480 *Macromolecules* **2000,** *33,* 480−489

Influence of Physical Aging on the Molecular Motion and Structural Relaxation in Poly(ethylene terephthalate) and Related Polyesters

Elizabeth-Anne McGonigle,[†] John H. Daly,[†] Stephen D. Jenkins,[‡]
John J. Liggat,[*,†] and Richard A. Pethrick[†]

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street,
Glasgow G1 1XL, UK, and Du Pont Polyester, Wilton Research Centre, Middlesbrough TS90 8JE, UK

Received June 9, 1999

ABSTRACT: A combination of dielectric relaxation, dynamic mechanical thermal analysis, and positron annihilation measurements is reported on melt-cast films of poly(ethylene terephthalate), poly(ethylene naphthalate), and their copolymers. The effects of change in the chemical structure of the polyesters are rationalized in terms of increased restriction of the mobility of the polar segments of the chain by the incorporation of the bulky naphthalate structure. All the quenched samples exhibit physical aging when raised to elevated temperatures, the rate depending on the degree of undercooling used in the aging experiments. The free volume surprisingly does not change significantly with temperature and leads to the suggestion that the reduction in the dielectric permittivity is a consequence of a reduction in the mobility of the local segments. The increased storage modulus is also consistent with a reduction in mobility. This proposal is further confirmed by the observation of a good correlation between the rates and extents of the physical aging as detected by dynamic mechanical and dielectric relaxation measurements. Similarities in the activation energies of the β relaxation process for all the polymers investigated indicate that the dipole relaxation processes have a common origin and can be ascribed to motion of the linking polar entity. This study implies that aging is accompanied by an increase in ordering within these polyesters.

Introduction

The relaxation behavior of poly(ethylene terephthalate) (PET) and related polyesters has been investigated using a variety of techniques,[1−7] and the molecular origins of the principal molecular relaxation features are well-defined. However, a close inspection of these studies indicates that while the influence of crystallinity is recognized, little or no attention has been paid to the effects of sample preparation on the observed relaxation behavior. The phenomenon of *physical aging* has significant effects on the physical properties of glassy polymers and might be expected to also influence partially crystalline polyesters. Physical aging gives rise to an increase in mechanical moduli, the appearance of endothermic enthalpic recovery peaks in differential scanning calorimetry [DSC] scans, and a reduction in volume.[8] Such effects are associated with a decrease in the free volume leading to an increase in both the mechanical relaxation time and the thermal energy required to initiate molecular rearrangements necessary for enthalpic recovery.[9] Using positron annihilation lifetime spectroscopy [PALS], the connection between changes in the molecular relaxation spectrum and free volume in glassy polymers has been established.[10−13] Free volume controls to a large extent the molecular mobility of large segments of the polymer chain, which in turn influences many of the physical and mechanical properties of polymers.[14,15] Tseng et al.[13] found two pronounced discontinuities in the plots of the ortho-positronium intensity against temperature in the range −80 to 60 °C from their PALS studies of PET and attributed the change in behavior to the onset of structural relaxation associated with the *trans*−*gauche* transition and glass to rubber transition [T_g].

Increases in crystallinity have been observed to lead to a decrease in the amplitude of the dielectric relaxation process.[16] The shape of the α relaxation process is strongly influenced by the degree of crystallinity. The half-width of the relaxation curve increases with increasing crystallinity, and the curve becomes broader on the low-frequency side of the relaxation, the asymmetry increasing with increasing degree of crystallinity. Close correlation between the morphology and the mechanical properties of PET and melt film has been reported.[17] The rate of segmental motion became more intense at small draw ratios but decreased with further increase in the draw ratio. The effects of humidity have been explored for the dielectric relaxation, and it was observed that the intensity of the β relaxation increased linearly with moisture content.[18] Similar observations have been reported on the basis of dynamic mechanical observations.[19]

In this paper, the effects of thermal aging on PET, poly(ethylene naphthalate) (PEN), and a series of poly(ethylene terephthalate-*co*-ethylene naphthalate) (PETN) polyesters are presented. The techniques used allow comparison between the changes in the free volume and molecular relaxation processes and help to clarify some of the previously reported effects of morphology on the physical properties of these materials.

Experimental Section

Materials. The PET, PEN, and PETN copolymers were supplied by ICI Polyester and were used as melt-cast amorphous films (~230 μm). Samples for the aging studies were quenched directly from the melt into a dry ice bath and stored in a freezer until the commencement of the aging experiment. Density measurements indicated that no detectable levels of crystallinity were incorporated during the quenching process

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[†] University of Strathclyde.
[‡] Wilton Research Centre.
* To whom correspondence should be addressed.

10.1021/ma9909197 CCC: $19.00

Table 1. Details of the Polymer Samples Used

material	mole % PEN	M_w	M_n	IV (dL/g)	T_g (°C)	ΔH_c (kJ/kg)	T_m(°C)	ΔH_m (kJ/kg)	density (g/cm^3)
PET	0	106 000	37 400	0.809	70	−32	251	37	1.3352
PETN3	3	111 000	34 400	0.806	78	−26	253	36	1.3347
PETN8	8	100 000	35 700	0.780	79	−20	242	26	1.3343
PETN12	12	98 100	39 200	0.718	84	−19	232	22	1.3339
PETN16	16	97 100	38 100	0.819	92				1.3336
PETN84	84	73 900	29 000	0.839	110				1.3276
PETN95	95	65 300	27 600	0.789	121	−32	265	37	1.3269
PEN	100	69 300	28 700	0.836	116	−35	272	34	1.3267
BLEND	*a*	81 600	31 700	0.780	90				1.3323

[a] Mixture of PETN3 and PETN95 copolymers at 50:50 wt %.

(Table 1). Densities were measured at 25 °C using a density column containing solutions of toluene and Arklone (1,1,2-trichloro-1,2,2-trifluoroethane). A blend was also included to highlight differences between blends and the copolymers. The numerical designate # in the code PETN# indicates the percentage of naphthalate in the copolymer (Table 1).

Differential Scanning Calorimetry. DSC measurements were made on a Perkin-Elmer DSC-2 interfaced to a BBC microcomputer, using software developed by Dr. J. Hay at the University of Birmingham, and all data were transferred to a networked PC for subsequent analysis. Samples of ~8 mg were sealed in crimped aluminum sample pans, and temperature scans were performed from 30 to 300 °C at a rate of 10 °C min^{-1}, using a range of 10 mcal. A dry nitrogen atmosphere was used to prevent oxidative degradation during preparation and measurement, and indium was used to calibrate the instrument. The T_g was taken to be a point midway between the glass and rubbery state.[20] The crystallization temperatures (T_c) and melting temperatures (T_m) were defined by the peak maximum value.

Dynamic Mechanical Thermal Analysis. Dynamic mechanical measurements were carried out using a Polymer Laboratories Ltd. dynamic mechanical thermal analyzer [DMTA]. A rectangular sample (15 mm × 5 mm × ~2 mm) was clamped using a single cantilever mode clamping arrangement using 40 N of torque. Temperature scans were performed from −100 to 150 °C at a rate of 3 °C min^{-1} using a frequency of 1 Hz. Samples were reclamped at low temperatures to minimize slippage. Isothermal experiments were performed, the assembly being equilibrated to the desired aging temperature and the storage modulus, E', measured using a frequency of 1 Hz and a strain of ×4. Temperature control was better than ±0.1 °C, and a standard deviation of ±0.02 Pa·s in the storage modulus was determined.

Positron Annihilation Lifetime Spectroscopy (PALS). The PALS measurements made using a conventional fast−slow coincidence system which has been described previously.[10] A ^{22}Na−Kapton foil source (13 μm) was sandwiched between two slabs of sample with dimensions 15 mm × 15 mm × ~2 mm and then placed in a Pyrex tube. The PAL measurements were made using two BaF_2 scintillators coupled to fast photomultipliers mounted in-line on an Oxford Instruments DC-2 cryostat. Lifetime spectra were collected at 25 °C for 6 h, giving approximately 1 million counts. Measurements were made in triplicate.

Isochronus aging experiments using PALS have failed to show any meaningful trends in the past and are inherently prone to errors.[21] However, isothermal aging experiments have the advantage of eliminating instrumental errors due to changes in sample positioning and source geometry. A potential problem concerning isothermal measurements is the possibility of the sample becoming charged and mask changes that might occur in I_3 caused by *real* structural effects. In the preliminary tests with PET, the collection time, location in the cell, and the use of metal foil earthing indicated that the values of the PALS parameters were constant, allowing the assumption to be made that changes observed may be attributed to real molecular effects. Similar to the dielectric experiments, the sandwich was equilibrated for 1 h at the aging temperature before the first measurement was taken. Spectra were collected at suitable intervals over a 4 h period, providing over 500K counts. The data were processed using the PATFIT program[22] consisting of RESOLUTION and POSITRONFIT fitting programs. The RESOLUTION of the instrument was determined using a single crystal of benzophenone having a well-defined lifetime. The POSITRONFIT is a least-squares program that fits both a lifetime (τ_i) and intensity (I_i) to each of the exponentials making up the spectra. Three lifetimes were defined, but the long lifetime components (τ_3, I_3) characteristic of orthopositronium (o-Ps) annihilation are the important quantities for polymers. The free volume cavity size is related to τ_3, and the number of o-Ps annihilation sites is related to I_3. The short lifetime component (τ_1) corresponding to para-positronium (p-Ps) annihilation was fixed at 0.125 ns, and the intensities I_3:I_1 constrained at a ratio of 3:1.

Dielectric Spectroscopy. Dielectric measurements were performed using a computer-controlled dielectric spectrometer, which has been detailed previously.[23] The following parameters were used: an applied voltage of 9 V, time constant of 10 s, and a feedback capacitance of 100 pF. Silver electrodes were coated onto the polymer films using an Edwards coating system E306A to provide maximum electrical contact. Temperature control of the spectrometer was better than ±0.1 °C. Spectra were collected over the frequency range 0.1−6.5 × 10^4 Hz at 10 deg intervals from −70 to −30 °C. Low temperatures were achieved using a liquid nitrogen cooling system. Isothermal scans were performed on samples equilibrated in the spectrometer at the desired aging temperature (T_a) for 1 h, and dielectric spectra recorded over the frequency range 0.01−65 × 10^4 Hz at specified intervals.

Results and Discussion

The study is divided into two sections: the first dealing with a study of the nature of the molecular motion in the polyesters and the second concerned with the process of physical aging.

A. Influence of Chemical Structure on Molecular Dynamic Properties of the Polyesters. *Differential Scanning Calorimetry [DSC] and Density Measurements.* The DSC scans of the as-supplied films exhibited three features: a glass transition, a cold crystallization peak, and a crystalline melt (Figure 1). The net effect of incorporating naphthalate by blending and/or copolymerization was to reduce the heat of fusion and implicitly the degree of organization. However, at certain naphthalate compositions (PETN16, PETN84) cold crystallization was not detected during the heating regime, although the polymers will crystallize if held isothermally. The blend also failed to crystallize, suggesting that some transesterification may have occurred. The T_g was observed to increase in an almost linear manner, consistent with the rotational restrictions introduced by the incorporation of the inflexible naphthalate moieties. Interestingly, a small exotherm seems to follow the glass transition process. This “peak” is attributed to the effects of entropic relaxation and is

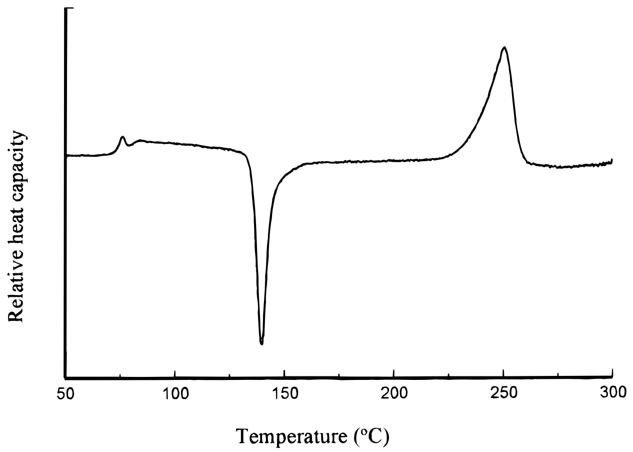

Figure 1. DSC curve for cast amorphous PET, as supplied.

a consequence of the fact that the films used were quenched from the melt. Although these films are not stretched, the extrusion process does freeze in a small amount of molecular orientation in the extrusion direction. When the films are heated in the DSC, the aligned molecular segments in the amorphous regions relax to a more thermodynamically stable state, and this structural reorganization leads to the small exotherm detected by DSC. The variation of T_g and T_m with naphthalate content are summarized in Table 1. The inhibition of the crystallization process is attributed to the inability of these systems to form densely packed structures and reflects a lack of regularity in the sequencing of the monomer units along the polymer chain. Furthermore, density measurements revealed that all of the materials used were essentially amorphous (Table 1).

DMTA Measurements. A typical DMTA scan is shown in Figure 2. The loss modulus (E'') data revealed two mechanical relaxations in all of the samples investigated: the α-relaxation associated with the glass transition and a very broad β-relaxation ranging from −70 to −55 °C. Each of the cast amorphous films displayed the rather unusual mechanical characteristic of exhibiting a rise in the storage modulus (E') just before the α-relaxation occurred, which we will define E'(max). This "peak" is attributed to the effects of entropic relaxation discussed earlier. When the films are heated in the DMTA in the vicinity of T_g, the aligned molecular segments in the amorphous regions relax to a more thermodynamically stable state, and the structural reorganization leads to an increase in E'. The temperature of this maximum in E', and also of E''(max) for the cast PETN polyesters as a function of naphthalate content, is presented as a function of the naphthalate content in Figure 3. The temperature of the maxima in E' and E'' appears to be independent of the naphthalate content at high naphthalate values.

Positron Annihilation Lifetime Spectroscopy. The PALS data for components associated with self-annihilation of positrons (τ_2, I_2) and o-Ps annihilation are presented in Table 2. The data show that only slight differences in τ_3 and I_3 exist in these films. The average free volume size (V_F) for spherical cavities can be calculated using

$$V_F = \frac{4\pi R^3}{3} \tag{1}$$

The cavity radius, R, is calculated from the o-Ps lifetime results:

$$\tau_3 = \frac{1}{2}\left[1 - R(R + \Delta R) + \left(\frac{1}{2\pi}\right)\sin(2\pi R/(R + \Delta R))\right]^{-1} \tag{2}$$

where ΔR represents an electron layer thickness and is estimated as 0.166 nm by fitting τ_3 to known vacancy sizes of molecular crystals.[24] Equation 2 can be used to calculate R from experimentally measured τ_3 results (Table 2), and V_F is then evaluated using eq 2. A larger hole size was observed for the blend. The variation of the hole size as a function of naphthalate content (Figure 4) does not vary monotonically with composition. Incorporation of naphthalate at 8, 12, and 16 mol % resulted in an increase in V_F relative to the value for PET, which subsequently decreased at the higher naph-

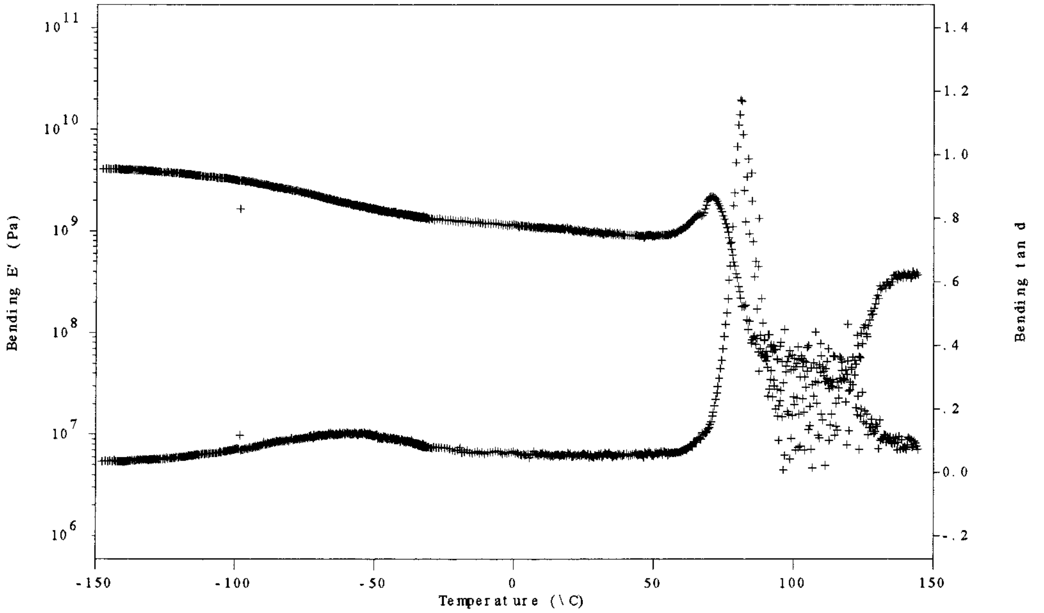

Figure 2. Typical dynamic mechanical spectrum of the storage modulus (E') and tan δ responses for PET at 1 Hz for cast polyester films.

Table 2. PALS Properties of the Melt-Cast Films Used in This Study

material	τ_2 (±0.02 ns)	I_2 (±0.4%)	τ_3 (ns)	I_3 (%)	R (nm)
PET	0.374	69.3	1.59 ± 0.02	23.0 ± 0.2	0.245 ± 0.02
PETN3	0.391	68.1	1.59 ± 0.02	23.9 ± 0.3	0.244 ± 0.03
PETN8	0.378	68.9	1.61 ± 0.02	23.3 ± 0.2	0.247 ± 0.02
PETN16	0.401	69.6	1.66 ± 0.02	22.8 ± 0. 3	0.252 ± 0.02
PETN84	0.364	69.8	1.59 ± 0.02	22.6 ± 0.2	0.244 ± 0.03
PETN95	0.395	69.0	1.58 ± 0.02	23.2 ± 0.3	0.243 ± 0.02
PEN	0.374	69.6	1.56 ± 0.02	22.8 ± 0.2	0.241 ± 0.02
BLEND	0.376	71.4	1.67 ± 0.02	21.4 ± 0.3	0.253 ± 0.02

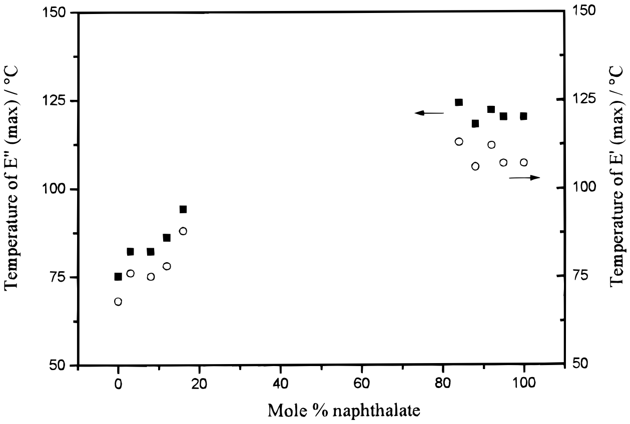

Figure 3. Variation of the transition temperatures for the cast PETN polyesters as a function of naphthalate content: E''(max) defines the α-relaxation, (■) and E'(max) represents the inherent stress relaxation peak (○).

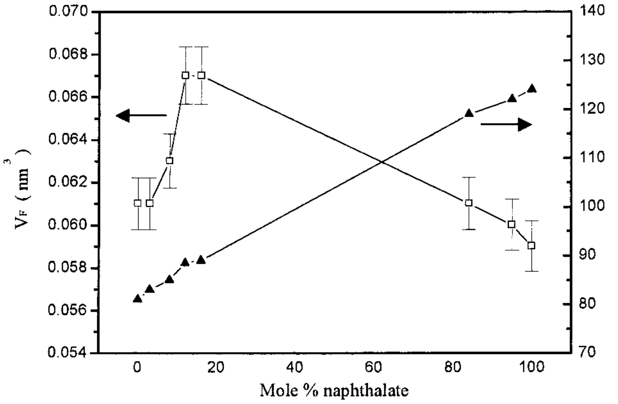

Figure 4. Free volume (V_F) calculated using the spherical cavity assumption and the glass transition temperature measured at 10 °C min^{-1} by DSC versus mol % naphthalate.

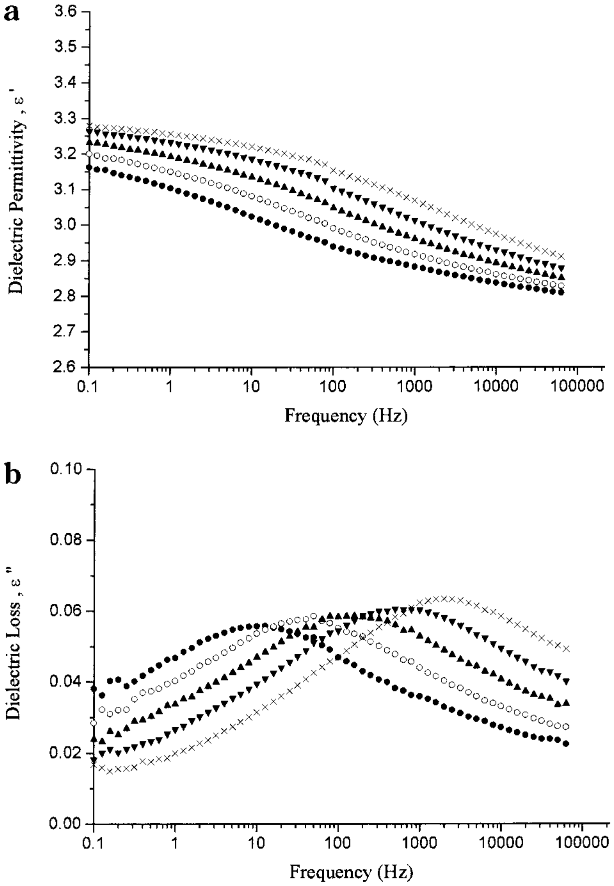

Figure 5. Typical dielectric β-relaxation spectrum for the cast polyesters: (a) the dielectric permittivity (ϵ') and (b) the dielectric loss (ϵ'') responses for PETN16 at −70 °C (●), −60 °C (○), −50 °C (▲), −40 °C (▼), and −30 °C (×).

thalate contents (84, 95, and 100 mol %). It is interesting to note that an increase in naphthalate content in the PETN series causes an almost linear increase in T_g. Kharul and Kulkarni[25] have found for poly(arylates) that the changes in packing density parameters calculated from interchain spacing (wide-angle X-ray diffraction) and fractional free volume (calculated from density measurements and Bondi's group contribution method[26]) showed a significant variation from the expected monotonic trend with increasing naphthalate content. Incorporation of ≤40% naphthalate disrupted chain packing because of the random distribution of naphthalene-based moieties in the polymer chain.

Dielectric Spectroscopy: Temperature Scans. Dielectric spectra were measured as a function of temperature, and a typical plot is presented in Figure 5. Complex plane (Cole−Cole) plots were constructed from the dielectric data, and fits of the experimental data were performed according to the Havriliak−Negami expression[27] (eq 3); the analyses carried out use a program written in Mathcad 6.0.

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{(1 + (i\omega\tau)^{1-\alpha})^\beta} \tag{3}$$

From the analysis was obtained the dielectric relaxation strength or oscillator strength, ($\epsilon_s - \epsilon_4$), f(max) the relaxation frequency, the distribution parameters α and β, and ϵ''(max) as a function of temperature and percent of naphthalate. The magnitude of ϵ''(max) varies linearly with naphthalate content in these PETN systems (Figure 6a,b), as does the frequency of the relaxation process. The dielectric relaxations are generally assumed to be thermally activated and take an Arrhenius form:

$$\frac{1}{\tau} = f(\max) = A \exp\left[\frac{-E_a}{RT}\right] \tag{4}$$

where f(max) is the frequency of the loss maximum and

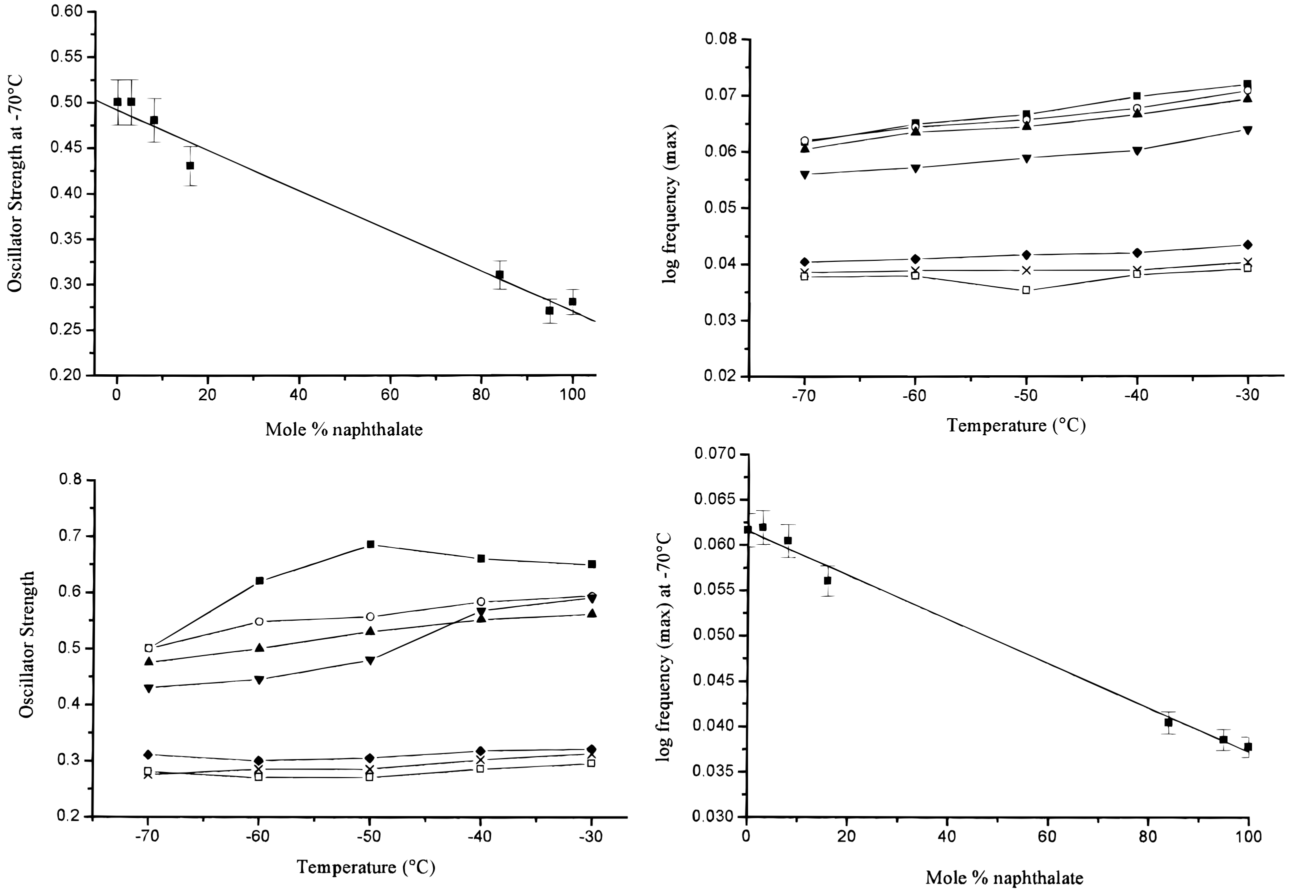

Figure 6. Dielectric parameters for PETN polyesters: (a) variation of oscillator strength with naphthalate composition from dielectric data at −70 °C; (b) variation of oscillator strength with temperature for PET (■), PETN3 (○), PETN8 (▲), PETN16 (▼), PETN84 (◆), PETN95 (×), and PEN (□); (c) variation of log frequency (max) with temperature for PET (■), PETN3 (○), PETN8 (▲), PETN16 (▼), PETN84 (◆), PETN95 (×), and PEN (□); (d) variation of log frequency (max) at −70 °C with polymer composition. For clarity, the error bars are not shown in (b) but are of the same magnitude as in (a).

E_a is the average activation energy. If the relaxation is a true thermodynamic process, then a plot of the logarithmic value of *f*(max) versus reciprocal temperature (K) should be linear with a slope of $-E_a/R$. An example of the data for several of the melt-cast films is presented in Figure 7a, showing that all of the data fall on essentially the same line. The calculated activation energies are presented in Table 3 and agree well with previously cited values.[28,29] These results indicate that the relaxing entity is the polar segment between the aromatic rings, since the value of the activation energy does not vary with the naphthalate composition. The distribution parameters (α and *β*) taken from the data at −70 °C, do, however, vary with naphthalate content (Figure 7b). Changes in α and *β* were interpreted in terms of changes in the order of the local environment or in the multiplicity of the pathways involved in the relaxation process. The α and *β* values, corresponding to the breadth and asymmetry of the relaxation, respectively, exhibited little variation for a particular sample with temperature. Generally, the *β*-relaxation process in all the cast film systems studied was broad (α values of 0.3−0.5), reflecting the differing types of local environments experienced by the dipoles and the nonuniformity of the glassy state. As naphthalate content was increased, a progressive decrease in *β* was noted which showed an increase again for PEN. This is indicative of the presence of different environments in the copolymer systems. The PETN3/PETN95 (50/50 wt %) blend had a particularly low value of *β* (0.43) consistent with it being a blend of polymers.

The oscillator strengths ($\epsilon_s - \epsilon_\infty$) were extracted from the complex plane analysis for each system at each temperature, and the values are plotted in Figure 6a,b. The magnitude of the oscillator strength was found to increase for a particular sample with temperature; for example, it increased from 0.43 to 0.59 in going from −70 to −30 °C for PETN16. The extent of the increase in ($\epsilon_s - \epsilon_\infty$) with temperature was observed to decrease with increasing naphthalate content. Moreover, the oscillator strength was found to decrease with increasing naphthalate content, and ($\epsilon_s - \epsilon_\infty$) provides a representation of the strength of molecular dipole involved in the relaxation.[30] According to the Onsager's equation[31]

$$\epsilon_s - \epsilon_\infty = \frac{N}{\epsilon_v}\left[\frac{\epsilon_\infty + 2}{3}\right]\left[\frac{3\epsilon_s}{2\epsilon_s + \epsilon_\infty}\right] \tag{5}$$

where ϵ_v is the vacuum permittivity, *N* is the number of segments per unit volume, and α_0 is the equilibrium polarizability of the main chain segment. Changes in oscillator strength reflect the presence of dipolar interactions, intramolecular interactions, or changes in molecular configurations. The data indicate that in the naphthalate systems the dipole strength is less than that of PET, due to the reduced dipolar density when the aromatic nature of the polymer is increased.

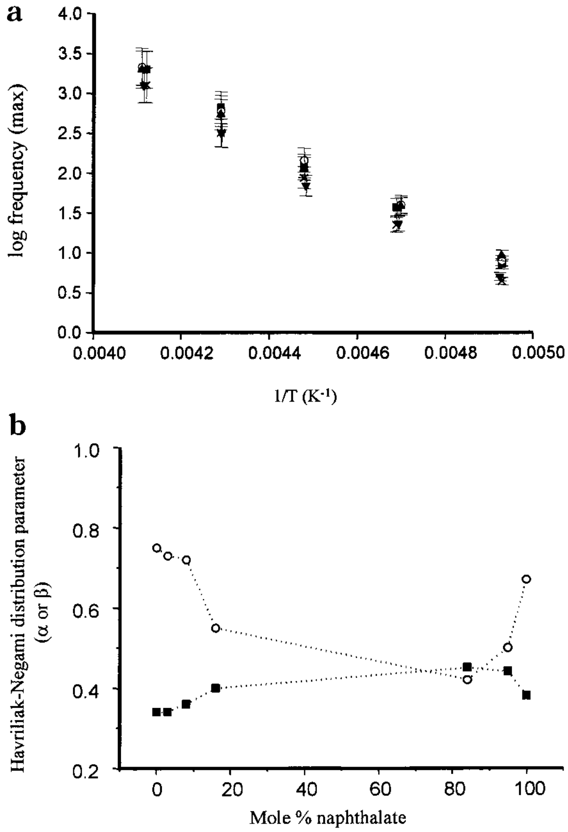

Figure 7. (a) Arrhenius activation energy plots for the β-relaxation in the PETN polyesters: PET (■), PETN8 (○), PETN16 (▲), PETN84 (▼), and PEN (×); (b) variation of the Havriliak–Negami distribution parameters, α (■) and β (○), with naphthalate composition, from the data at −70 °C.

Table 3. Activation Energies for the β-Relaxation in the Melt-Cast Films

material	E_a (kJ/mol)	material	E_a (kJ/mol)
PET	57.9 ± 2.0	PETN84	56.0 ± 2.4
PETN3	55.8 ± 1.0	PETN95	52.2 ± 2.2
PETN8	57.2 ± 1.0	PEN	57.4 ± 1.0
PETN16	54.8 ± 2.5	BLEND	59.4 ± 1.0

Conclusions. The data presented indicate that change of the composition of the polyesters leads to subtle variations in the way the chains pack which are reflected in the variation of the values of T_g and the extent to which a crystalline ordered phase is created. The local chain dynamics as reflected in the β process are, however, not dramatically influenced by changes in composition.

B. Physical Aging Effects in Polyesters. The samples used in this study were melt-cast and then rapidly quenched to 60 °C below T_g. This process will freeze into the solid an equilibrium structure that is representative of the melt temperature. Increase of the temperature allows molecular motions to occur which may lead to structural rearrangement and observation of the phenomenon of physical aging. In an attempt to explore the connection between the various processes which may be occurring, measurements of the change in the dynamic mechanical, dielectric, and positron annihilation characteristics were carried out.

Dynamic Mechanical Thermal Analysis: Isothermal Experiments. For all of the samples, E' increased with aging time at a rate dictated by the extent of undercooling which takes place, and this behavior is illustrated for PET (Figure 8). The changes in E' ($\Delta E'$)

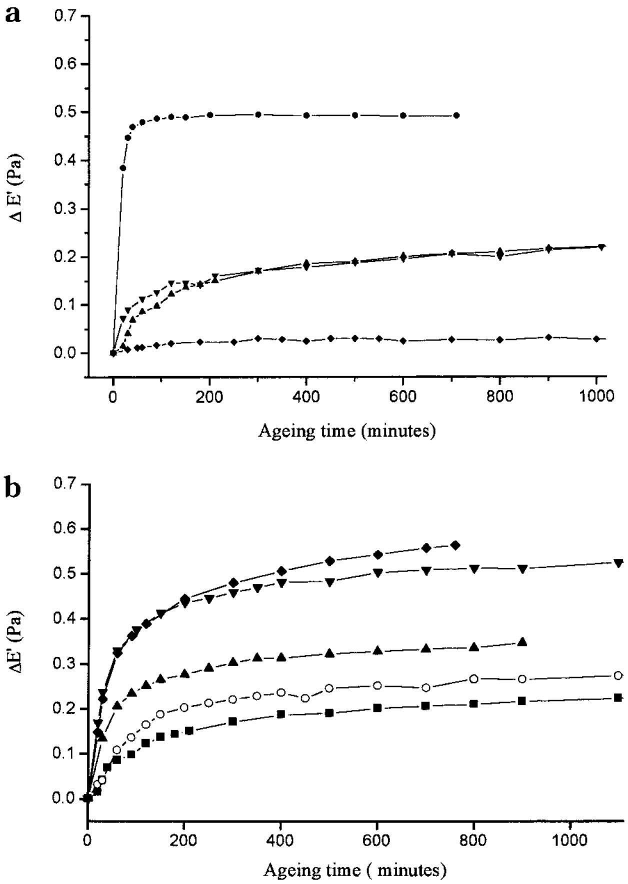

Figure 8. Relative changes in mechanical storage modulus ($\Delta E'$) with aging time for (a) PET held isothermally at (◆) 40 °C, (▲) 50 °C, (▼) 60 °C, and (●) 70 °C and (b) the PETN polyesters at similar undercoolings [°C]: (■) PET [21 °C], (○) PETN8 [25 °C], (▲) PETN16 [19 °C], (▼) PETN84 [19 °C], and (◆) PEN [20 °C].

Table 4. Values of the Storage Modulus (E') after 700 min of Aging for PETN Polyesters

	storage modulus (E') after 700 min at aging temp [°C]			
PET	8.93 [40]	8.83 [50]	8.95 [60]	9.13 [70]
PETN8	8.84 [40]	8.85 [50]	8.80 [60]	9.14 [70]
PETN16	8.68 [50]	8.84 [60]	8.95 [70]	9.13 [80]
PETN84	8.70 [70]	8.81 [90]	9.05 [100]	9.00 [110]
PEN	8.65 [70]	8.68 [90]	8.86 [100]	9.05 [110]

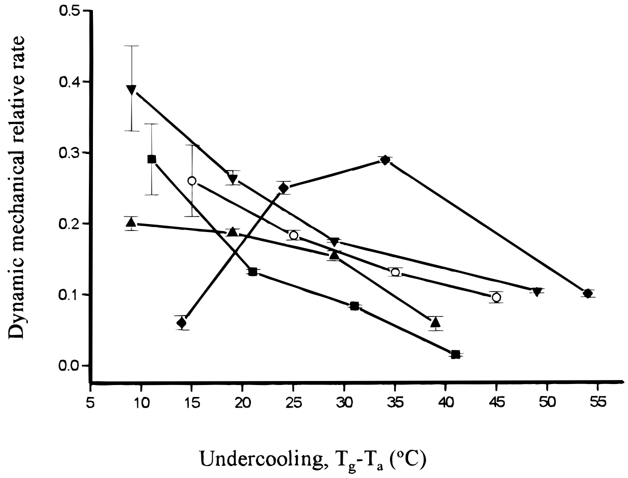

Figure 9. Relative rates of aging calculated from the gradient of the linear fits to $\Delta E'$ versus aging time (log scale) against undercooling for (■) PET, (●) PETN8, (▲) PETN16, (▼) PETN84, and (◆) PEN.

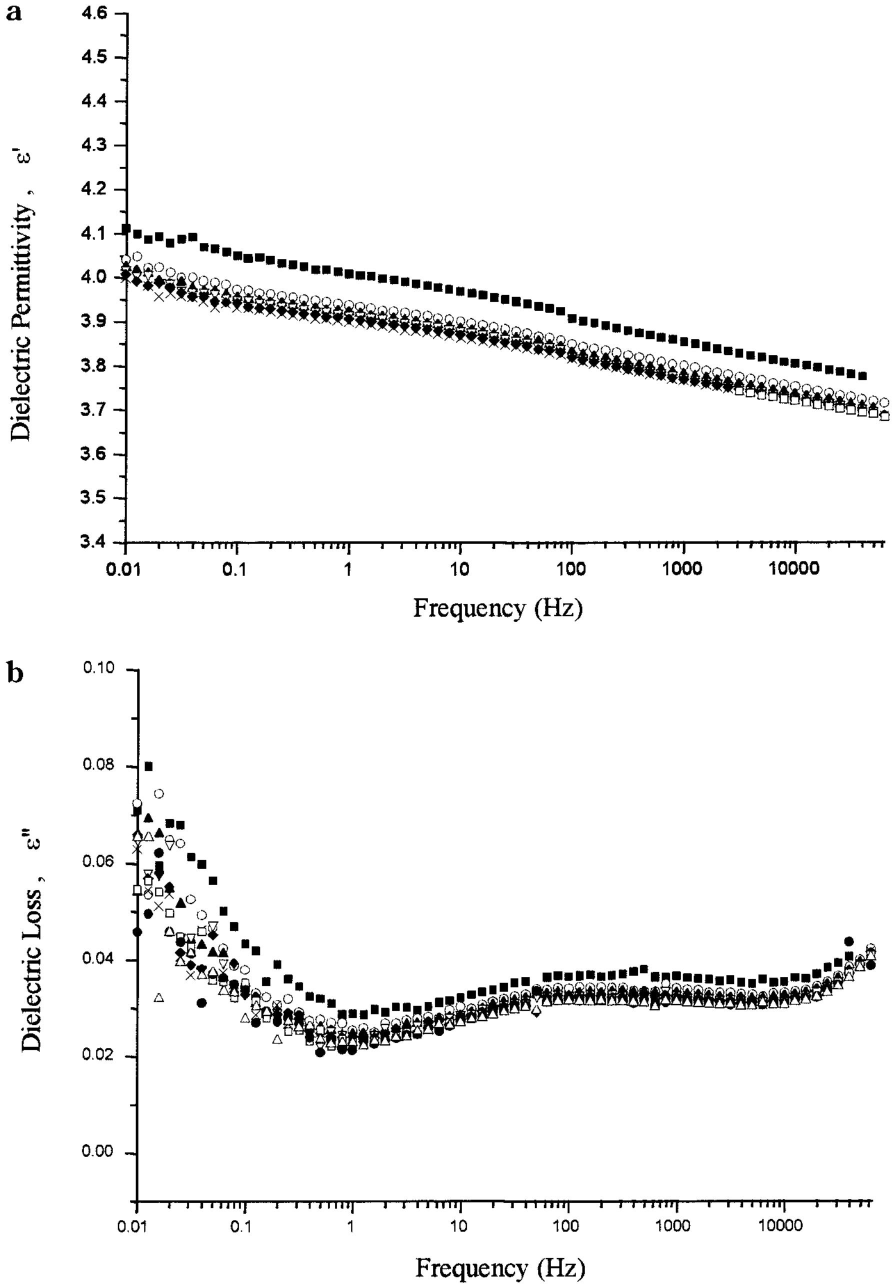

Figure 10. Examples of (a) dielectric permittivity (ϵ') and (b) dielectric loss (ϵ'') spectra for PETN84 held isothermally at 100 °C. Aged 1 h (■), 2.5 h (○), 4 h (▲), 5.5 h (▽), 7 h (◆), 8.5 h (×), 10 h (□), 11.5 h (●), and 16 h (△).

relative to the initial value were recorded at 40, 50, 60, and 70 °C. As the degree of undercooling relative to the T_g is reduced so the rate of the relaxation becomes faster. Changes in the mechanical properties have in the past been attributed to a gradual embrittlement of the PET[32] which may be associated with an increase of T_g due to aging. An increase in the modulus is accompanied by a reduction in the value of tan δ that is indicative of a reduction of the extent of the molecular motion in the sample. Values of E' measured after 700 min of aging (Table 4) and corresponding to the asymptotic value at the highest T_a indicated that there is a general increase in this limiting value, which is contrary to what would intuitively have been expected to happen for an amorphous polymer. An increase in limiting value of E' suggests that the material is becoming more restricted and indicates that molecular ordering is possibly occurring. The formation of ordered domains has been reported from PET.[33-35]

To calculate a relative rate of aging, the $\Delta E'$ data were plotted against aging time on a log scale, and a linear fit was made to the data.[36,37] Correlation coefficients ranging from 0.93 to 0.99 were obtained. The largest errors were associated with the data for the lowest undercoolings where a plateau was quickly established. The relative rates of aging are plotted against undercooling in Figure 9. The form of these graphs is similar to those predicted by Struik.[14] The apparently low rate for PEN at 110 °C (the smallest undercooling) is an artifact, the sample undergoing relaxation that is too fast to be measured accurately.

The presence of a local maximum in the PEN curve is nevertheless probably real, reflecting the role of internal stress on aging. Vieth et al.[38] have, in a discussion of their aging work on extruded PET films, suggested that such factors can have an important influence. The particular behavior here of PEN may reflect the additional constraints imposed by the devel-

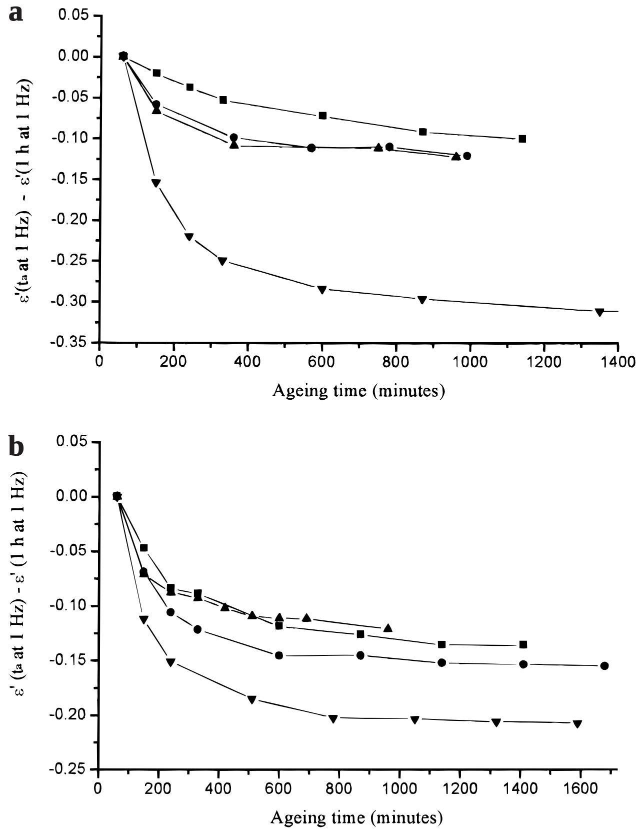

Figure 11. Relative changes in dielectric permittivity ($\Delta\epsilon'$) at 1 Hz for (a) PET held isothermally at 40 °C (■), 50 °C (●), 60 °C (▲), and 70 °C (▼) and (b) PETN84 held isothermally at (■) 70 °C, (●) 90 °C, (▲) 100 °C, and (▼) 110 °C.

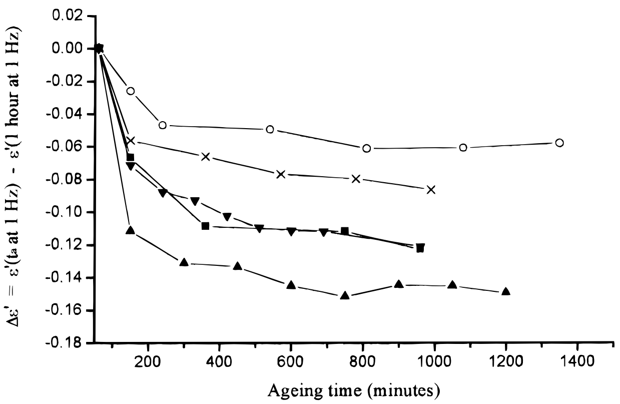

Figure 12. Changes in dielectric permittivity ($\Delta\epsilon'$) with aging time for the PETN polyesters at similar undercoolings [°C]: (■) PET [21 °C], (×) PETN8 [25 °C], (▲) PETN16 [19 °C], (▼) PETN84 [19 °C], and (○) PEN [20 °C].

opment of local order in the form of parallelization of the naphthalate moieties.

Dielectric Spectroscopy: Isothermal Experiments. The mechanical data imply that aging is restricting the motion of the polymer chains, and an ideal way of probing such changes is to study isothermally the dielectric relaxation spectra. An example of the type of data obtained is presented in Figure 10. The dielectric permittivity decreases as aging occurs and is indicative of a reduction in the amplitude of the contributing dipole relaxation. Since no variations in dimension or thickness were observed in any of the samples during aging, these changes were genuinely attributable to aging. Before data collection, the sample was equilibrated for 1 h at the aging temperature. The aging process may be conveniently represented as the difference in the value of ϵ' first scan with respect to the subsequent scans of the aged samples. The values of $(\Delta\epsilon') = \epsilon'$ (t_a at 1 Hz) $-$ ϵ' (1 h at 1 Hz) are presented in Figure 11 for PET and PETN84. In all cases the dielectric permittivity was found to decrease with sub-T_g annealing time. The extent and rate of reduction were greatest at the lowest degrees of undercoolings. The dielectric loss spectra for PETN84 and PEN contained an additional relaxation process that moved to higher frequencies with increasing aging temperature. This relaxation, defined as β^*, has been attributed to motions of the naphthalene rings and corresponds to the β_1 relaxation process noted for the dynamic mechanical measurements. Similar observations have been reported by other workers.[39,40] Corresponding plots for the polyesters at a similar degree of undercooling are presented in Figure 12. The relative magnitude of the changes in ϵ' for PEN were much lower than for the other polyesters and reflects a decreased strength of the molecular dipoles in PEN due to the influence of the naphthalene rings. Although a loss in dipole activity was observed for all temperatures, the largest reduction was observed at the lowest undercoolings. Changes in permittivity can be related to changes in density using the Clausius–Mossotti equation if the dipole contribution is assumed to be constant:

$$P = \frac{M}{\rho}\frac{\epsilon_s - 1}{\epsilon_s + 2} = \frac{N_A \alpha}{3\epsilon_0} \tag{6}$$

where N_A is Avogadro's number, P is the polarization, and M is the molar mass. Equation 6 indicates that if the dipole contribution is constant, then a reduction in permittivity can be related to a densification of the system during aging. At the temperatures used in this study the β-relaxation process will occur at frequencies above those used and therefore will contribute to its amplitude of the low-frequency permittivity. Moreover, the data reflect an inhibition of localized chain motions associated with β-relaxation process, and this feature is known to contribute to physical aging.[41] Thus, motions associated with the β-relaxation are believed to be a factor in the physical aging process. In the absence of any changes in sample morphology, an increase in temperature should result in an increase of ϵ'; this is, however, not the case. Since we do not have access to the high-frequency limiting values of ϵ', it is not possible to unambiguously analyze the contributions to the changes observed. However, the data do suggest that chain packing is occurring, producing a more densely packed structure with diminished mobility and/or number of molecular dipoles per unit volume. Chain packing toward a more ordered arrangement where the chain segments align giving *trans*-ethylene glycol, coplanar CO units, and a parallelization of benzene rings[42,43] would be consistent with these observations. The PETN polymers showed similar variations in ϵ' to PET, pointing to the fact that aging in the naphthalate systems also involved a densification toward a more closely packed structure. It was interesting to note the somewhat "anomalous" value of ϵ' obtained after 1000 min at 60 °C (i.e., 25 °C undercooling) for PETN8. This peculiar behavior was not limited to the dielectric technique, and low values of E' and $\Delta E'$ were obtained from the dynamic mechanical measurements (Figure 13).

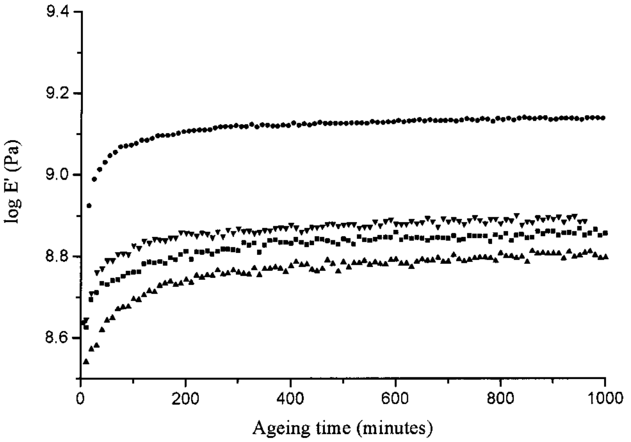

Figure 13. Variation of log E' for PETN8 as a function of aging time at (■) 40 °C, (▼) 50 °C, (▲) 60 °C, and (●) 70 °C.

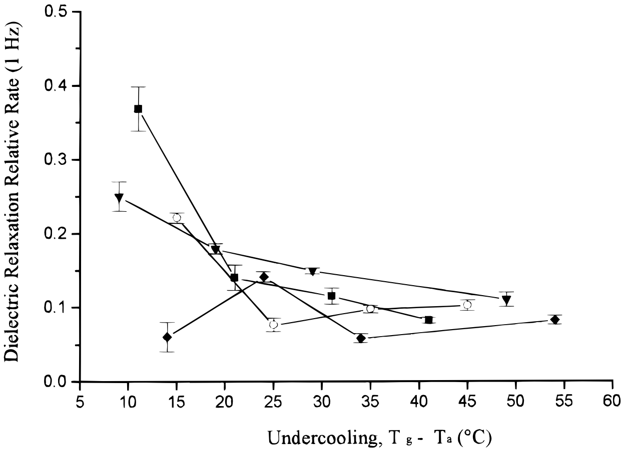

Figure 14. Relative rates of aging calculated from the gradient of the linear fits of $\Delta\epsilon'$ versus aging time (log scale) against undercooling for (■) PET, (○) PETN8, (▼) PETN84, and (◆) PEN. The lines are included to act as guides for the eye.

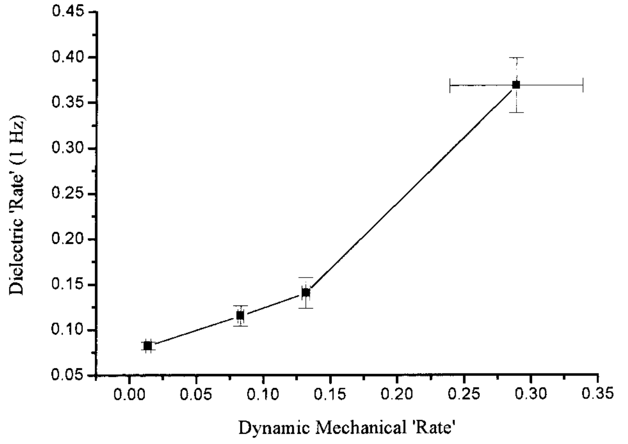

Figure 15. Correlation between aging "rates" of PET from dielectric spectroscopy and dynamic mechanical measurements.

Using the same approach as that used with the mechanical data, it was possible to calculate relative rates of aging, and correlation coefficients in the range 0.91 and 0.98 were obtained (Figure 14). As expected, an increase in rate was observed with increasing T_a which correlated well with the dynamic mechanical rates, suggesting again that the same process was being probed. Again, the apparently low rate for PEN at 110 °C (the smallest undercooling) is an artifact, the sample undergoing relaxation that is too fast to be measured accurately. A clear correlation does exist between the dielectric and dynamic mechanical data as shown for PET in Figure 15, suggesting that the same underlying processes are leading to the observed changes.

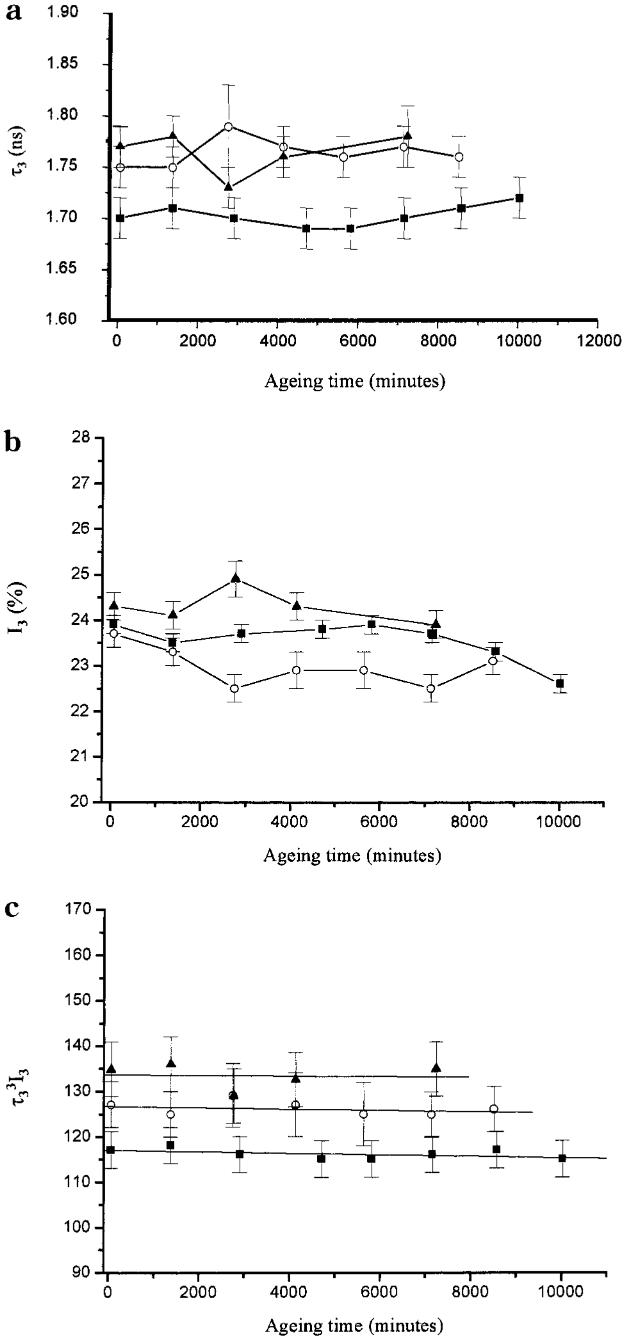

Figure 16. (a) Changes in PALS parameter τ_3 with aging time for PET held isothermally at (■) 40 °C, (○) 50 °C, and (▲) 60 °C. (b) Changes I_3 with aging time for PET held isothermally at (■) 40 °C, (○) 50 °C, and (▲) 60 °C. (c) Changes in PALS free volume, represented by the product $\tau_3^3 I_3$, with aging time for PET held isothermally at (■) 40 °C, (○) 50 °C, and (▲) 60 °C.

Positron Annihilation Lifetime Spectroscopy (PALS). In the dielectric study it was pointed out that the decrease in the permittivity might be attributed to densification of the matrix; if this is the case, then PALS data might be expected to reflect these changes. Isothermal PALS data showing the variation of τ_3 and I_3 with aging time are given for PET in Figure 16a,b.

Although the PALS results for PET failed to show significant free volume changes upon aging, they were useful for rationalizing some of the unusual observations from the dynamic mechanical (pseudorate and $\Delta E'$) and dielectric (pseudorate, ϵ' and $\Delta\epsilon'$) experiments. The isothermal PALS experiments revealed that the τ_3 component for the samples aged at 50 and 60 °C were very similar, in contrast to the expected increase in hole size with increasing temperature. However, the distribution of free volume term, I_3, was lower at 50 °C (Figure 16b), and the discrepancy was resolved by considering the product $\tau_3^3 I_3$ (Figure 16c), which is indicative of the total hole size distribution in a material.[44,45] The total hole distribution in PET is surprisingly invariant compared with the usual time dependence observed for most amorphous polymers. The data show that complex processes are involved in terms of hole size changes with time and temperature but that the local free volume does not change significantly with temperature.

Conclusions

The apparent invariance of the free volume with time implies that the reduction in the dielectric permittivity must be attributed to order developing in the solid leading to a reduction in the amplitude of the β process. This conclusion is consistent with the increased storage modulus on aging. The presence of internal stresses in the film appears to facilitate the aging process. An excellent correlation was found between the rates of aging from both techniques, suggesting that the same underlying structural changes were being assessed. Positron annihilation lifetime spectroscopy aging experiments suggested that aging in PET was not merely a free-volume-controlled event but was more consistent with chain redistribution with changes in local order.

Acknowledgment. The authors thank ICI (now Du Pont) and the EPSRC for funding the work. Special thanks to Paul Davis (Du Pont Polyester) for preparing the amorphous PET samples used in this study and Dr. D. Hayward for assistance with the measurements presented in this paper.

References and Notes

(1) Colomer, P.; Montserrat, S.; Belana, J. *J. Mater. Sci.* **1998**, *33*, 7, 1921.
(2) Neagu, E. R.; Neagu, R. M. *Phys. Status Solidi A* **1994**, *144*, 2, 429.
(3) Hofmann, A.; Kremer, F.; Fischer, E. W. *Physica A* **1993**, *201*, 1−3, 106.
(4) Xia, Z. F.; Yang, G. M.; Sun, X. M. *IEEE Trans. Electr. Insul.* **1992**, *27*, 4, 702.
(5) McCrum, N. G.; Reid, B. E.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Materials*; Wiley: Chichester, 1967.
(6) Bailey, R. T.; North, A. M.; Pethrick, R. A. *Molecular Motion In High Polymers*; Oxford: New York, 1985.
(7) Jaffe, M.; Menczel, J. D.; Bessey, W. E. *Thermal Characterization of Polymeric Materials*, 2nd ed.; Academic Press: San Diego, 1997; pp 1866, 2006.
(8) Song, H.-H.; Roe, R.-J. *Macromolecules* **1987**, *20*, 2723.
(9) Montserrat, S.; Cortes, P. *Makromol. Chem., Macromol. Symp.* **1988**, *20/21*, 389.
(10) Davies, W. J.; Pethrick, R. A. *Eur. Polym. J.* **1994**, *30* (11), 1289.
(11) Nakanishi, H.; Jean, Y. C.; Smith, E. G.; Sandreczki, T. C. *J. Polym. Sci., Part B: Polym. Phys.* **1989**, *27*, 1419.
(12) Nakanishi, H.; Jean, Y. C. *Macromolecules* **1991**, *24*, 6618.
(13) Tseng, P.-K.; Chang, S.-P.; Chuang, S.-Y. In *Positron Annihilation*; Coleman, P. G., Sharma, S. C., Diana, I. M., Eds.; North-Holland Publishing Company: Dordrecht, 1987; p 730.
(14) Struik, L. C. E. In *Physical Aging in Amorphous Polymers & Other Materials*; Elsevier: Amsterdam, 1978.
(15) Hutchinson, J. M. Physical Aging of Polymers. *Prog. Polym. Sci.* **1995**, *20*, 703.
(16) Ishida, Y.; Matsuo, M.; Togami, S.; Yamafuji, K.; Takahanagi, M. *Kolloid Z.* **1962**, *183*, 74.
(17) Mascia, L.; Fekkai, Z. *Polymer* **1993**, *34*, 1418.
(18) Lightfoot, S.; Xu, G. *Polym. Plast. Technol. Eng.* **1993**, *32*, 21.
(19) Tatsumi, T.; Ezure, H.; Ito, E.; *Kobunshi Ronbunshu* **1992**, *49*, 521.
(20) Campbell, D.; White, J. R. *Polymer Characterization*, Chapman and Hall: New York, 1989.
(21) Davies, W. J. Ph.D. Thesis, University of Strathclyde, Glasgow, G1 1XL, 1995.
(22) Kirkgaard, P.; Eldrup, M.; Morgensen, O. E.; Pedersen, N. J. *Comput. Phys. Commun.* **1981**, *23*, 307.
(23) Pethrick, R. A.; Hayward, D.; Mahboubian-Jones, M. G. B. *J. Phys. E: Sci. Instrum.* **1984**, *17*, 683.
(24) Hill, A. J.; Weinhold, S.; Stack, G. M.; Tant, M. R. *Eur. Polym. J.* **1996**, *32* (7), 843.
(25) Kharul, U. K.; Kulkarni, S. S. *Polymer* **1998**, *39* (10), 2011.
(26) Bondi, J. *J. Chem. Phys.* **1964**, *68*, 441.
(27) Havriliak, S.; Havriliak, S. J. *Dielectric and Mechanical Relaxation in Materials*; Hanser Publishers: Munich, New York, 1997.
(28) Tatsumi, T.; Ito, E.; Hayakawa, R. *J. Polym. Sci., Phys. Ed.* **1992**, *30*, 701.
(29) Ezquerra, T. A.; Baltá-Calleja, F. J.; Zachmann, H. G. *Acta Polym.* **1993**, *44*, 18.
(30) Blythe, A. R. In *Electrical Properties of Polymers*; Cambridge University Press: Cambridge, 1979.
(31) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.
(32) Petrie, S. E. B. *J. Macromol. Sci., Phys.* **1976**, *B12* (2), 225.
(33) Bove, L.; D'Aniello, C.; Gorrasi, G.; Guadagno, L.; Vittoria, V. *Polym. Bull.* **1997**, *38*, 579.
(34) Baltá-Calleja, F. J.; Santa Cruz, C.; Asano, T. *J. Polym. Sci., Phys. Ed.* **1993**, *31*, 557.
(35) Vittoria, V.; Petrillo, E.; Russo, R. *J. Macromol. Sci., Phys.* **1996**, *B35*, 147.
(36) Guest, M. J.; Daly, J. H. In *Polymer Yearbook 10*; Pethrick, R. A., Zaikov, G. E., Naoyoki Koida, T. T., Eds.; Harwood Academic Publishers: London, 1993; p 141.
(37) Aref-Azar, A.; Hay, J. N. *Polymer* **1982**, *23*, 1129.
(38) Vieth, W. R. In *Diffusion in and Through Polymers: Principles and Applications*; Hanser Publishers: Munich, 1990.
(39) Light, R. R.; Seymour, R. W. *Polym. Eng. Sci.* **1982**, *22* (14), 857.
(40) Ezquerra, T. A.; Baltá-Calleja, F. J.; Zachmann, H. G. *Acta Polym.* **1993**, *44*, 18.
(41) Bigg, D. M. *Polym. Eng. Sci.* **1996**, *36* (6) 737.
(42) Koenig, J. L.; Kormos, D. E. *N. Y. Acad. Sci.* **1981**, *371*, 87.
(43) Rodríguez-Cabello, J. C.; Quintanilla, L.; Pastor, J. M. *J. Raman Spectrosc.* **1994**, *25*, 335.
(44) Pethrick, R. A. Positron Annihilation—A probe for nanoscale voids and free volume. *Prog. Polym. Sci.* **1997**, *22*, 1.
(45) Eldrup, M. *Positron Methods for the Study of Defects in Bulk Materials*; Industrial Applications of Positron Annihilation; Europhysics Ind. Workshop, March 1994.

MA9909197