Thermal Properties and Enthalpy Relaxation of Tyrosine-Derived Polyarylates

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ABSTRACT: Sixteen degradable, tyrosine-derived polyarylates with well-defined chemical structures were used to study the effect of polymer structure on the glass transition temperature and enthalpy relaxation kinetics (physical aging). These polyarylates compose a model system where the number of methylene groups present in either the pendent chain or the polymer backbone can be altered independently and in a systematic fashion. Quantitative differential scanning calorimetry was employed to measure the glass transition temperature and the enthalpy relaxation kinetics. Correlations between these material properties and the polymer structure were established. The glass transition temperature of this family of polymers ranged from 13 to 78°C. The addition of methylene groups to either the pendent chain or the polymer backbone made a fairly constant contribution to lowering the glass transition temperature. The rate of enthalpy relaxation increased with an increasing number of methylene groups in the polymer backbone, but was independent of the number of methylene groups in the pendent chain. This observation indicated that the rate of enthalpy relaxation in these polymers was limited by the mobility of the polymer backbone. The enthalpy relaxation data was fitted to the Cowie–Ferguson model and the relaxation times obtained ranged from 44 min to about 100 min. Although these structure–property correlations facilitate the design of new materials with predictable thermal properties, they are rarely investigated for biomedical polymers. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1441–1448, 1997

Key words: physical aging; enthalpy relaxation; glass transition temperature; differential scanning calorimetry; tyrosine; biomaterial; biopolymer; structure–property correlation

INTRODUCTION

Polyarylates (also referred to as polyphenolates) are a subclass of polyesters and are among the most widely investigated liquid crystalline polymers.[1] Polyarylates with useful engineering properties have been obtained by copolyesterification of aromatic diacids and industrially available di-

phenols such as bisphenol-A. Recently, the synthesis of polyarylates was reported using desaminotyrosyl–tyrosine alkyl esters (derivatives of tyrosine dipeptide) and aliphatic diacids as monomers (Fig. 1).[2–4] These polymers were degradable under physiological conditions and had significantly improved engineering properties as compared to most conventional poly(amino acid)s.[5–7] Based on preliminary studies, tyrosine-derived polyarylates were identified as promising materials for the design of degradable medical implants.[3,4,8,9] To further optimize the material properties of these materials, a better understanding is needed of their structure–property relations,
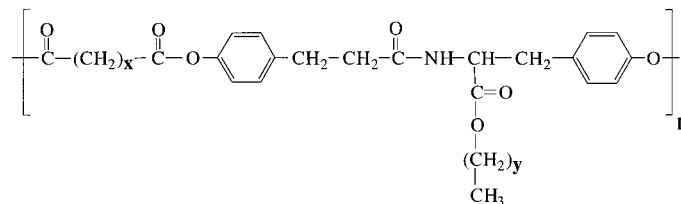
diacid component (backbone)	ester component (pendent chain)
X = 2; succinate	Y+1= 2; desaminotyrosyl-tyrosine ethyl ester (DTE)
X = 4; adipate	Y+1= 4; desaminotyrosyl-tyrosine butyl ester (DTB)
X = 6; suberate	Y+1= 6; desaminotyrosyl-tyrosine hexyl ester (DTH)
X = 8; sebacate	Y+1= 8; desaminotyrosyl-tyrosine octyl ester (DTO)

Figure 1 Chemical structure of the polyarylates used in this study. The structure of the polymer backbone includes a spacer of X methylene groups. The length of the pendent chain (Y + 1) can be varied independently. The "flexibility index" was defined as the total number of carbon atoms (X + Y + 1) contained in the backbone spacer and the alkyl ester chain.

their thermomechanical properties, and their long-term performance under various conditions.

In addition to their possible practical applications as biomaterials, tyrosine-derived polyarylates are a convenient model system for the systematic study of correlations between the chemical structure of the polymer and selected material properties. To modify the length of the polymer pendent chain, four desaminotyrosyl–tyrosine alkyl esters (Fig. 1) were prepared having an ethyl, butyl, hexyl, and octyl ester group, respectively. To modify the structure of the polymer backbone, a series of four nontoxic, natural diacids was identified (succinic, adipic, suberic, and sebacic acid). These diacids differ in the number of methylene groups between the carboxylic acid end groups and provide a mean to introduce variable "methylene spacers" into the polymer backbone (Fig. 1). By copolymerizing either of the four diphenols with either of the four diacids, a "two-dimensional" grid comprising a family of 16 polymers was obtained, covering all available combinations of pendent chain length and backbone structure (Table I).

In preliminary studies, correlations between the chemical structure of tyrosine-derived polyarylates and selected material properties were observed. For example, the surface tension, as measured by the air–water contact angle, was a more sensitive function of the number of methylene groups in the pendent chain than of the number of methylene groups in the backbone.[3,5] The rate of release of a model dye (p-nitroanilline) from thin polymer films was correlated with the pendent chain length[2] and variations in attachment

and growth of several cell lines on polyarylate surfaces are currently under investigation.

In continuation to preliminary investigations of the glass transition temperature (T_g) and the enthalpy relaxation of selected polyarylates,[3,5,10] we report here correlations between the number of methylene groups present in either the pendent chain and/or the polymer backbone and the glass transition temperature and the relaxation kinetics of a group of 16 tyrosine-derived polyarylates.

When a polymer in a nonequilibrium state is stored below its T_g, structural relaxation to an equilibrium state will take place. This relaxation process (referred to as enthalpy relaxation or physical aging)[11] results in a reduction of the enthalpy and the free volume of the polymer matrix. Enthalpy relaxation can be monitored conveniently by differential scanning calorimetry (DSC) and manifests itself by an endothermic peak in the vicinity of the glass transition region of the DSC thermogram whenever an aged polymer specimen is heated from below to above its glass transition temperature. The rate of this relaxation depends on structure, aging temperature (storage temperature), and the thermal history of the polymer. Since the process of enthalpy relaxation can lead to changes in the dimensions and the mechanical properties (e.g., increased brittleness) of a polymeric specimen, an evaluation of the enthalpy relaxation process in glassy polymers is critical to many practical applications.[12–17] Surprisingly, in biomedical engineering, and, in particular, in the evaluation of biodegradable polymers, the study of enthalpy relaxations has received very little attention. Al-

Table I Glass Transition Temperatures and Molecular Weights of Polyarylates Used in This Study

Polymer Name	Poly(DTE succinate)	Poly(DTB succinate)	Poly(DTH succinate)	Poly(DTO succinate)
X^a	2	2	2	2
$Y + 1^a$	2	4	6	8
T_g (°C)	78	67	53	48
M_w $(M_w/M_n)^b$	74,000 (1.5)	80,000 (1.5)	51,000 (1.6)	120,000 (1.6)
Polymer Name	**Poly(DTE adipate)**	**Poly(DTB adipate)**	**Poly(DTH adipate)**	**Poly(DTO adipate)**
X^a	4	4	4	4
$Y + 1^a$	2	4	6	8
T_g (°C)	61	46	38	28
M_w $(M_w/M_n)^b$	114,000 (1.3)	130,000 (1.5)	104,000 (1.4)	56,000 (1.7)
Polymer Name	**Poly(DTE suberate)**	**Poly(DTB suberate)**	**Poly(DTH suberate)**	**Poly(DTO suberate)**
X^a	6	6	6	6
$Y + 1^a$	2	4	6	8
T_g (°C)	50	37	27	21
M_w $(M_w/M_n)^b$	72,000 (1.7)	65,000 (1.6)	105,000 (1.5)	66,000 (1.5)
Polymer Name	**Poly(DTE sebacate)**	**Poly(DTB sebacate)**	**Poly(DTH sebacate)**	**Poly(DTO sebacate)**
X^a	8	8	8	8
$Y + 1^a$	2	4	6	8
T_g (°C)	44	30	20	13
M_w $(M_w/M_n)^b$	77,000 (1.5)	99,000 (1.5)	123,000 (1.5)	53,000 (1.9)

[a] X = no. methylene groups present in the flexible spacers of the polymer backbone and (Y + 1) = length (no. carbon atoms) present in the alkyl ester pendent chain (see Fig. 1).
[b] Molecular weight given for the polymer sample used for determination of T_g.

though poly(L-lactic acid) is one of the most intensively investigated biodegradable polymers, the first study of the enthalpy relaxation kinetics in poly(lactic acid) was published only in 1992.[18] The importance of enthalpy relaxation processes in the evaluation of biodegradable polymers was illustrated by a recent report indicating that aged specimens of poly(lactic acid) exhibit a reduced rate of enzymatic surface degradation as compared to unaged specimens.[19]

In a previous study, tyrosine-derived polycarbonates were used to investigate the effect of pendent chain length on the enthalpy relaxation kinetics.[20] In that study, the relaxation time (τ) was independent of the length of the pendent chain, indicating that the structural relaxation in tyrosine-derived polycarbonates was controlled by the segmental mobility of the polymer backbone. One of the limitations of the previous study was that the structural design of tyrosine-derived polycarbonates allowed for the systematic variation of the pendent chain only. The use of tyrosine-derived

polyarylates made it possible to circumvent this limitation.

EXPERIMENTAL

Synthesis

Polyarylates were prepared according to previously published procedures.[2,4,8] The polymers had weight-average molecular weights ranging from 51,000 to 130,000 g/mol (Table I) and polydispersity values of about 1.6.

Polymer Characterization

The chemical structure of the polymers was confirmed by IR and NMR spectroscopy. Molecular weights were determined on a GPC chromatographic system consisting of a Perkin-Elmer Model 410 pump, a Waters Model 410 refractive index detector, and a Perkin-Elmer Model 2600

computerized data station. Two GPC columns (10^5 and 10^3 Å pore size, 30 cm in length; Polymer Laboratories, Ltd., Church Stretton, UK) were operated in series at a flow rate of 1 mL/min in THF. Molecular weights were calculated relative to polystyrene standards (Polymer Laboratories, Ltd.) without further corrections. Samples (5 mg/mL) were filtered through a 0.45 μm membrane filter prior to injection.

Glass Transition

Previously described methodology was used.[20] Briefly, a thermal analyzer Model DSC 910 (TA Instruments, Newcastle, DE) was employed to follow the changes in the specific heat capacity from the glassy to the rubbery region. The heating rate was 10°C per minute and the glass transition temperature was determined in the second scan by the midpoint of the endothermic changes associated with the glass transition. The reproducibility of the T_g measurements was within 1°C.

Measurement of the Relaxation Process (Aging)

Following previously described methodology,[20] one sample of each polymer was used for all measurements to minimize run-to-run variation. First, the previous thermal history of each sample was erased by heating to approximately 60°C above the T_g.[18,21] After quenching to the appropriate aging temperature (defined here as $T_a = T_g - 15$°C), each sample was aged for a predetermined time (t_a). Then, the aged sample was quenched to $T_g - 50$°C, and the data acquisition scan was immediately started (heating rate: 10°C/min). All measurements were performed in closed aluminum pans under a nitrogen atmosphere.

Estimation of Excess Enthalpy

Enthalpy relaxation was determined by the integration of the endothermic peak below the extended sigmoidal base line from the glassy region to the rubbery region of the thermogram, as described previously.[14,20–22] The changes in enthalpy were monitored as a function of aging time for each polyarylate.

RESULTS AND DISCUSSION

Due to differences in monomer solubility and the typical variability of small-scale condensation po-

lymerizations, some differences in molecular weight among the polymer samples could not be avoided. However, care was taken to select polymer samples with similar polydispersity values (Table I) and symmetrical, Gaussian molecular weight distributions. In addition, for all polymer samples, the degree of polymerization was sufficient so that the physicomechanical properties of the polymers were no longer a sensitive function of the molecular weight. These precautions ensured that the results obtained were comparable among the 16 polyarylates used in this study. In addition, to facilitate the comparison of data between different studies, the methodology described previously[20] was used without changes and the way in which the physical aging experiments were conducted in this study is comparable to the methodology used by other investigators.[18,19]

Glass Transition Temperature

The glass transition temperature (T_g) is one of the most important characteristics of amorphous polymers. In the literature, T_g values are reported either at the "onset" or the "midpoint" of the baseline shift in the DSC thermogram. Since the midpoint values were found to be more reproducible,[23,24] this method of reporting T_g values was used here.

In this group of polymers, structure–property correlations can be defined in terms of the number of carbon atoms contained within the variable portion of the polymer backbone (labeled as "X" in Fig. 1) and the number of carbon atoms present in the alkyl pendent chain (labeled as "Y + 1" in Fig. 1). For ease of presentation, the combined number of carbon atoms (X + Y + 1) was defined as the "flexibility index."

The glass transition temperature decreased with increasing flexibility index. The reduction in the T_g was similar when methylene groups were added either to the pendent chain or the polymer backbone (Fig. 2). This observation suggested that, to a first approximation, the effect of additional methylene groups on polymer mobility and packing efficiency was independent of the position of the methylene groups within the polymer molecule. However, more careful analysis of the T_g values shown in Table I revealed several subtle trends. When the backbone unit was held constant, the addition of six methylene groups to the pendent chain of the polymer lowered the T_g by about 31 ($\pm$2)°C. On the other hand, keeping the
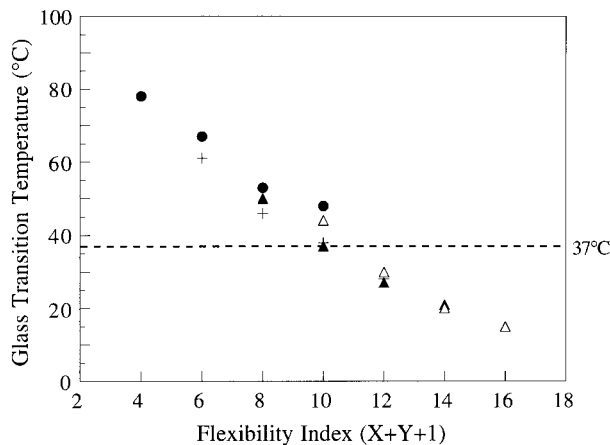
Figure 2 Detailed analysis of the effect of polymer structure on T_g. Each data point represents the T_g of a specific polyarylate. To illustrate the subtle variations in T_g as a function of the polymer structure, polymers were grouped according to length of the backbone spacer: succinate: (●) X = 2; (+) adipate: X = 4; (▲) suberate: X = 6; (△) sebacate: X = 8.

pendent chain constant and adding six methylene groups to the polymer backbone had a slightly greater effect and reduced the T_g by 35 (±2)°C. For instance, the T_g of poly(*DTO* succinate) was 30°C lower than the T_g of poly(*DTE* succinate), while the T_g of poly(DTE *sebacate*) was 34°C lower than the T_g of poly(DTE *succinate*) (see Table I). This observation indicated that the mobility of the polymer backbone made a slightly greater contribution to lowering the glass transition temperature than did the increasing bulkiness of the pendent chain.

The 16 available polyarylates can be divided into seven isomeric subgroups, based on their "flexibility index" as defined above (4, 6, 8, 10, 12, 14, and 16 respectively, see Figs. 1 and 2). Within each isomeric subgroup, the polymer with the least flexible backbone tended to have a slightly higher T_g than that of the other members of the subgroup. For example, among the subgroup of four polymers having a flexibility index of 10, poly(DTO succinate) had a slightly higher T_g than that of any of the other isomeric polymers (Fig. 2).

Polymers in which the number of methylene groups was distributed equally between the backbone and the pendent chain tended to have the lowest T_g values within each isomeric subgroup. For example, among the polymers having a flexibility index of 8, poly(DTB adipate) had the lowest T_g.

In considering practical applications as a biomaterial, the morphological state of the polymer within the body of the patient is an important consideration. For high strength and/or load-bearing applications (e.g., bone fixation devices), the polymer should be in the glassy state. On the other hand, for drug-delivery systems, it is often desirable to use polymers that are rubbery at body temperature (37°C). For this group of polyarylates, polymers will be rubbery at 37°C if their flexibility index is greater than 10, while polymers with a flexibility index ≤10 will be in the glassy state at body temperature (Fig. 2).

Enthalpy Relaxation Kinetics (Physical Aging)

All polyarylates were aged at an aging temperature (T_a) of 15°C below their respective T_g. Representative DSC thermograms of poly(DTE suberate) for increasing aging times are shown in Figure 3(A). Similar thermograms were obtained for all other polyarylates tested. All thermograms could be well superimposed in both the glassy and the rubbery regions, indicating that no irreversible changes were induced in the polymer during repeated DSC scans. The endothermic peak in the vicinity of T_g, corresponding to the recovery of the heat lost during the enthalpy relaxation process, became clearly noticeable after 15 min of aging. The temperature at which the enthalpy peak reached its maximum shifted to higher temperatures with increasing aging time. As the polymer aged, the shift of the endothermic aging peak was attributed to a substantial decrease in molecular mobility. A reduction of molecular mobility is widely regarded as a general feature of the structural relaxation of glassy polymers.[14–17,21]

A linear relationship was observed between the relaxation enthalpy (ΔH) and the logarithm of the aging time for all tested polyarylates. This observation is in agreement with the studies by Bauwens-Crowet and Bauwens.[16] A representative plot, derived from the enthalpy relaxation data for poly(DTE suberate), is shown in Figure 3(B).

The enthalpy relaxation data at each aging time, $\Delta H(t_a)$, was analyzed using a phenomenological multiorder parameter model based on eq. (1)[12,13]:

$$\Delta H(t_a) = \Delta H_\infty\{1 - \phi(t_a)\} \qquad (1)$$

where

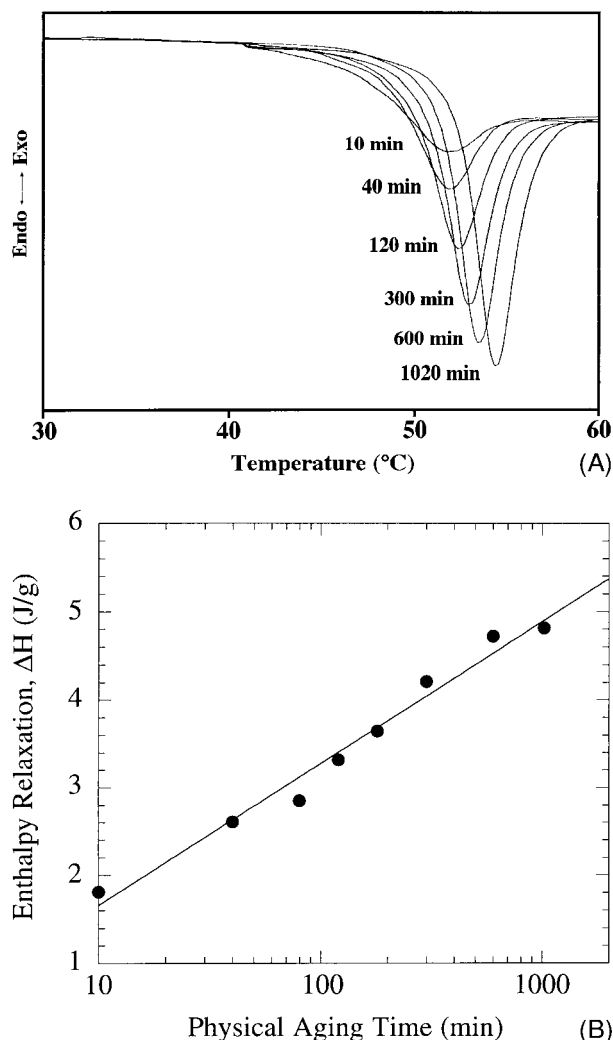$$\phi(t_a) = \exp\{-(t_a/\tau)^\beta\} \qquad (2)$$

Figure 3 (A) Representative DSC thermogram in the glass transition region of poly(DTE suberate) aged at $T_a = T_g - 15°C$ for increasing aging periods. (B) Enthalpy relaxation (ΔH) as a function of the logarithm of aging time.

Here, t_a is the aging time and ΔH_∞ is the equilibrium enthalpy relaxation at infinite aging time. The relaxation function, $\phi(t_a)$, describes the kinetics of the approach of the system to the equilibrium state. The most widely used relaxation function is the empirical Williams–Watts function which is given in eq. (2).[12,13] τ is the characteristic relaxation time, and β ($0 < \beta \leq 1$) is a parameter that characterizes the width of the distribution of the relaxation times. A small value of β (e.g., $\beta = 0.2$) implies a very broad distribution of relaxation times, while a value close to 1 implies a very narrow distribution.

In this work, the value of ΔH_∞ was determined experimentally by conducting the aging experi-

ments for periods long enough to ensure that the polymer had come close to equilibrium. In this way, only τ and β remained as adjustable parameters, which were determined by nonlinear fitting analysis using the Cowie–Ferguson model.

To study the correlation between polymer structure and enthalpy relaxation in more detail, two test series of polyarylates were selected. In the first test series, consisting of poly(DTE succinate), poly(DTE suberate), and poly(DTE sebacate), the length of the flexible spacer in the polymer backbone was changed while the pendent chain was kept constant. In the second test series, consisting of poly(DTE succinate), poly(DTH succinate), and poly(DTO succinate), the length of the pendent chain increased while the polymer backbone was kept unchanged.

The effect of the backbone structure on the enthalpy relaxation kinetics is shown in a plot of the relaxation enthalpy (ΔH) as function of the aging time (t_a) [Fig. 4(A)]. At a constant pendent chain length, the relaxation time decreased with an increasing number of methylene groups in the polymer backbone (Table II). This correlation indicated that the rate of enthalpy relaxation is controlled by the segmental mobility of the polymer backbone. This behavior is consistent with the results obtained in a previous study of the physical aging of tyrosine-derived polycarbonates.[20] A similar correlation was also obtained by Cheng and co-workers[17] for semicrystalline polyimides. For all tested polyarylates, the distribution of relaxation times, β, was about 0.4 and was independent of the number of methylene groups in the polymer backbone. When interpreting the β value, it is important to note that β is simply used to describe the shape of the experimentally determined relaxation curve vs. time. The relaxation time τ and the parameter β do not represent a specific molecular process.[14] Indeed, it is well known that "presentations of τ and β are purely empirical and that the relaxation times obtained in our studies cannot be attributed to specific atomic processes."[25]

Figure 4(A) also illustrates that the equilibrium enthalpy (ΔH_∞) was strongly affected by the number of methylene groups in the polymer backbone. Poly(DTE succinate) had the largest ΔH_∞ and poly(DTE sebacate) had the lowest ΔH_∞ in the test series. This can be explained in the following fashion: At the onset of the aging process, polymers with stiffer chains deviate more from equilibrium as compared to more flexible polymers, since stiffer chains release less of their excess free
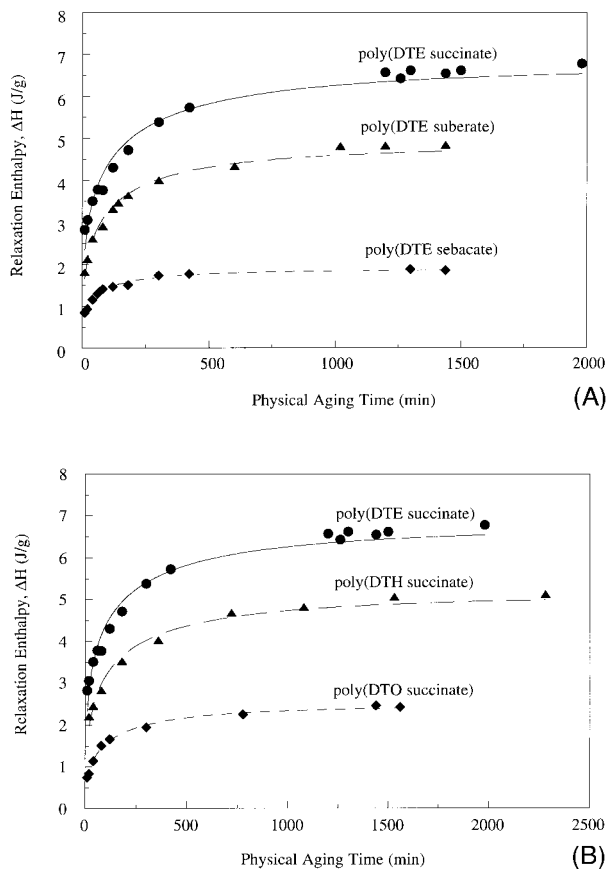
Figure 4 (A) The effect of polymer backbone structure on enthalpy relaxation was studied in (●) poly(DTE succinate), (▲) poly(DTE suberate), and (♦) poly(DTE sebacate) aged at $T_a = T_g - 15°C$ for increasing aging periods. (B) The effect of pendent chain length on enthalpy relaxation kinetics was studied in (●) poly(DTE succinate), (▲) poly(DTH succinate), and (♦) poly(DTO succinate) aged at $T_a = T_g - 15°C$ for increasing aging periods.

volume during cooling as compared to more flexible chains. Consequently, at the onset of the aging experiment, the stiffer poly(DTE succinate) was further removed from its equilibrium state than was the more flexible poly(DTE sebacate).

The effect of pendent chain length on the enthalpy relaxation process was studied by comparing the results for poly(DTE succinate), poly(DTH succinate), and poly(DTO succinate) [Figure 4(B)]. At a constant backbone structure, the relaxation time predicted by the Cowie–Ferguson model for these polymers was about 100 min and independent of pendent chain length (Table II). This observation suggested that the dimensions of the pendent chain did not affect the limited segmental mobility occurring in the glassy

state. Thus, for the tested polyarylates, the rate of physical aging was controlled exclusively by the mobility of the polymer backbone.

As observed for the previous test series, the equilibrium enthalpy, ΔH_∞, could be related to the flexibility of the polymer [Fig. 4(B) and Table II]: ΔH_∞ was larger for poly(DTE succinate) than for poly(DTO succinate), indicating that polymers with the shorter pendent chains deviated more from equilibrium at the onset of the aging process than did polymers with longer pendent chains.

CONCLUSIONS

Tyrosine-derived polyarylates provided a convenient and systematic model to study the effect of polymer structure on the glass transition temperature and the enthalpy relaxation kinetics. Both T_g and the enthalpy relaxation process were influenced to a significant degree by polymer structure. T_g decreased with an increasing number of methylene groups in either the pendent chain or polymer backbone. To a first approximation, T_g was linearly correlated with the "flexibility index" (defined as the total number of carbon atoms contained in the variable backbone spacer and the alkyl ester pendent chain). For isomeric polymers having an identical "flexibility index," the exact value of T_g was predominantly determined by the structure of the polymer backbone and by the distribution of methylene groups between the pendent chain and the backbone spacer.

The enthalpy relaxation time τ decreased with an increasing number of methylene groups in the polymer backbone, but was independent of the length of the pendent chain. This observation indicated that for the tested polyarylates the rate of physical aging is limited by the segmental mobility of the polymer backbone. The equilibrium relaxation enthalpy, ΔH_∞, was correlated with the flexibility of the polymer and was reduced with an increasing number of methylene groups in either the polymer backbone or the pendent chain.

This study represents one of the first reports of a detailed evaluation of structural relaxation processes (physical aging) in biodegradable polymers. The structure–property correlations found in this study can be used in the efficient design of new polymers with predictable thermal properties.

Table II   Equilibrium Relaxation Kinetics of Five Selected, Tyrosine-derived Polyarylates

Polymer	Methylene Groups in the Polymer Backbone	Carbon Atoms in the Polymer Pendent Chain	τ (min)[a]	ΔH_∞ (J/g)[b]	β
Poly(DTE succinate)	2	2	91 ± 8	6.8	0.4
Poly(DTE suberate)	6	2	77 ± 5	4.8	0.4
Poly(DTE sebacate)	8	2	42 ± 2	1.9	0.4
Poly(DTE succinate)	2	2	91 ± 8	6.8	0.4
Poly(DTH succinate)	2	6	110 ± 10	5.1	0.4
Poly(DTO succinate)	2	8	101 ± 6	2.5	0.5

[a] The enthalpy relaxation time τ and the distribution factor β were determined by nonlinear regression analysis of the aging data using the Cowie−Ferguson model, substituting ΔH_∞ with the experimentally observed value shown in this table.
[b] Experimental value of the equilibrium enthalpy relaxation measured at the plateau reached after extensive aging.

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