg) corresponded to (±0.2%) water content.

2.4. TSDC experiments

The TSDC experiments were performed from 80 to 350 K. With this technique, the dipoles are first oriented by applying an electric field at a temperature at witch they are mobile, then the sample is cooled to freeze this polarization, and finally, the field is switched off and the temperature-relaxation phenomena is observed by measuring the depolarization current while the sample is been heated at a constant rate. To examine sub-T_g relaxations separately from relaxation phenomena associated with the glass transition, two polarization temperatures were used. They were carefully chosen in order to orient the species under study and also to isolate two different regions of the spectra. A polarization temperature, T_p, of 228 K was used to examine sub-T_g relaxations over a temperature range of 80 to 240 K. A higher T_p of 328 K was used to examine relaxations over a temperature range of 250–350 K typically associated with the glass transition. To avoid significant differences in aging states, each specimen was heated well above the glass transition temperature and then rapidly cooled (55 K/min) to the desired polarization temperature.

A specimen was placed between two spring-loaded metallic electrodes in contact with the specimen's Al-coated surfaces. The TSDC measuring cell, after being evacuated to 10^{-7} Torr, was filled with dry nitrogen at a pressure of 600 mmHg. The temperature was controlled by immersion of the cell in liquid nitrogen and by heating with a resistive element soldered to the external walls of the cell. The polarizing DC field, E_p 100 kV/m, was applied for 3 min to orient the species under study. With the external field applied, the sample was then rapidly quenched (55 K/min) to 80 K. At this temperature, the field was switched off and the cell was evacuated for a second time and filled with dry helium (100 mmHg), which was used as an interchange gas due to its high purity and good thermal conductivity. A highly sensitive electrometer, Cary 401M, connected in series with the sample, detected the depolarization current density J_D, originating in the variations of the polarization $P(T)$, as the temperature was increased at a controlled, constant rate b, (typically 6 K/min). The sensitivity of the system was 10^{-17} A and the signal to noise ratio was close to 500. The analog output from the electrometer and the temperature were recorded concurrently by a voltmeter scanner and were stored in a PC computer for subsequent analysis.

2.5. Analysis of TSDC spectra

Direct signal analysis (DSA) is a curve fitting procedure developed to analyze complex TSDC peaks. The DSA procedure was used to analyze the TSDC peaks as previously described [14].

3. Results and discussion

The low temperature TSDC spectra were obtained over a temperature range 80–240 K using a polarization temperature of 228 K to ensure that the spectra was isolated from the glass transition. The polymer specimens had two degrees of hydration (h), ca. $h = 0.5\%$ and $h < 0.5\%$ (w/w), respectively [7]. The less hydrated specimen will be referred to as 'dry' or 'non-hydrated' specimen. High temperature TSDC spectra were obtained at 250–350 K using only the dry specimens. In hydrated specimens, diffusion of water was problematic. The TSDC spectra were normalized to the same polarizing field and sample size [14,17]. A representative TSDC spectrum for poly(DTH adipate) ($y = 4$) over both temperature ranges is shown in Fig. 2. The broad peak

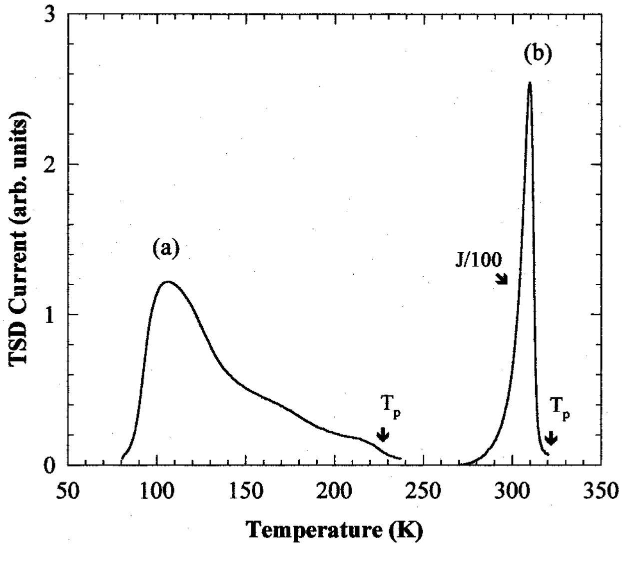

Fig. 2. TSDC spectrum for poly(DTH adipate) ($y = 4$) over both the low and high temperature ranges. The polarization temperatures are indicated.

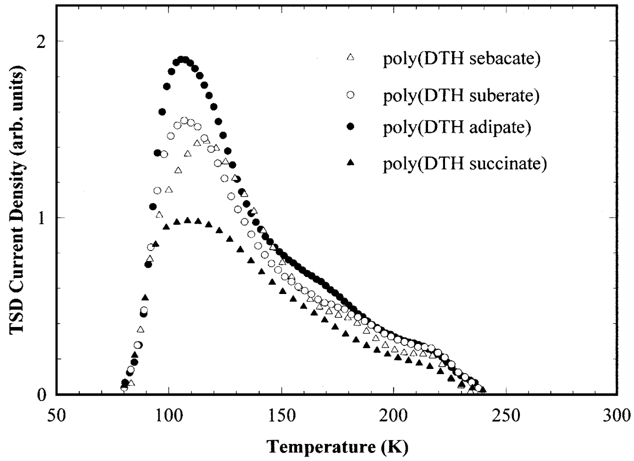

Fig. 3. Superposition of the low temperature TSDC spectra obtained at the low hydration state for each of the four polyarylates.

in the low temperature range is the β band and the sharp signal in the high temperature range is the α peak.

3.1. Low temperature polarization

3.1.1. TSDC analysis of non-hydrated polyarylate specimen

The low temperature TSDC spectra for the non-hydrated polymer samples are shown in Fig. 3. These spectra are the superposition of numerous molecular relaxation processes whose relative and absolute contributions vary as a function of the number of methylene groups in the polymer backbone. Deconvolution of these spectra by DSA gave the individual relaxation processes [14]. These low temperature relaxation processes result from localized motions of molecular segments of variable length molecules. Arrhenius relaxation times were assumed in the analysis of these spectra. Four relaxation processes with Gaussian distributions were determined and labeled in the order of increasing energy as β_1, β_2, β_3, and β_4. These relaxation processes were analogous with those in previous studies of polycarbonates **4** and poly(DTH succinate) [7,17] and was expected since both the polyarylates **3** and polycarbonates **4** are derived from the same tyrosine-derived diols and possess the same dipolar moieties. The identities for each β_i component of the polyarylates **3** was established in prior study of polycarbonates **4** and shown in Fig. 4. The β_1 peak corresponded to the orientable dipoles of the CH_3 end groups on the pendent chain, β_2 peak resulted from the motions of the carbonate carbonyl groups, β_3 peak was associated with the motions of the ester-bonded carbonyl, and the β_4 was assigned to the amide carbonyl. The percent contributions for each β_i component to the total low temperature polarization is shown in Fig. 5. DSA analysis provided the mean energies and Gaussian distribution widths for each β_i component (Table 1).

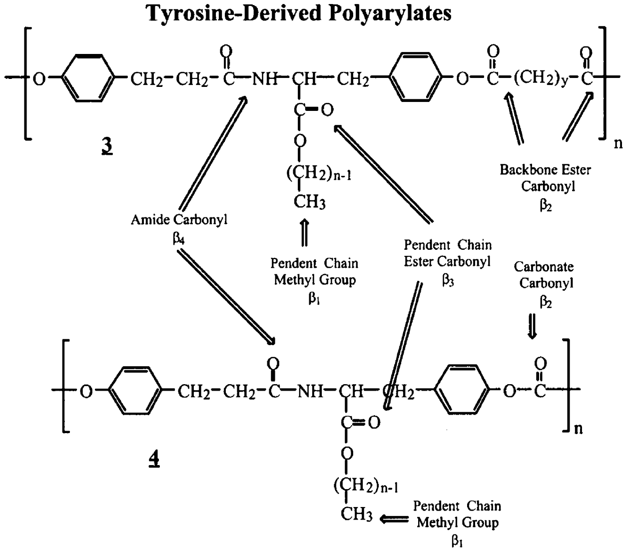

Fig. 4. Structural features in the tyrosine-derived polyarylates **3** and polycarbonates **4** which lead to the dipolar relaxation processes derived by the DSA analysis of the TSDC spectra.

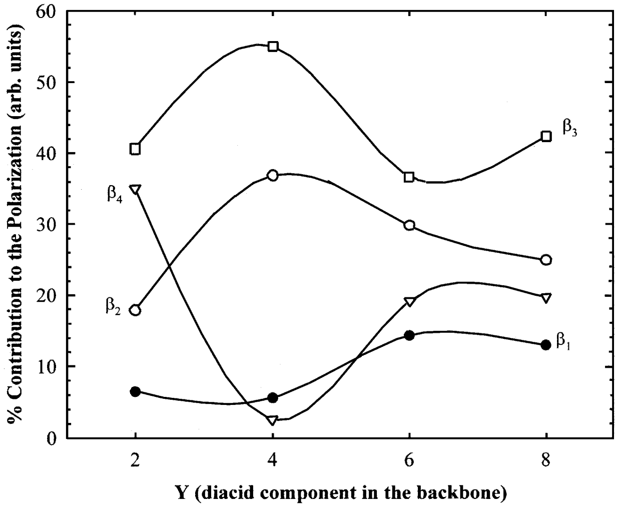

Fig. 5. The contributions for the relative polarization of each β_i component in the low hydrated specimen as a function of the number of methylene groups ($y = 2$–8). The lines are drawn to guide the eye.

The relative contribution of each moiety varied as methylene groups were added to the polymer backbone with each β_i component exhibiting different responses to the addition of methylene groups. The relative contribution of the β_1 process changed little as the number of methylene groups were increased from $y = 2$ to 4. The implication was that the β_1 relaxation process was localized in the polymer matrix and not influenced by the addition of these two backbone methylene groups [4,19]. In contrast at $y = 4$ methylene groups, the relative intensities exhibited by the β_2 and β_3 components were a maximum and for the β_4 component a minimum (Fig. 5).

Enhanced polymer flexibility and cooperative molecular motions were expected as the number of backbone methylene groups was increased. This may account for the

Table 1
Comparison of the mean energies and width distributions for each β_i component obtained from the low temperature TSDC spectra for the four polyarylates in both hydration states. Air–water contact angles were standard sessile drop measurements [1,18] and the densities were measured in a defined volume of a solution of water and sugar

y	Hydration state	$E_{0\beta_1}(\sigma_{\beta_1})$ (eV)	$E_{0\beta_2}(\sigma_{\beta_2})$ (eV)	$E_{0\beta_3}(\sigma_{\beta_3})$ (eV)	$E_{0\beta_4}$ (σ_{β_4}) (eV)	Density (g/cm^3)	θ
2	Non-hydrated	0.17 (0.01)	0.21 (0.03)	0.28 (0.07)	0.41 (0.12)	1.19	81.0
	Hydrated	0.17 (0.02)	0.22 (0.04)	0.36 (0.08)	0.55 (0.05)		
4	Non-hydrated	0.16 (0.02)	0.20 (0.05)	0.31 (0.12)	0.52 (0.02)	1.16	83.7
	Hydrated	0.18 (0.02)	0.23 (0.04)	0.37 (0.08)	0.56 (0.04)		
6	Non-hydrated	0.19 (0.02)	0.24 (0.04)	0.33 (0.07)	0.57 (0.14)	1.14	84.4
	Hydrated	0.19 (0.02)	0.23 (0.04)	0.36 (0.08)	0.56 (0.07)		
8	Non-hydrated	0.19 (0.03)	0.25 (0.04)	0.34 (0.08)	0.59 (0.09)	1.12	90.3
	Hydrated	0.20 (0.02)	0.24 (0.04)	0.36 (0.08)	0.56 (0.06)		

increase in the β_2 contribution as methylene groups increased from $y = 2$ to 4 in the polymer backbone. The β_3 process increased to a maximum at $y = 4$ methylene groups. This process was probably influenced by its proximity to the backbone amide moiety as well as in changes to the polymer flexibility. Small amounts of water may have been loosely associated with the pendent chain carbonyl due to its proximity to the backbone amide [7]. This trace water may have more readily undergone simultaneous dipolar reorientation as the polymer flexibility increased thus heightening the contribution of the β_3 process.

Both inter and intramolecular amide hydrogen bonds with water and differing bound water species were observed in poly(DTH succinate) and other polymers [7,20–22]. These water derived associations were expected to exert a significant influence on the β_4 contribution. For example, tightly bound water lowered the number of reorientable free amide carbonyls for poly(DTH succinate) in the hydrated state causing a decrease in the β_4 contribution. The minimum contribution observed for the β_4 process was may due to increased polymer flexibility allowing greater association of the amide dipole with trace water.

The addition of two more backbone methylene groups ($y = 6$) caused the contributions of the β_1 and β_4 processes to increase and the β_2 and β_3 processes to decrease (Fig. 5). Chain entanglements may have become important with the addition of these two methylene groups. Although entanglement effects in concentrated polymer solutions and melts are observed after a critical molecular weight, changes in polymer structure also effect the onset of entanglements [23,24]. While increased polymer flexibility might be expected to increase chain entanglements, these two types of conformational mobility, e.g. flexibility and entanglement may influence dipolar reorientation processes in an opposing manner. Entanglement points would constrain chain motions and lower the number of reorientable dipoles. This would result in decreased contributions for these dependent processes [17]. Thus, the lower relative contributions of both the β_2 and β_3 processes from $y = 4$ to 6 methylenes may have been due to the onset of chain entanglement effects. However, chain entanglements may disrupt the network of amide hydrogen bonds. This would lead to lower packing efficiency causing an increase the relative number of amide carbonyls participating in the β_4 relaxation process. The result would be an increase contribution of the β_4 process.

The profile of the relative contributions at $y = 8$ methylenes was similar to that at $y = 6$. The β_1 and β_4 contributions remained essentially unchanged while β_2 continued to decrease and β_3 was slightly higher. Entanglement effects may be responsible for the slight decrease in β_2. The β_3 increase may be due to a slight increase in the amount of loosely bound water resulting from a decrease in packing efficiency of the polymer chains thus heightening the β_3 contribution.

As the number of methylene groups in the polyarylate backbone increased, the number of dipolar groups per unit volume decreased. Based on density measurements it was expected that the absolute polarization would decrease with increasing backbone methylene groups. However, from $y = 4$ to 8 methylene groups the total low temperature

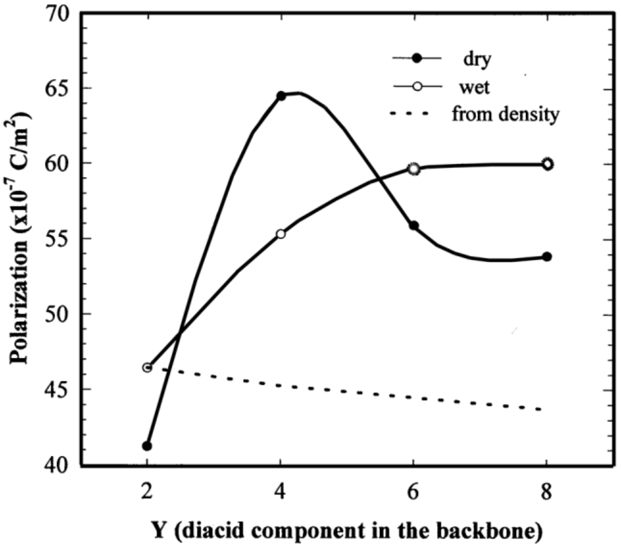

Fig. 6. The variation of the total low temperature polarization with the number of methylene groups for both the hydrate and non-hydrated specimen (the lines are drawn to guide the eye). The change in polarization calculated from the polymer density is shown by the dotted line.

polarization was higher than calculated from the polymer density and with a maximum polarization observed at $y = 4$ methylenes. This was followed by an approximate 13% decrease in polarization as the number of methylene groups increased (Fig. 6). The total low temperature polarization initially increased with increasing polymer flexibility as the number of methylene groups increased to $y = 4$, but then the onset of entanglement effects at $y > 4$ resulted in a decrease in the total polarization. This suggests that the low temperature dielectric relaxation profile of these polyarylates **3** was dependent on polymer backbone structure. This was not the case in the polycarbonate **4** study where methylene groups were added to the pendent chain [17]. It was inferred in that study that low temperature dielectric relaxations were independent of the pendent chain mobility since the observed total low temperature polarization was that expected from changes polymer density. However, the total low temperature polarization did decrease for the case of the polycarbonate **4** with the longest pendent chain ($n = 8$) where entanglement effects may no longer be negligible.

3.1.2. TSDC analysis of hydrated polyarylates

Each of the four polyarylates was hydrated to ca. $h = 0.5\%$ (w/w) and the low temperature TSDC spectra were obtained (Fig. 7). The spectra of the hydrated specimens exhibited a broad peak at about 160 K. This peak was absent in the TSDC spectra of the less hydrated specimens (Fig. 3). The broad peak at 160 K was associated with loosely bound states of water.

DSA analysis provided the mean energies and Gaussian distribution widths for each β_i component (Table 1). The mean energies of β_1 and β_2 components remained relatively constant and independent of changes in hydration. In the hydration study of poly(DTH succinate), the uptake of small amounts of water predominantly affected the β_3 and β_4 components [7]. The mean energies of the β_3 and β_4 components were greater for the hydrated vs. the non-hydrated specimens at $y = 2$ and 4 with the greatest difference being exhibited at $y = 2$. This suggested that water was localized nearest to these dipolar moieties. However, the differences became negligible as the number of methylene groups increased further to $y = 6$ and 8. The surface hydrophobicity as measured by the air–water contact angle increased with the addition of methylene groups in the backbone indicating an increase in bulk hydrophobicity (Table 1). Although changes in polymer hydrophobicity may have caused some variation in the degree of hydration and its manifestation, changes in polymer packing and chain entanglement with increasing number of backbone methylene groups also influences hydration.

The relative contributions for each β_i component in the hydrated specimen are shown in Fig. 8. Compared with the non-hydrated specimen at $y = 2$ methylene groups (Fig. 5), the β_3 process exhibited a higher contribution and the β_4 process, a lower contribution. A similar trend was also observed at $y = 4$ and 8 methylene groups. Different bound states of water molecules were localized at the amide carbonyl and pendent chain ester carbonyl [7]. The decrease in β_4 resulted from tightly bound water decreasing the number of reorientable amide carbonyl dipoles. Conversely, loosely bound water around the pendent chain ester underwent simultaneous reorientation with the ester carbonyl and increased the contribution of the β_3 process compared to the non-hydrated specimen.

Also, while the addition of methylene groups was most proximate to the backbone ester carbonyl groups, the contribution differences for the β_2 process for the two hydration states were somewhat more complex. These issues may have been due to a combination of water plasticization effects and differences in polymer hydrophobicity.

Interestingly, at $y = 6$ methylene groups where the onset of entanglement effects had been inferred, the relative contributions of all the β_i components were similar for

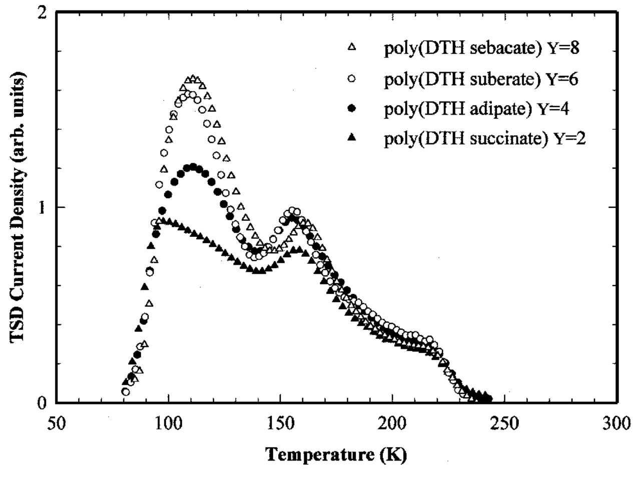

Fig. 7. Superposition of the low temperature TSDC obtained at the higher hydration state for each of the four polyarylates.

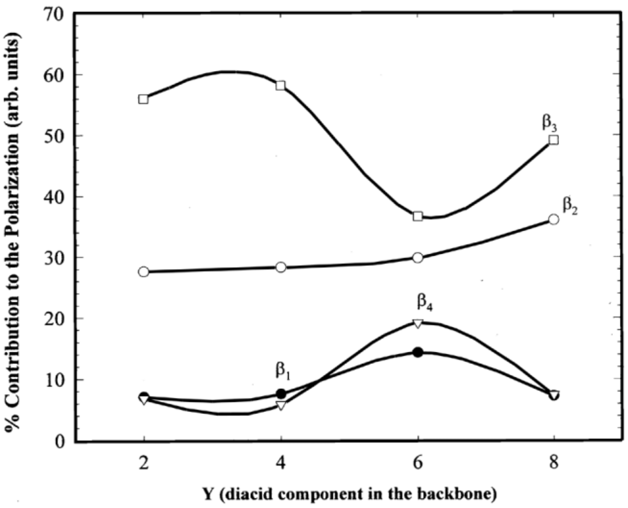

Fig. 8. The contributions for the relative polarization of each bicomponent in the hydrated specimen as a function of the number of methylene groups ($y = 2$–8). The lines are drawn to guide the eye.

both the hydrated and non-hydrated specimen (Figs. 5 and 8). This may be the result of the disruption of hydrogen bonding at the amide carbonyl by tightly bound water resulting in similarities in the chain packing efficiency for the hydrated and non-hydrated specimens.

The total low temperature polarization of the polyarylates in the hydrated state ($h = 0.5\%$) increased with increasing methylene groups in the backbone reaching a plateau at $y = 6$ (Fig. 6). The maximum polarization for the hydrated specimen was less than the maximum observed for the non-hydrated specimen at $y = 4$. Hydration effects seemed to exert a dominant influence on the low temperature relaxation processes in the polymer with $y = 2$ methylene groups. As the number of methylene groups in the backbone increased, chain flexibility becomes more dominant resulting in the absolute low temperature polarization for the non-hydrated specimen being greater than for the hydrated specimen. Hydration may have stiffened the polymer through hydrogen bonding at the amide carbonyl group lowering the total polarization relative to the non-hydrated specimens. Similar phenomena have been observed in other polyamides [25]. At $y = 6$ and 8 methylene groups, the solubility of water within the polymer matrix may have been lower than with the polymers possessing $y = 2$ and 4 methylene groups. Water plasticization could increase the flexibility for the polyarylates reducing the influence of chain entanglements resulting in a higher absolute polarization compared to the corresponding non-hydrated specimen.

3.2. High temperature polarization in dry samples

Higher temperature TSDC spectra provided the α relaxation processes associated with the glass transition temperature (T_g) (Fig. 9). These TSDC derived T_g values were the same as the values obtained by differential scanning calorimetry (DSC) experiments (Fig. 10) [1,18,26]. The similarity in the peak maxima temperatures obtained by TSDC and DSC is accountable to the comparable working frequencies of the two techniques (about 1 mHz). The addition of methylene groups to the polymer backbone caused a decrease in T_g from 326 K for $y = 2$ to 292 K for $y = 8$. The total high temperature polarization (inset, Fig. 9) increased as the number of methylene groups increased from $y = 2$ to 4, but then decreased 22% as the number of methylene groups increased to $y = 6$. These changes in polarization from $y = 2$ to 6 methylene groups were similar to that observed in the low temperature TSDC spectra for the dry specimen. However, increasing the number of methylene groups to $y = 8$ caused an increase in polarization.

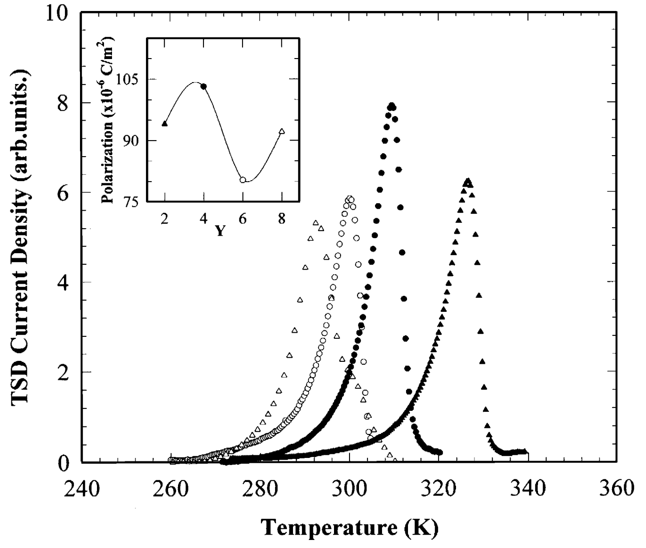

Fig. 9. Superposition of the high temperature TSDC spectra for each of the four polyarylates. The inset shows the total high temperature polarization.

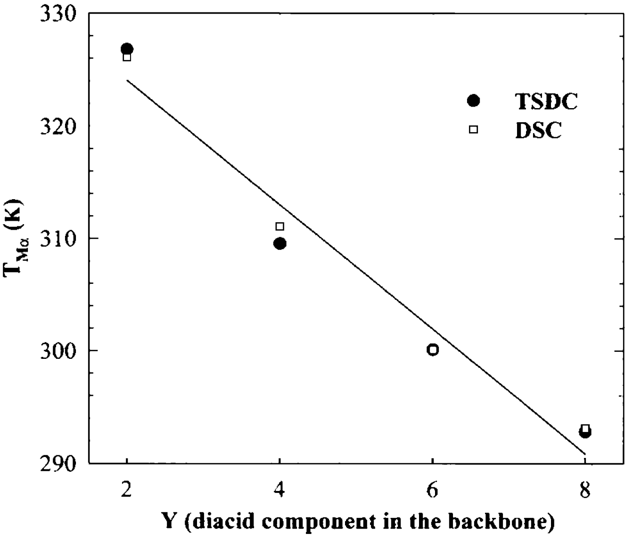

Fig. 10. Variation of the temperature of the maximum of the TSDC α-peaks and the DSC derived glass transition temperatures for each of the four polyarylates.

These variations in polarization with the number of backbone methylene groups can be interpreted in a manner similar to the low temperature β processes. The polarization increase from $y = 2$ to 4 methylene groups was caused by increased polymer flexibility while the polarization decrease from $y = 4$ to 6 methylenes was caused by the onset of entanglement effects. At $y = 8$ methylene groups, further increases in chain flexibility resulted in an increase in the total polarization (Fig. 9).

Several studies have described the influence of polymer flexibility and chain entanglements on the relaxation behavior of nylons. Studying the amorphous phase of nylon-12, Varlet reported that the intensity for the α relaxation processes at various temperatures was a function of chain entanglements [27]. Pathmanathan determined that chain entanglements influenced the dielectric magnitude and lowered the temperature position of the α peak [28]. Additionally, Boyd found that an elementary site for relaxation in nylons was a flexible polymer segment containing a constant number of repeat units [29]. Thus, nylons with

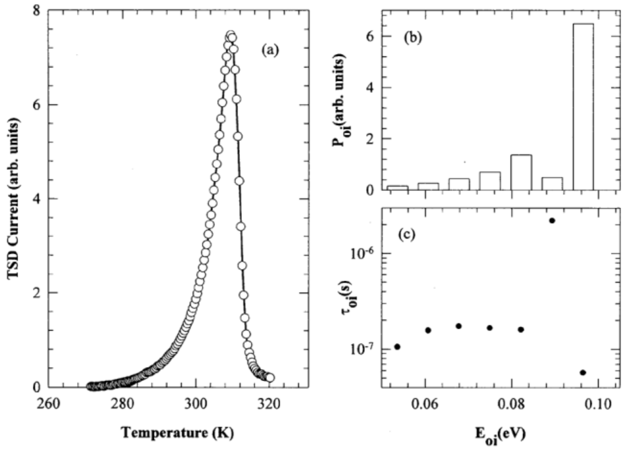

Fig. 11. DSA analysis of the α-peak in poly(DTH adipate): (a) experimental and fitted peak, (b) energy histogram of the contribution to the polarization for each energy bin, and (c) the variation of the pre-exponential factor with the activation energy.

longer repeat units were predicted to have α relaxations of higher intensity.

DSA analysis of the α processes for the polyarylates were convergent when the relaxation temperature dependencies were modeled by the Vogel–Fulcher model [11,17,30,31]. A representative DSA analysis for poly(DTH adipate) is presented in Fig. 11. Although the energy histogram depicts a well-defined monoenergetic process, the P_{0i} distribution located on the left side of the mean Vogel–Fulcher relaxation was probably due to Arrhenius type local reorientations of chain segments that occurred prior to the glass transition. The presence of these dipolar contributions was not unexpected since no cleaning procedure was used on the data to avoid distortion of the primary α process. The characteristic fitted parameters of the mean Vogel–Fulcher processes are presented in Table 2. The fitted T_o values are a decreasing function of the number of backbone methylene groups. This was in agreement with the experimental dependence of $T_{M\alpha}$ with backbone length. According to Adam and Gibbs theory, the values of $T_{M\alpha} - T_o = (55 \pm 4)$ K are constant within 10% [32].

The DSA analysis for the three polyarylates with $y = 2$–6 methylene groups all provided consistent results by the Vogel–Fulcher model. However, an asymmetrically distributed Vogel–Fulcher process was obtained for poly(DTH sebacate), the polymer with the largest number of backbone methylene groups ($y = 8$). The broadening of the fitted Vogel Fulcher histogram above the T_g for this specimen agreed with the shoulder observed in the TSDC spectrum in Fig. 9. The maximum of this shoulder is located around 298 K and the mean Vogel–Fulcher energy and pre-exponential factor are 0.066 eV and 9×10^{-5} s, respectively. Since poly(DTH sebacate) appears to be completely amorphous [1,18], this shoulder is not related to interfacial phenomena or to space charge effects which can occur at higher temperature.

Table 2
Glass transition peak values for each of the four polyarylates

Methylene groups (y)	Energy (eV)	T_o (K)	τ_o (s)
2	0.106	265.2	7.1×10^{-8}
4	0.096	254.2	5.7×10^{-8}
6	0.086	248.4	1.4×10^{-7}
8	0.061	241.1	5.2×10^{-5}

The presence of additional relaxation processes at temperatures greater than the glass transition has been observed in other polymers. DSC under swelling conditions, also called swelling differential scanning calorimetry (SDSC), and thermomicroscopy studies with several polymers, particularly acrylic fibers, have identified a broadening of the thermogram associated with macromolecular entanglements [33–36]. This peak broadening varied with polymer molecular weight and flexibility. The same authors compared the results measured by SDSC and by rheological and dynamic modulus analysis of polyacrylic fibers with different number-average molecular weights [34]. It was concluded that the broadened thermogram was attributed to the dissociation of the macromolecular entanglement structure. Polarizing photon correlation measurements over a wide temperature range on bulk polybutadiene also detected relaxation processes at temperatures higher than the T_g which were derived from subchain motions related to disentanglement effects [37]. These authors also measured longitudinal and shear waves by acoustic methods to determine the dynamic volume viscosity of polybutadiene and poly(ethylene glycols) of different molecular weights. Entanglement effects were quantified and found to contribute to volume and shear viscosity of the concentrated polymeric solutions and melts [38].

The contribution on the high temperature side of the glass transition for poly(DTH sebacate) ($y = 8$) was most probably related to the dielectric relaxation of an entanglement structure which became increasingly significant in the polyarylate structure after $y = 6$ methylene groups were used. Although chain entanglements in the polyarylates increased with the addition of methylene groups, the onset of these entanglement effects may also be associated with a critical molecular weight (M_c) [24,39]. According to the molecular interpretation postulated by Chee [39] for the correlation between the unperturbed parameter (K_q) and the critical molecular weight for flexible polymers, a linear relation between $\ln(K_q)$ vs. $\ln(M_c)$ was expected. This yielded the expression $K_q M_c^{1/2} r^{1/2} = 12.9 \pm 1.8$ ml/g, where r is the density of bulk polymer. Assuming poly(DTH suberate) was at least at the critical molecular weight, the value for the unperturbed parameter, K_q was 0.0375 ml/g in close agreement to values reported for various high molecular weight flexible polymers [39–41]. The abrupt changes observed in the low and high temperature polarization at $y = 6$ methylene groups could also be explained assuming that poly(DTH suberate) was at the critical molecular weight for the onset of entanglement effects.

4. Conclusion

Low and high temperature TSDC spectra were obtained and analyzed for a series of structurally related tyrosine-derived polyarylates. Polymer structure was precisely varied by addition of methylene groups in the polymer backbone. The low temperature TSDC spectra were obtained with the polymer specimen prepared at two hydration states and compared to a detailed study of the effects of hydration on poly(DTH succinate) [7]. The individual relaxation processes, β_1, β_2, β_3, and β_4 were elucidated by DSA and compared with a previous study of a series of tyrosine-derived polycarbonates where structure had been precisely varied by the addition of methylene groups in the pendent chain [17].

The relative contributions of the β_i components varied differently in the low temperature TSDC studies as methylene groups were added to the backbone of the polyarylates. In the less hydrated specimens, the onset of entanglement effects was observed with $y = 6$ methylene groups. The total low temperature polarization increased with polymer flexibility up to $y = 4$ methylene groups and then the polarization decreased with further methylene group additions. This decrease was attributed to entanglement effects. Contrarily, a monotonously decrease of this polarization is predicted by density measurements in polymers with increasing backbone length. Such an abrupt change in the measured total low temperature polarization suggested that the low temperature dielectric relaxation profile for the tested polyarylates was dependent on polymer backbone structure. This was not the case in the polycarbonate study [17] where the total low temperature polarization followed closely the expected decay predicted by the decrease in the measured density as the pendent chain length increased up to 6 methylene groups. This behavior was explained assuming that the dielectric profile for the tested polycarbonates was independent of the methylene group structure variation in the pendent chain.

Low temperature TSDC spectra were then obtained for hydrated specimens. Small amounts of water also affected the individual relaxation processes differently as a function of the number of backbone methylene groups. Presumably this was due to a combination of flexibility and entanglement phenomena. Since water was localized near the β_3 and β_4 dipoles it was not surprising these processes exhibited the greatest differences compared to the non-hydrated specimen. Interestingly these effects were only observed in the two polymers with $y = 2$ and 8 methylene groups while there were slight differences in the relative contributions of the individual processes at $y = 6$ and 4 methylene groups. Hydration effects were dominant in the more hydrophilic polymer with $y = 2$ methylene groups. As methylene groups were added ($y = 4$) to the backbone, hydration may have stiffened the polymer compared to the non-hydrated state and lowered the absolute polarization. The entanglement effects at $y = 6$ and 8 were then offset with hydration because of water plasticization effects in the more hydrophobic polymer matrix. This caused the polymer to be more flexible compared to the non-hydrated specimen and the corresponding absolute low temperature polarization was thus higher. For specimens with 2, 4, and 6 methylene groups the α relaxation process associated with the glass transition temperature was an almost monoenergetic Vogel–Fulcher relaxation. The position of this peak for the whole family of polymers was in correspondence with the glass transition temperature measured by DSC. Entanglement effects were also observed in the high temperature TSDC studies. The most apparent evidence was the dielectric manifestation of disentanglement effects observed in the polymer with the highest number of methylene groups in the backbone, poly(DTH sebacate) ($y = 8$). Assuming poly(DTH suberate) ($y = 6$) was at least at the critical molecular weight for the onset of entanglement effects, the value of 0.0375 ml/g obtained for the unperturbed parameter (K_q) was in close agreement with those reported for various high molecular weight flexible polymers. The onset of entanglement effects at $y = 6$ methylene groups could also explain the abrupt changes reported in the variations of the low and high temperature polarization with backbone length.

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