Conformational and Relaxation Studies on Polyesters Derived from Terephthalic Acid and Propylene and Dipropylene Glycol†

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ABSTRACT: Poly(propylene glycol terephthalate) (PPT) and poly(dipropylene glycol terephthalate) (PDPT) were obtained by condensation of propylene glycol and dipropylene glycol with dimethyl terephthalate, respectively. The dielectric constants of benzene solutions of PDPT chains were measured in the temperature range 30–60 °C. The values of the dipole moment ratio $\langle\mu^2\rangle/nm^2$, where nm^2 is the mean-square dipole moment of a freely jointed chain, amounted to 0.715 at 30 °C and 0.750 at 60 °C. These results indicate that PDPT is more polar than PPT, since the dipole moment ratio of the latter polymer is only 0.582 at 30 °C. The theoretical analysis of the dipole moment ratio of PDPT suggests that gauche states about $CH(CH_3)$–CH_2 bonds, which place an oxygen atom between a methyl group and another oxygen atom, have higher energy than the alternative gauche states. The mechanical spectra of both PDPT and PPT present prominent α-absorptions, associated to the glass–rubber relaxation, which are centered at 43 and 98 °C, respectively, at 1 Hz. A well-developed β subglass relaxation, which seems to be the result of two overlapping β_1 and β_2 absorptions, appears in the mechanical spectrum of PPT chains; however, this relaxation is weak and diffuse in PDPT. The dielectric loss tangent versus temperature plots exhibit a single prominent β absorption in both polymers. The critical interpretation of the dielectric and mechanical results seems to suggest that the β subglass absorptions are caused by conformational transitions about $CH(CH_3)$–CH_2 bonds of the glycol residue. The high activation energy (37 kcal mol^{-1}), associated to the β_1 mechanical absorptions of PPT chains, is probably caused by molecular motions in which more than a single unit intervene.

Introduction

Terephthalic acid based polyesters with an ether group in the structural unit, and general formula $-OOCC_6H_4COO(CH_2)_xO(CH_2)_x-$, can schematically be obtained by substituting the central methylene group for an oxygen atom in polyesters with structural unit $-OOCC_6H_4COO(CH_2)_{2x+1}-$. The physical properties of these polyesters differ significantly from those of their poly(methylene terephthalate) counterparts. One of the polyesters best studied, in this regard, is poly(diethylene glycol terephthalate) (PDET),[1-4] which can schematically be derived from poly(pentamethylene terephthalate) (PPMT). In comparing the physical behavior of PDET and PPMT, one can see that the former polyester hardly crystallizes from the bulk in a foreseeable time[4] but only from dilute solutions, whereas the latter readily crystallizes from the melt. The conformational characteristics of both polymers may explain these differences. Thus gauche states about CH_2–CH_2 bonds in PDET, which give rise to first-order O···O interactions, are strongly favored over the alternative trans states,[3] whereas the remaining skeletal bonds are either restricted to trans states as the O–CO bonds or show a strong preference for these states as it occurs with O–CH_2 bonds.[1-3] On the contrary, gauche states about CH_2–CH_2 bonds in PPMT, which cause first-order interactions between CH_2 groups and O atoms, are only slightly favored over the alternative trans states, whereas gauche states about CH_2–CH_2 bonds, which give rise to first-order interactions between two methylene groups, have an energy of 0.5 kcal mol^{-1} above that of the corresponding trans states.[5] Consequently, one can infer that PPMT is more flexible than PDET and the accessibility to the all-trans conformation, necessary to pack the chains in the crystal, is easier in the former polymer than in the latter. With an increasing number of methylene groups in polyesters with an ether group in the structural unit, the feasibility of crystallization of the polymer also increases. Thus poly(ditrimethylene glycol terephthalate) (PDTT) crystallizes from the bulk, presumably as consequence of the fact that gauche states about CH_2–CH_2 bonds, which cause CH_2···O interactions, are favored by only 0.1 kcal mol^{-1} over the alternative trans states.[6]

It is important to study how the introduction of asymmetry in the chains will affect their conformation-dependent properties and their relaxation behavior. This is the aim of this work, where the dipole moments of poly(dipropylene glycol terephthalate) (PDPT), a polymer that can be considered derived from PDET, were studied. An inspection of the structural unit of the polymer suggests that if the reduction in the flexibility of the chains, by action of the methyl side groups, compensates the increase in flexibility caused by the diminution of the fraction of gauche states about CH_2–CH_2 bonds in PDET, then the glass transition temperatures of PDET and PDPT should have similar value. Another goal of this work was to investigate how the substitution of a hydrogen atom of one of the methylene groups of poly(ethylene terephthalate) (PET) for a methyl group will affect the relaxation behavior of the resulting polymer, poly(propylene terephthalate) (PPT).

Experimental Section

Synthesis of Dipropylene Glycol. 1,1′-Oxydi-2-propanol (DPG), an isomer of dipropylene glycol, was prepared from propylene oxide and propylene glycol, using sodium as catalyst, as reported by Sexton and Britton.[7] The fraction boiling between 73 and 77 °C at 1 mmHg was collected and used for the preparation of the polymer. The purity of this fraction was higher than 93%, as determined by HPLC and ^1H and ^{13}C NMR spectroscopy. The impurity was considered to be the primary–secondary isomer of dipropylene glycol.

Synthesis of the Polymers. Poly(dipropylene glycol terephthalate) (PDPT) and poly(propylene glycol terephthalate) (PPT) were obtained by the standard melt phase procedure from DPG and propylene glycol, respectively, and dimethyl terephthalate, in the presence of isopropyl titanate, using an initial mole ratio of diester to glycol of 1:2.2. The polycondensation

† This paper is dedicated to Prof. G. M. Guzmán on the occasion of his 65th birthday.

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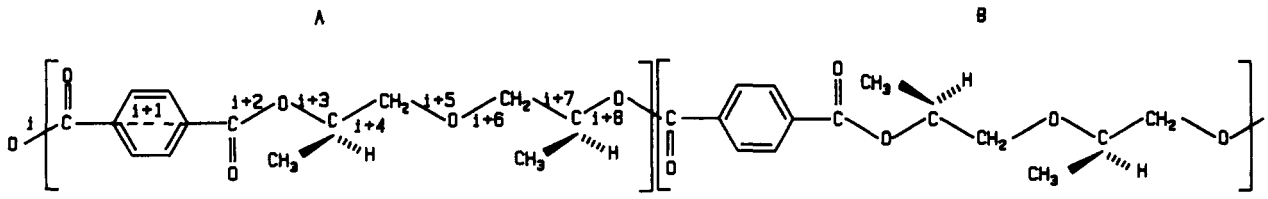

Figure 1. Schematic representation of A and B units of poly(dipropylene glycol terephthalate) in the all-trans conformation.

proceeded in two steps. In the first step, the ester interchange was complete after 2–3 h at 180–200 °C, with elimination of the theoretical amount of methanol; in the second step, the polycondensation was carried out at 220 °C under vacuum (0.1 mmHg). The polymer was dissolved in chloroform and precipitated several times with methanol, in order to remove the low molecular weight species and cyclic olygomers.

The polymers were fractionated at room temperature, using chloroform/methanol as the solvent/nonsolvent system. Fractions of number-average molecular weight 10 000 and 12 000 were used in both the dielectric and mechanical experiments on PDPT and PPT, respectively. The glass transition temperatures of PDPT and PPT, measured with a Du Pont 943 TMA apparatus, at a heating rate of 5 °C/min, amounted to 31 and 92 °C, respectively.

Characterization of the Polymers. PDPT chains were characterized by ^1H and ^{13}C NMR spectroscopy. The spectra were recorded at room temperature with a Varian XL-300 apparatus, operating at 300 MHz (^1H) and 75.4 MHz (^{13}C), on solutions of the polymer in deuterated chloroform, using tetramethylsilane as internal standard. Owing to the presence of the two glycol isomers in the starting mixture, two different structures (A and B in Figure 1) in the ratio 85/15 were detected in the polymer. The fact that the composition of PDPT is different from what would be expected from the initial ratio of the two glycol isomers (93/7) is attributed to the higher reactivity of the primary alcohols with respect to the secondary ones. Details on the characterization of PPT are given elsewhere.[8]

Dynamic Mechanical and Dielectric Measurements. Dynamic mechanical experiments were performed with a PL-DMTA apparatus, at a heating rate of 1 °C/min, and the measurements proceeded from low to high temperature. Dielectric measurements were carried out on solids and solutions with three terminal cells and a capacitance bridge (General Radio, Type 1620), at nine frequencies lying in the range 0.2–100 kHz in the former case and at a single frequency of 10 kHz in the latter. The dielectric measurements on solids were performed from low to high temperatures in 10 °C steps; about 20 min was required to stabilize the temperature in each step.

Experimental Results

(A) Mechanical and Dielectric Relaxations. The mechanical loss tangent versus temperature plot, corresponding to PDPT, presents a well-developed absorption, ostensibly to be attributed to the glass–rubber transition, followed by a weak and wide subglass relaxation extending from about −60 to −140 °C. A detailed representation of the glass–rubber relaxation, labeled α relaxation, at three frequencies (0.1, 1, and 10 Hz), is shown in Figure 2. As expected, the peaks are shifted to higher temperature with increasing frequencies, the temperature associated to the maximum of the peak increasing from 41 °C, at 0.1 Hz, up to 48.5 °C, at 10 Hz. A small shoulder can be devised at low frequencies, on the left side of the α peak, that is attributed to small amounts of solvent, remaining in the strip, which could not be removed. Actually, the shoulder becomes more prominent as the amount of solvent inside the sample increases. The mechanical subglass absorption, labeled β, is weak and the values of the loss tangent in the relaxation lie below 0.033.

The dependence of the mechanical loss tangent on temperature of PPT chains is shown in Figure 3. The mechanical spectrum exhibits a prominent absorption of 0.1 Hz, associated to long-range motions of the glass–rubber relaxation. The absorption, labeled α, also presents

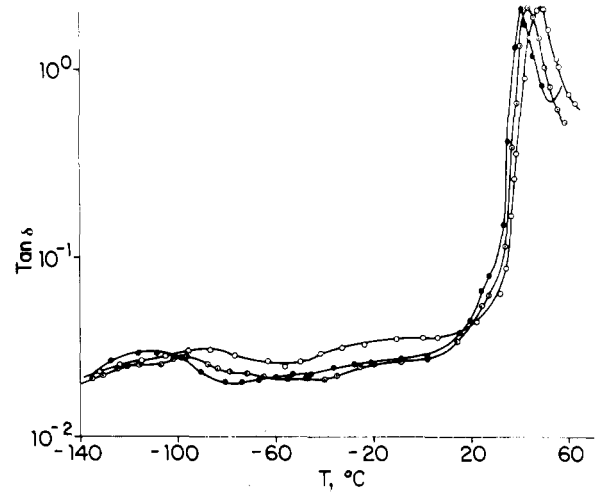

Figure 2. Mechanical loss tangent versus temperature plots for poly(dipropylene glycol terephthalate) (PDPT) at three frequencies: (●) 0.1, (○) 1, (⊙) 10 Hz.

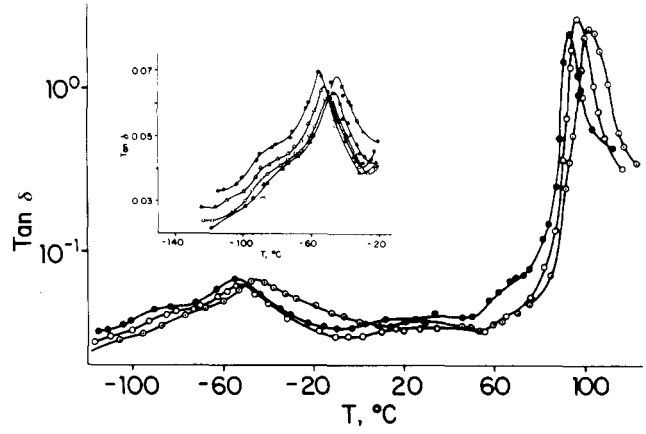

Figure 3. Mechanical loss tangent dependence on temperature for poly(propylene glycol terephthalate) (PPT): (●) 0.1, (△) 0.33, (○) 1, (▲) 3, (⊙) 10 Hz.

a small shoulder on its low-temperature side, presumably caused, as above, by the solvent. A subglass B absorption, which seems to be the result of two overlapping relaxations, extends from 0 to −120 °C. Thus the spectrum at 0.1 Hz presents a sharp peak (β_1), centered at −55 °C, followed by a diffuse peak (β_2), whose maximum seems to be located in the vicinity of −90 °C. It is worthy to point out that the strength of the mechanical subglass relaxation is noticeably higher for this polymer than for PDPT chains.

Values of the dielectric loss tangent for PDPT and PPT chains, as a function of temperature, are shown in Figures 4 and 5, respectively. On the high-temperature side of the spectra a prominent absorption appears, labeled the α relaxation, which can be considered as the result of the relaxation of dipoles in the glass–rubber transition, followed by a well-defined β peak, extending from about 10 to −140 °C for the former polymer and from about 70 to ca. −100 °C for the latter. As in the case of the mechanical spectra, the dielectric β peak corresponding to PPT chains shows higher symmetry and strength than its counterpart

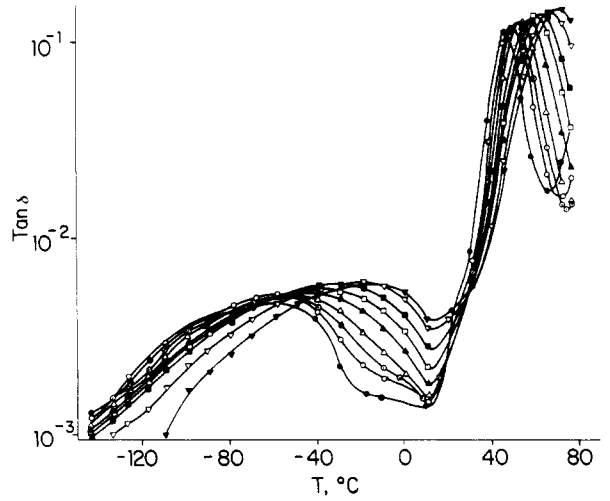

Figure 4. Dependence of the dielectric loss tangent on temperature for poly(dipropylene glycol terephthalate) (PDPT) at several frequencies: (●) 0.2, (○) 0.5, (⊙) 1, (△) 2, (▲) 5, (□) 10, (■) 20, (▽) 50, (▼) 100 kHz.

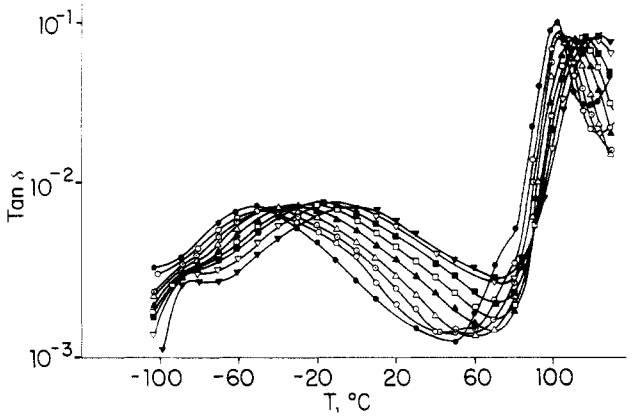

Figure 5. Dependence of the dielectric loss tangent on temperature for poly(propylene glycol terephthalate). (See Figure 4 for the values of the frequencies attached to the symbols indicated).

in PDPT. The dielectric results are fitted by the Havrilak–Nagami[9] equation that relates the complex dielectric constant to the central relaxation time τ_0

$$\epsilon^* = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty)[1 + (i\omega\tau_0)^\gamma]^{-\delta} \quad (1)$$

by using values of γ and δ of 0.12 and 0.88, respectively, for PPT at 112 °C. The values of these quantities for PDPT are 0.17 and 0.42, respectively, at 53.7 °C. Since γ and δ are a measure of the symmetry broadening about τ_0 and frequency skewing, respectively, the values obtained for these parameters indicate that the dielectric relaxation is rather narrow and it is skewed toward the high-frequency side.[10]

(B) Dipole Moments of PDPT Chains. The mean-square dipole moment $\langle\mu^2\rangle$ of PDPT chains was obtained by measuring the increments ($\Delta\epsilon = \epsilon - \epsilon_1$) of the dielectric constant (ϵ) of benzene solutions of the chains, with respect to that of the solvent (ϵ_1), as well as the increments of refractive indices of the same solutions ($\Delta n = n - n_1$). By plotting $\Delta\epsilon$ and Δn against the weight fraction w of polymer in the solutions, straight lines were obtained from whose slopes the values of $d\epsilon/dw$ and dn/dw were determined. Values of these quantities at 30, 40, 50, and 60 °C are shown in the third and fourth columns of Table I, respectively. The magnitude of $\langle\mu^2\rangle$, at each temperature of interest, was obtained by using the method of Guggenheim[11] and Smith,[12] in which the contribution of the

Table I
Summary of Dielectric Results for Poly(dipropylene glycol terephthalate) (PDPT)

T, °C	$d\epsilon/dw$	dn/dw	$\langle\mu^2\rangle/nm^2$	$(\langle\mu^2\rangle/nm^2)_{PPT}$[a]
30	2.826	0.098	0.715	0.582
40	2.727	0.103	0.726	0.585
50	2.646	0.110	0.741	0.596
60	2.552	0.116	0.750	0.609

[a] Taken from ref 16.

atomic polarization to the total polarization was considered to be negligible. The values of $\langle\mu^2\rangle$ were expressed in terms of $\langle\mu^2\rangle/nm^2$, where nm^2 is the mean-square dipole moment of the chains in the idealization that all the skeletal bonds are freely jointed. In the evaluation of nm^2 it was assumed that the dipole associated to each ester group[13] is 1.89 D, whereas the dipole corresponding to the CH_2–O ether group and CH_3–CH_2 groups is 1.07 and 0.00 D, respectively.[14,15] Values of $\langle\mu^2\rangle/nm^2$, with an extimated uncertainty of ±3%, are shown in the fourth column of Table I. It can be seen that the polarity of PDPT chains increases with increasing temperature and the temperature coefficient of the dipole moment, expressed as $d \ln \langle\mu^2\rangle/dT$, amounts to 1.6×10^{-3} K^{-1}. In the fifth column of Table I, and for comparative purposes, the values of the dipole moment ratio for PPT, taken from ref 16, are also shown. As can be seen, PPT exhibits a polarity that is significantly lower than that of PDPT.

Theoretical Dipole Moments

A schematic representation of the two units of PDPT in the all-trans conformation is shown in Figure 1. In the theoretical analysis of the dipole moment of PDPT, extensive use was made of the information on the conformational energies of PDET[2,3] and PPT[16] chains. Thus O–CO bonds were assumed to be planar trans,[13,17] whereas the terephthaloyl residue was considered to be restricted to cis and trans conformations, both forms having similar energy.[18] Bonds of type $i + 3$ in Figure 1 present two minima, located at −20° and −100° (20° and 100° in the case of $i + 8$ bonds), and the energy $E\sigma_k$ of the latter rotational state is 0.1 kcal mol^{-1} below that of the former. The potential curve around bonds of type $i + 4$ presents three minima at 5°, 120°, and 235°; the states located at 120° and 235° exhibit conformational energies $E\sigma_\alpha$ and $E\sigma_\beta$ whose values are 0.5 and 0.1 kcal mol^{-1}, respectively, below that of the alternative trans states.[16] It should be pointed out that for $i + 7$ bonds in Figure 5, $E\sigma_\alpha$ and $E\sigma_\beta$ are associated with the rotational states placed at 235° and 120°, respectively. As the rotational angles depart from zero in bonds of type $i + 5$, the interaction between methylene and methyl groups separated for four bonds increases, so that g^+ states are forbidden; for the same reason, g^- states about $i + 6$ bonds are not permitted. The alternative gauche states about these bonds have an energy $E\sigma'' \approx 1.2$ kcal mol^{-1} above that of the corresponding trans[14] states. Gauche rotations of different sign about consecutive pairs of bonds, which give rise to second-order $CH_2\cdots O$ and CO..O interactions, were considered to have energies Ew and Ew' of 0.45 and 1 kcal mol^{-1}, respectively.

Values of the mean-square dipole moment were calculated for hydroxyl-terminated chains of $M_n = 10\,000$ by using standard methods described in detail elsewhere.[18,19] It was assumed that the dipole moment associated to each ester group is 1.89 D, and it makes an angle of 123° with the direction of the C^{Ph}–CO bond.[13] The dipole moments corresponding to the ether and hydroxyl groups lie along the bonds, and their values are 1.07 and 1.70 D, respectively.[14] The statistical weight matrices associated with

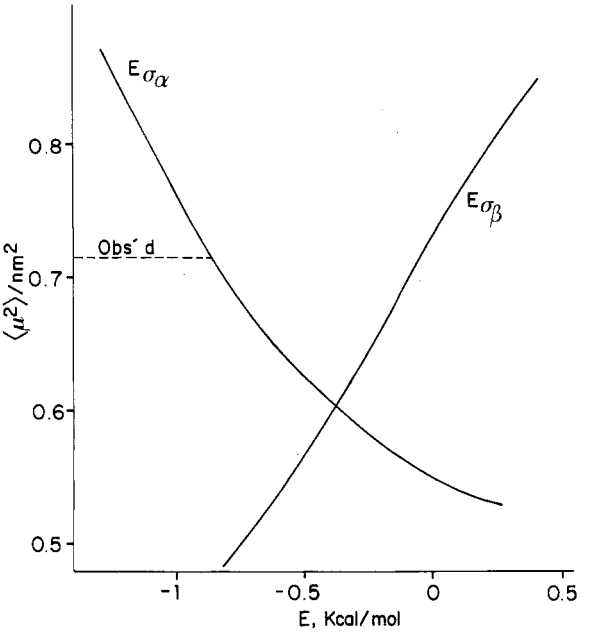

Figure 6. Theoretical values of the dipole moment ratio as a function of $E\sigma_\alpha$ (calculated assuming $E\sigma_\beta$ = –0.1 kcal mol^{-1}) and $E\sigma_\beta$ (calculated assuming $E\sigma_\alpha$ = –0.8 kcal mol^{-1}).

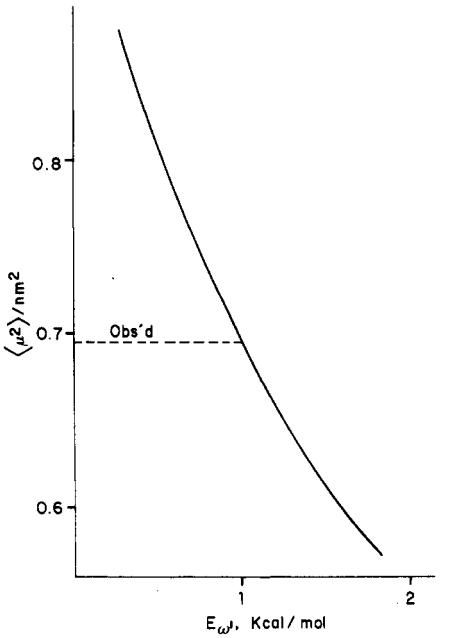

Figure 7. Changes of the dipole moment ratio with the energy associated to second-order CO···O interactions.

each skeletal bond of the A unit in the iso configuration, shown in Figure 1, were considered to be

$$\mathbf{U}_i = 1; \quad \mathbf{U}_{i+1} = [1 \quad 1]; \quad \mathbf{U}_{i+2} = \begin{bmatrix} 1 \\ 1 \end{bmatrix}$$

$$\mathbf{U}_{i+3} = [1 \quad 0 \quad \sigma_k]; \quad \mathbf{U}_{i+4} = \begin{bmatrix} 1 & \sigma_\alpha & \sigma_\beta \\ 0 & 0 & 0 \\ 1 & \sigma_\alpha w' & \sigma_\beta \end{bmatrix}$$

$$\mathbf{U}_{i+5} = \begin{bmatrix} 1 & 0 & \sigma'' \\ 1 & \sigma'' & \sigma w \\ 1 & \sigma w & 0 \end{bmatrix}; \quad \mathbf{U}_{i+6} = \begin{bmatrix} 1 & \sigma'' & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_{i+7} = \begin{bmatrix} 1 & \sigma_\beta & \sigma_\alpha \\ 1 & 0 & \sigma_\alpha w \\ 0 & \sigma_\beta w & \sigma_\alpha \end{bmatrix}; \quad \mathbf{U}_{i+8} = \begin{bmatrix} 1 & \sigma_k & 0 \\ 1 & \sigma_k & 0 \\ 1 & \sigma_k w' & 0 \end{bmatrix} \quad (2)$$

For the sake of simplicity, the statistical weight matrices corresponding to B units in Figure 1 are not shown, but they can easily be derived from the information given above. The statistical weight parameters were obtained from the conformational energies in the usual way, the main set of energies being $E\sigma_\beta$ = –0.1; $E\sigma''$ = 1.2; $E\sigma_\alpha$ = –0.5; $E\sigma_\beta$ = –0.1; Ew = 0.45, and Ew' = 1 kcal mol^{-1}. Preliminary calculations showed that the dipole moment is almost insensitive to the stereochemical composition and to the distribution of A and B units in the polymer.

An inspection of Figure 1 reveals that the dipoles associated to the CH_2OCH_2 group and to the two esters flanking the ether group are almost in parallel direction, so that departure from the trans conformation should reduce the polarity of the chains. Consequently, the dipole moment should be very sensitive to $E\sigma_\alpha$, $E\sigma_\beta$, and Ew'. Values of $\langle\mu^2\rangle/nm^2$ were calculated as a function of $E\sigma_\alpha$, assuming $E\sigma_\beta$ = –0.1 kcal mol^{-1}. The results obtained, shown in Figure 6, indicate that in increasing $E\sigma_\alpha$ from –1.3 to 0.2 kcal mol^{-1}, the dipole moment ratio decreases from 0.87 to 0.55, as a consequence of the fact that low values of $E\sigma_\alpha$ stabilize the g^+ states about i + 4 bonds and g^- states about i + 7 bonds, which places the dipoles of the ester groups in an almost parallel direction. Agreement between theory and experiment was found for $E\sigma_\alpha$ = –0.8 kcal mol^{-1}, ca. $^3/_{10}$ kcal mol^{-1} below that calculated from semiempirical potential functions. It is worthy to note that a similar energy was found for gauche states about OCH_2–CH_2O bonds in poly(diethylene glycol terephthalate). The sensitivity of the dipole moment ratio to $E\sigma_\beta$ is also shown in Figure 6. Here the curve was calculated by assuming that $E\sigma_\alpha$ = –0.8 kcal mol^{-1}. The calculations show that the dipole moment decreases as $E\sigma_\beta$ decreases, since the fraction of g^+g^+ states about i + 4, i + 7 bonds, which places the dipoles of the ester groups in an almost antiparallel direction, increases, thus opposing the enhancing effects that the alternative gauche states produce in the polarity of the chains.

Low values of Ew' stabilize the g^-g^+ conformations about the i + 3, i + 4 pair of bonds (g^+g^- about i + 7, i + 8 bonds), in which the dipoles associated to the CH_2OCH_2 and ester groups are placed in an almost parallel direction. Hence the polarity of the chains should increase as Ew' decreases, as can be seen in Figure 7, where the values of $\langle\mu^2\rangle/nm^2$ are plotted as a function of Ew'. By comparing theory and experiment, the reasonable value of Ew' = 1 kcal mol^{-1} was obtained. The dipole moment ratio is only moderately dependent on $E\sigma_k$ since it only changes by 6% when the energy increases from 0.1 to 0.7 kcal mol^{-1}. The sensitivity of the dipole moment ratio to $E\sigma''$ and Ew is even lower.

The temperature coefficient of the dipole moment ratio, calculated by using the best set of conformational energies, is positive, in agreement with the experimental result, but its value (1.3×10^{-4} K^{-1}) is almost 1 order of magnitude lower. In order to reproduce the experimental temperature coefficient it would be necessary to postulate that $E\sigma_\alpha$ = $E\sigma_\beta$ = –0.8 kcal/mol^{-1}, but then $\langle\mu^2\rangle/nm^2$ = 0.485, a value which is far below the experimental result. It should be pointed out that small errors in the measurements of the dipole moments can lead to big errors in the determination of d ln $\langle\mu^2\rangle/dT$ and, consequently, the dipole moment ratio is much better than the temperature coefficient for comparison of theory and experiment.

Discussion

Both the mechanical and dielecric β relaxations show Arrhenius behavior and the values obtained for the activation energies are given in Table II. The results show

Table II
Values of the Activation Energies E (in kcal mol^{-1}) Associated with the Mechanical and Dielectric β Processes of Poly(dipropylene glycol terephthalate) (PDPT) and Poly(propylene glycol terephthalate) (PPT)

polymer	E(mechanical)	E(dielectric)
PDPT	16 ± 1	10
PPT	37 ± 1	14

Table III
Glass Transition Temperature Related Parameters for Poly(dipropylene glycol terephthalate) (PDPT) and Poly(propylene glycol terephthalate) (PPT)

relaxation	polymer	ϕ_g/B	$10^4\alpha_f/B$
mechanical	PDPT	0.025	5.0
mechanical	PPT	0.029	5.8
dielectric	PDPT	0.033	6.6
dielectric	PPT	0.036	7.3

that the activation energy E_a involved in the β mechanical relaxation corresponding to PPT changes is more then twice the value of this energy for similar process in PDPT chains, whereas the value of E_a for the dielectric β relaxation is only somewhat higher. In both cases the activation energy involved in the β dielectric process is lower than that corresponding to the β mechanical relaxation.

The glass–rubber transition can be described in terms of the free volume theory, which assumes that the relaxation time τ_i associated to the viscoelastic or dielectric i mechanism in the transition is related to the relative free volume ϕ by the Doolittle equation[20]

$$\tau_i = A \exp(B/\phi) \tag{3}$$

where ϕ is defined as

$$\phi = (v - v_0)/v_0 \tag{4}$$

v and v_0 being the specific volume and the volume at which a relaxation process cannot take place, respectively. By assuming that v is a linear function of temperature, that is

$$v = v_0(1 + \alpha_f(T - T_\infty)) \tag{5}$$

eq 3 leads to the Vogel equation[21]

$$\ln \tau_i = A' + m/(T - T_\infty) \tag{6}$$

where T_∞ is the temperature at which the free volume would be zero were it not for the formation of the glassy state. The free volume and α_f at T_g are related to m by the following equations[22]

$$\phi_g/B = (T_g - T_\infty)/m \tag{7}$$

$$\alpha_f/B = 1/m \tag{8}$$

Values of the reciprocal of the relaxation times, associated to the maximum of both mechanical and dielectric glass–rubber processes in PDPT and PPT chains, are plotted as a function of $1/(T - T_\infty)$ in Figure 8. As can be seen, the experimental results fit the Vogel equation by assuming that T_∞ has a value 50 °C below the respective glass transition temperatures. The values of ϕ_g/B, obtained from mechanical and dielectric experiments, are shown in the third column of Table III. An inspection of these values reveals that the magnitude of ϕ_g/B, calculated from mechanical experiments, is lower than that determined from dielectric results, exceeding in the latter case the average value of 0.025 ± 0.005 reported for this quantity in most amorphous systems.[23] The larger values of ϕ_g/B, obtained from dielectric experiments, may be attributed to values of B other than unity, presumably as a consequence of the fact that the minimum hole size, required for local segmental motions, is probably lower in the dipolar relaxation than in the mechanical relaxation

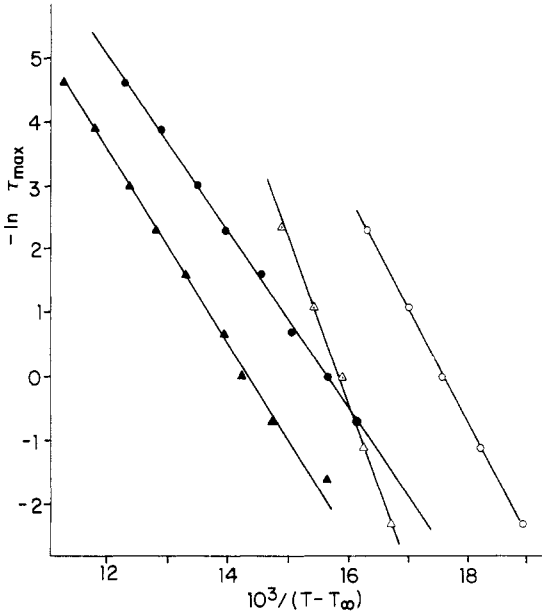

Figure 8. Plots of the relaxation times associated to the maximum of the peaks as a function of $1/(T - T_\infty)$: (△, ○) mechanical results for PDPT and PPT, respectively; (▲, ●) dielectric results for PDPT and PPT, respectively.

process.[23] The values of α_f/B, shown in the last column of Table II, follow the same trend as the values of ϕ_g/B, in the sense that the magnitude of α calculated from mechanical results is lower than that obtained from dielectric experiments. However, the fact that α_f turns out to be the correct magnitude for a thermal expansion coefficient supports the assumption that both, the mechanical and dielectric α relaxation processes, are governed by the volume.

The flexibility of molecular chains can be expressed in terms of the conformational partition function per skeletal bond z or, alternatively, by the conformational entropy S, which at different z, is independent of the rotational states taken as reference in its evaluation. S and z are related by the equation[24,25]

$$S = R[\ln z + (T/z)\, dz/dT] \tag{9}$$

The conformational entropy for PDPT was calculated by using the following conformational energies: $E\sigma_\alpha = -0.8$, $E\sigma_\beta = -0.1$, $E\sigma_k = -0.1$, $E\sigma'' = 1.2$, $Ew = 0.45$, and $Ew' = 1.0$ kcal mol^{-1}. The value obtained for S, 0.84 cal/K (mol bond), is somewhat lower than the value of 1.35, in the same units, reported for the conformational entropy of PDET chains.

The values of the glass transition temperature of PDPT and PPT do not follow the general trend observed in the homologous series of most polymers, in the sense that the lower the conformational entropy is the higher Tg is.[26,27] Thus the glass transition temperature of PPT is almost 60 °C above that of PDPT, in spite of the fact that the conformational entropies of these polymers are 1.00 and 0.84 cal/K (mol bond), respectively. These results suggest that dipolar intermolecular interactions, which probably involve the terephthaloyl residue, may be held responsible of the anomalous experimental values found for the glass transition temperatures of these polymers. Actually, the density of terephthaloyl residues along the chains is larger in PPT than in PDPT chains and, consequently, the dipolar intermolecular interactions would be larger in the former polymer than in the latter.

As was indicated above, both PDPT and PPT exhibit strong mechanical and dielectric processes associated to

the glass–rubber relaxation. However, whereas the α mechanical peak exhibits similar intensity in both polymers, the α dielectric process shows higher strength in PDPT than in PPT, as a consequence of the lower polarity of the latter polymer.

PPT presents an asymmetric β mechanical process slightly shifted to higher temperature with respect to the β mechanical absorption in PET. The relaxation can be resolved in a well-defined β_1 peak, centered at −55 °C at 1 Hz, overlapping with a diffuse β_2 peak, whose maximum lies in the vicinity of −90 °C. Two peaks, centered at −70 and −105 °C, were also reported for PET, and they were attributed to motions of the COO groups associated to the trans and gauche conformations of the CH_2–CH_2 bonds.[10,28,29] The β dielectric relaxation of PPT chains displays a single peak, centered at −55 °C at 0.2 kHz, which taking into account its activation energy (14 kcal mol^{-1}), would be located at −90 °C at 0.1 Hz. This behavior suggests that both the β_2 mechanical peak and the β dielectric absorption probably involve the same type of motions. Dielectric and mechanical activity can be obtained through cis/trans transitions in the terephthaloyl residue; for example, in cis/trans conformation the two dipoles are in the parallel/antiparallel direction, respectively, both conformers having similar energy. Also transitions from trans to gauche conformations about CH(CH_3)–CH_2 bonds would increase and decrease the polarity and dimensions of the chains, respectively.

The β mechanical absorption corresponding to PDPT chains is diffuse and its strength is small in comparison with the strength of the absorption in PPT. On the contrary, the β dielectric absorption is well defined but of lower intensity than a similar relaxation in PPT chains. By considering that the activation energy associated with the β dielectric process is 10 kcal mol^{-1}, one finds that this peak would be centered at −100 °C at 0.1 Hz, almost at the same temperature that the β mechanical peak appears. This suggests that similar motions are probably involved in both processes. It is worthy to note that if the motions would imply cis–trans transitions in the terephthaloyl residue, considerable mechanical activity would appear in PDPT, in sharp contrast with the experimental results which show a low activity. These considerations seem to rule out rotations about C^{Ph}–CO bonds as a cause of the relaxation and, consequently, the absorption should be produced by motions in which only skeletal bonds of the glycol residue intervene. Moreover, since the critical interpretation of the dipole moments of PDPT chains suggests that the polarity of the chains is very sensitive to the population of the rotational states about CH(CH_3)–CH_2 bonds, it is expected that the mechanical absorption preferently involves rotation about these bonds, rather than about other skeletal bonds. If this speculation is correct, then the β_1 mechanical relaxation in PPT would entail molecular motions in which more than a single repeating unit would intervene.

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Registry No. PDPT (SRU), 99037-56-6; PDPT (copolymer), 99022-60-3; PPT (SRU), 9022-20-2; PPT (copolymer), 40103-20-6.

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